Thermal Degradation of Cellulose Nanomaterials: Structural and Chemical Changes

AUTHORS:

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PRESENTED BY:

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TAPPI

Background

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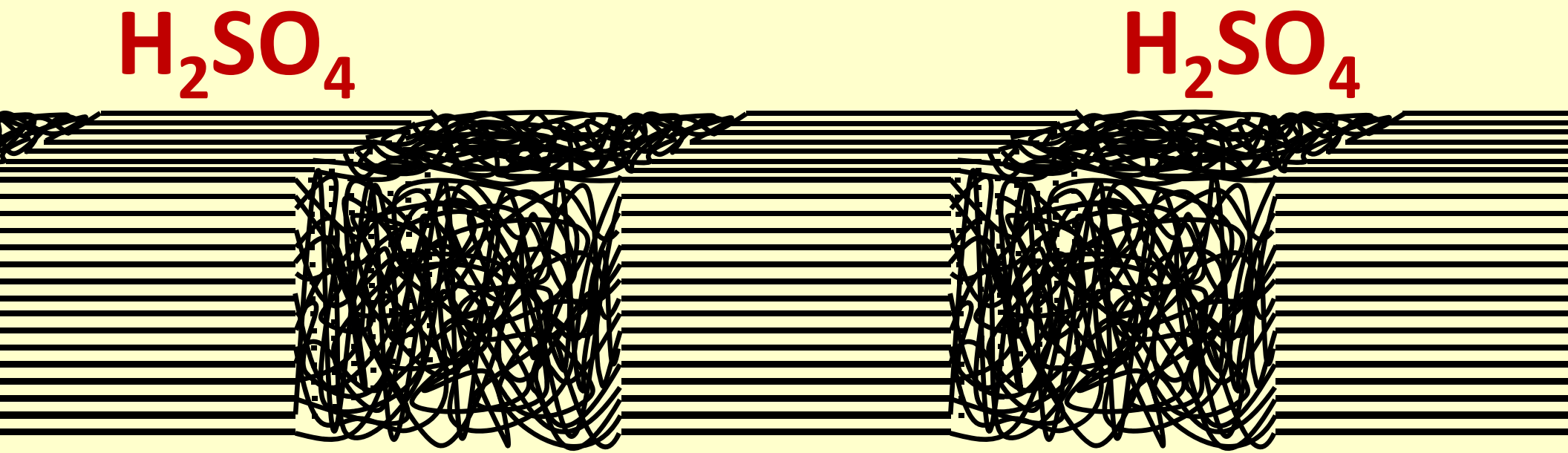

CELLULOSE NANOCRYSTALS

Background

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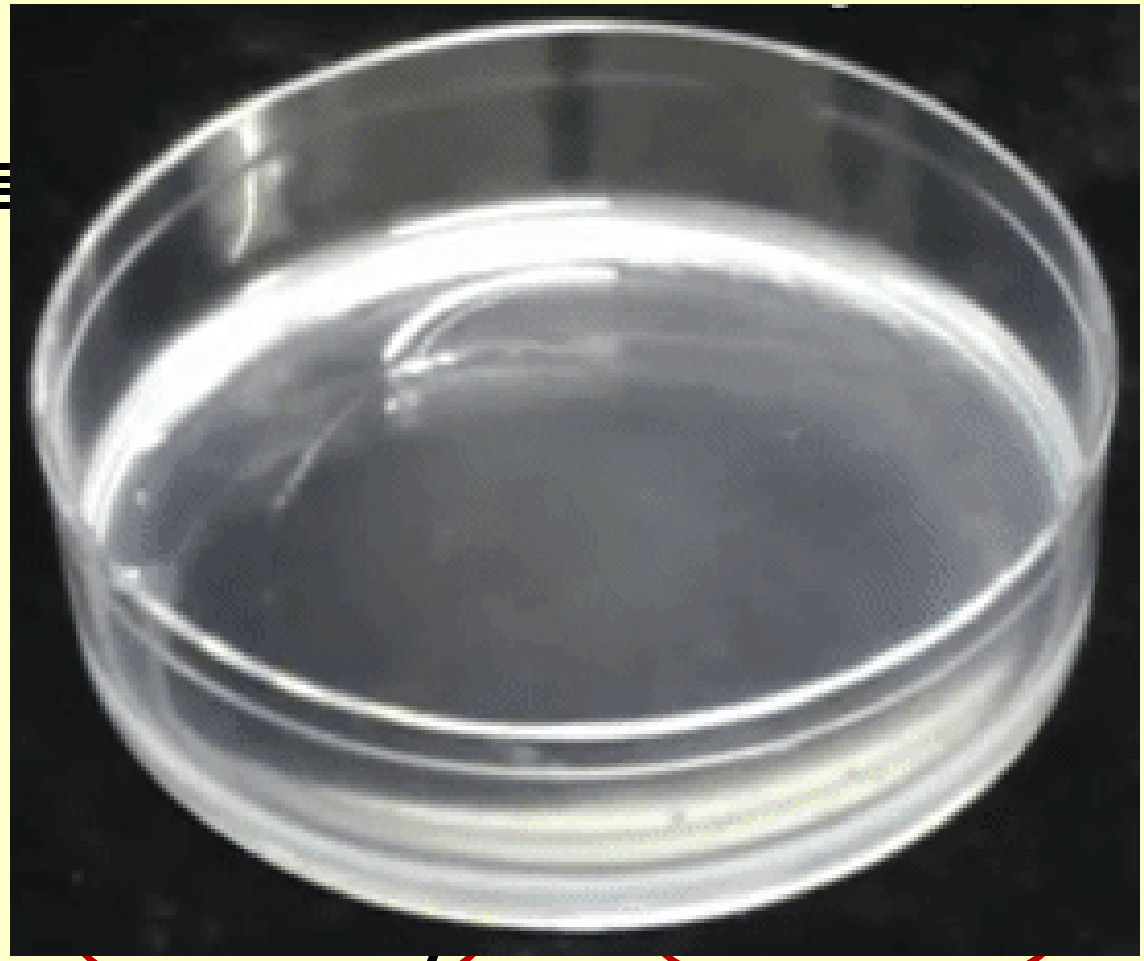

Composites

Foams

Packaging

Emulsions

Background

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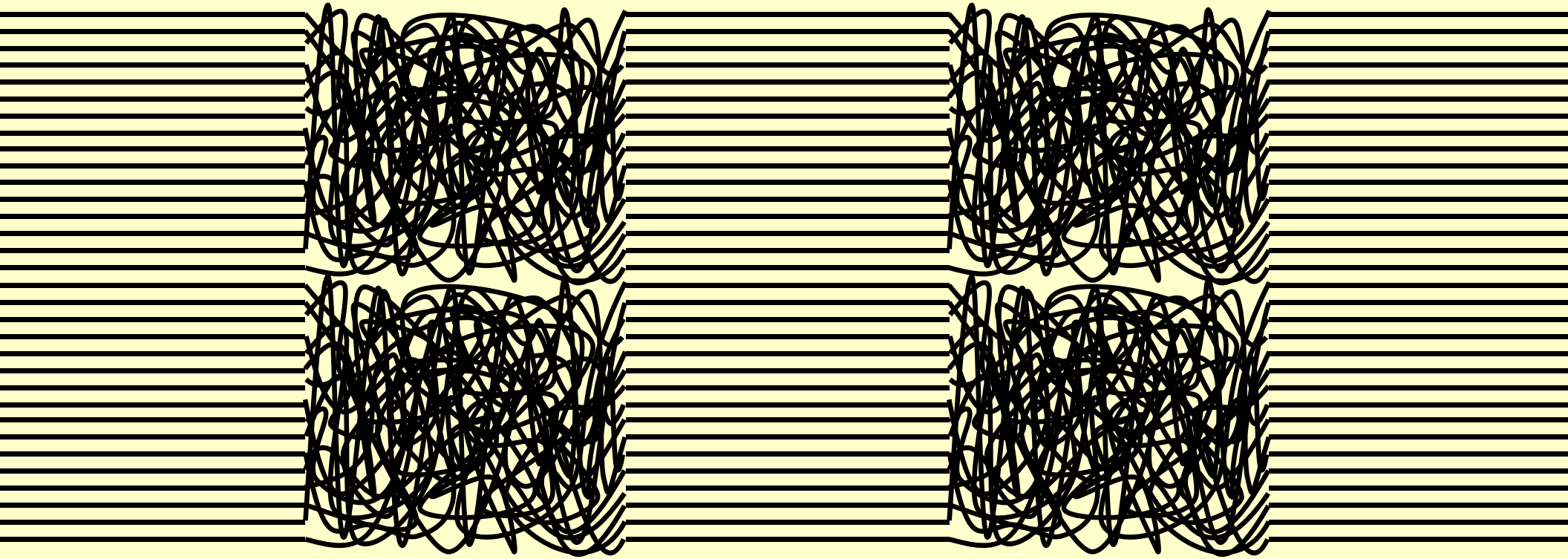

CELLULOSE FILAMENTS

Background

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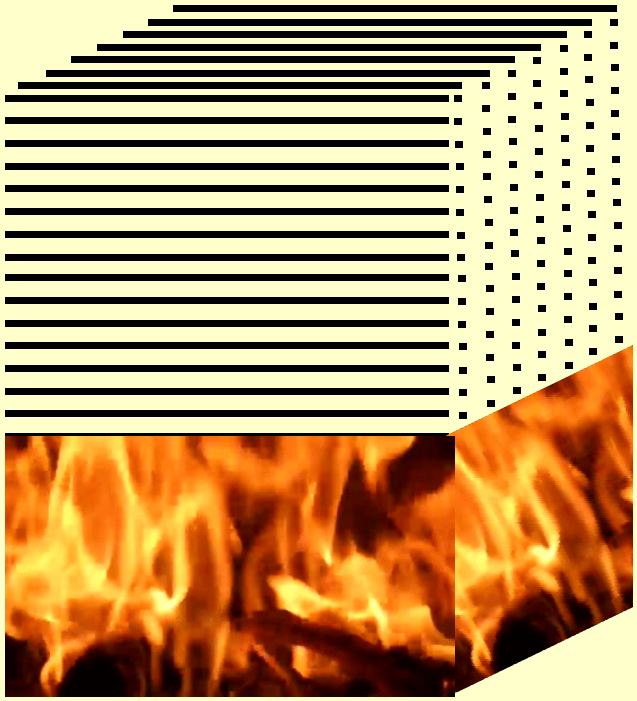

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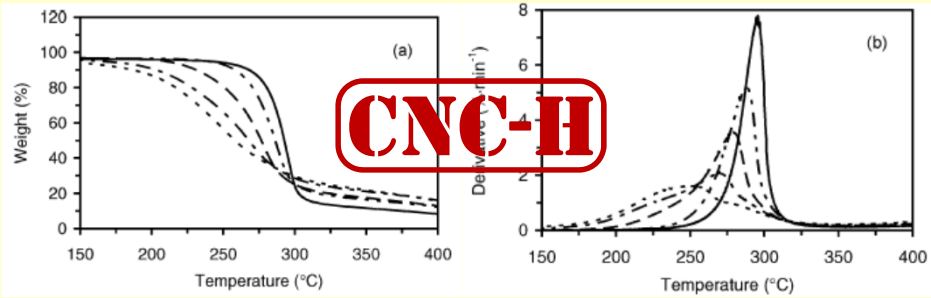
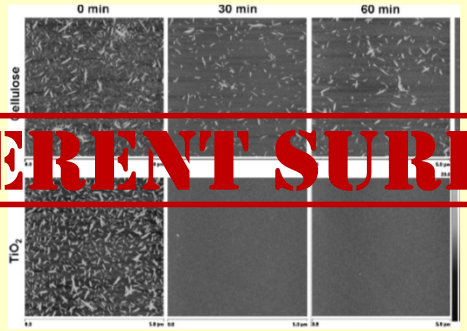
Roman, M.; Winter, W. T. *Biomacromol.* **2004**, *5*, 1671-1677.



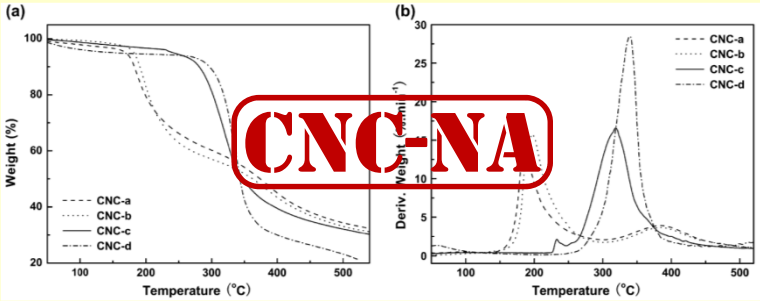
CNC-H

Suchy, M.; et al. *Macromol. Symp.* **2010**, *294*, 51-57.



DIFFERENT SURFACES

Wang, N.; et al. *Polymer* **2007**, *48*, 3486-3493.



CNC-NA

Chauve, G.; et al. *TAPPI Journal* **2016**, *15*, 383-391.

CNC-X

Vanderfleet, O. M.; et al. *Philos. Trans. Royal Soc. A* **2017**, *376*.

P-CNC-H

Motivation

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Motivation

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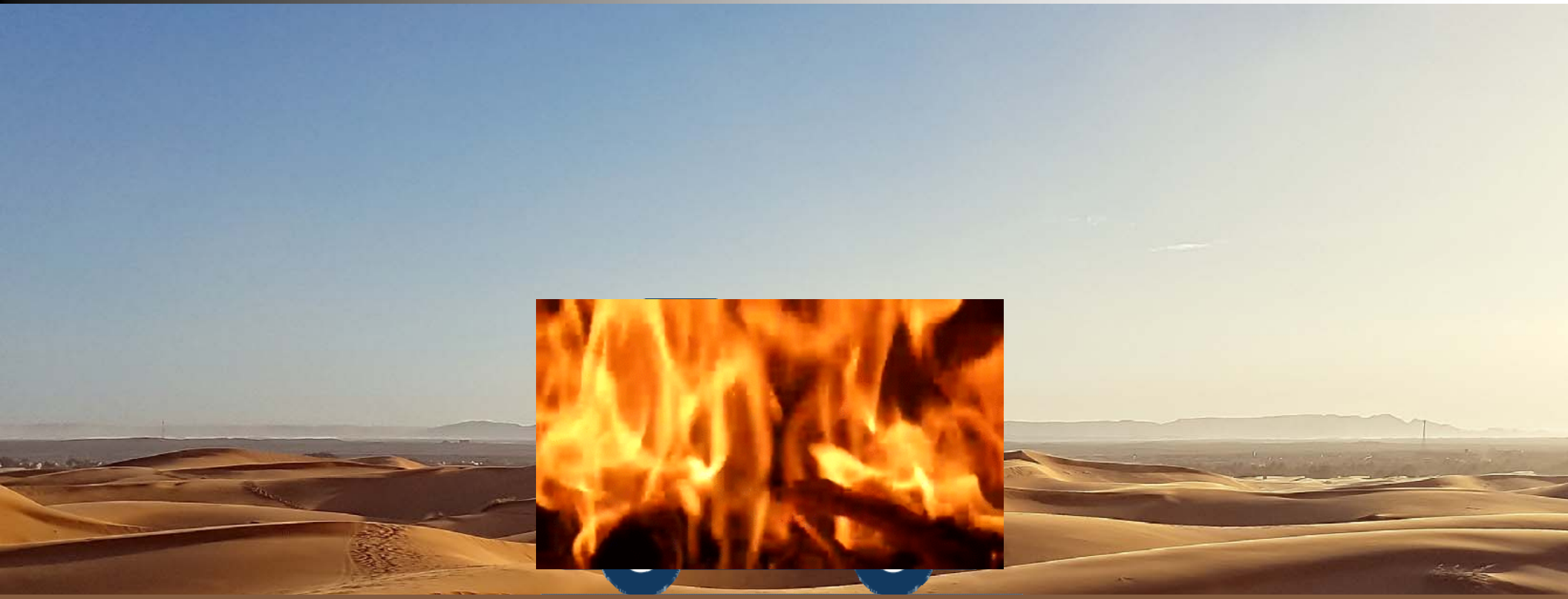

Objective

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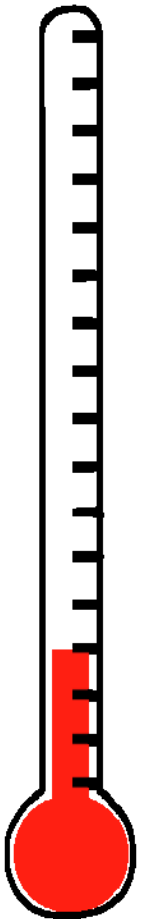


THERMAL DEGRADATION

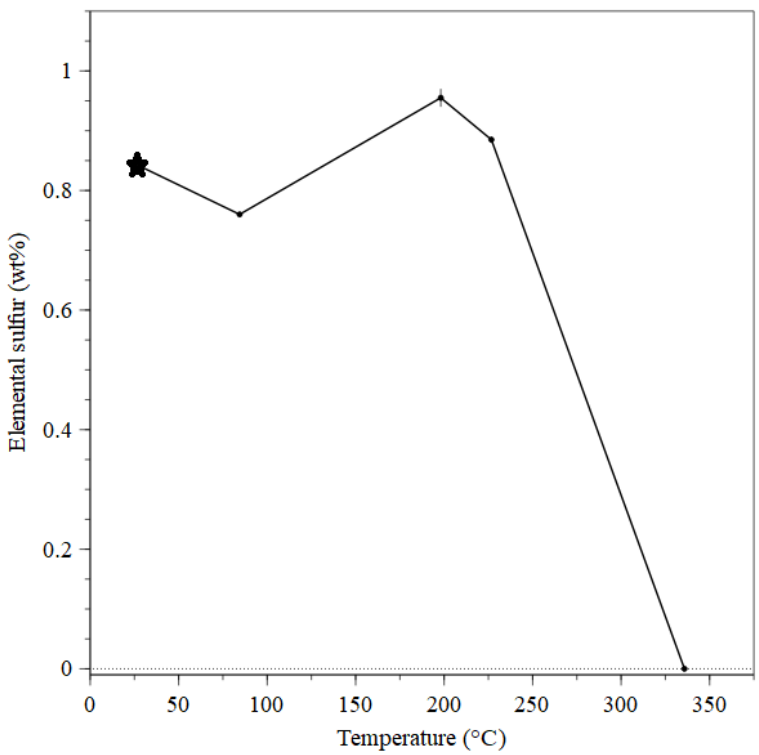
CNC-H CNC-Na CF

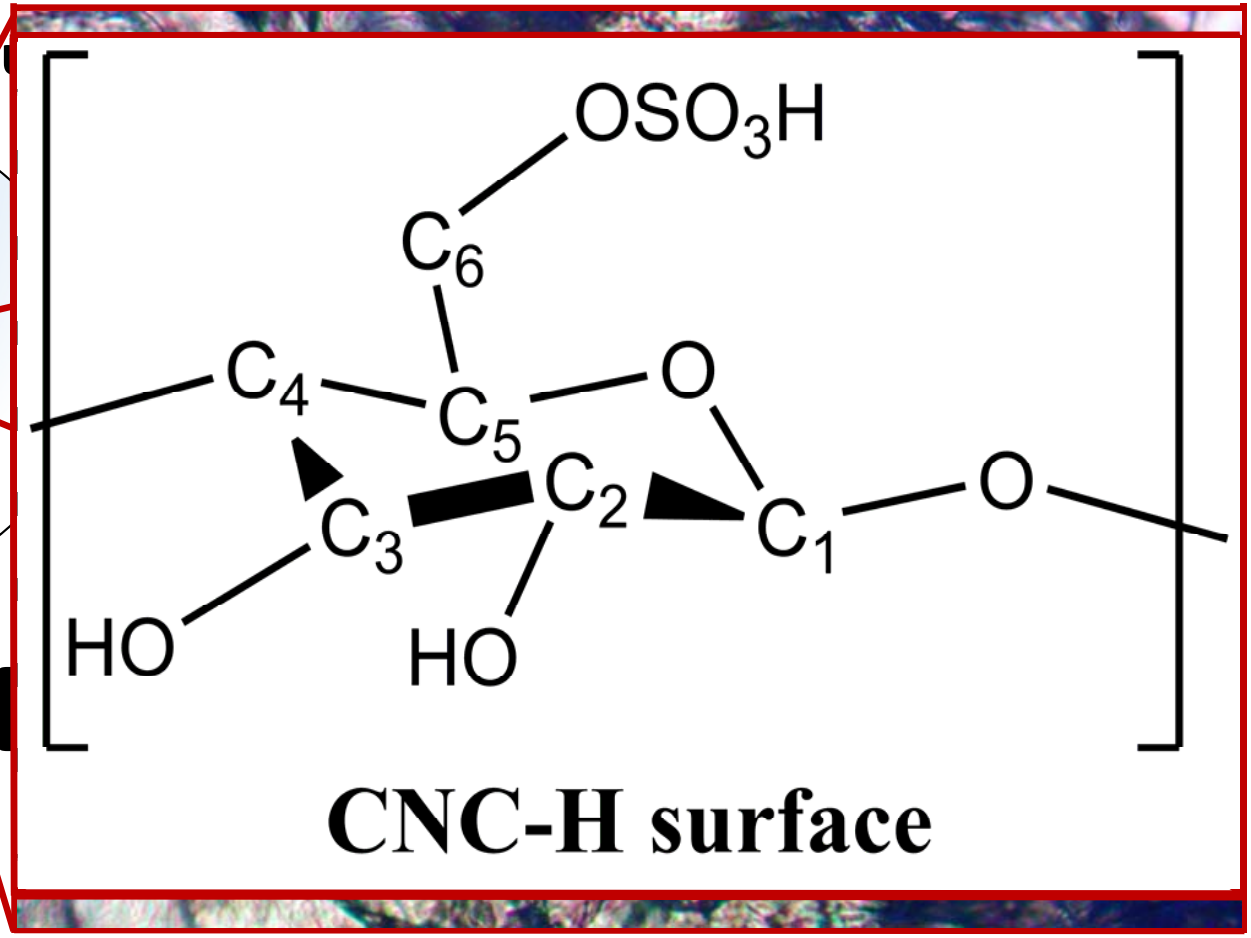
Structural changes?

Chemical changes?

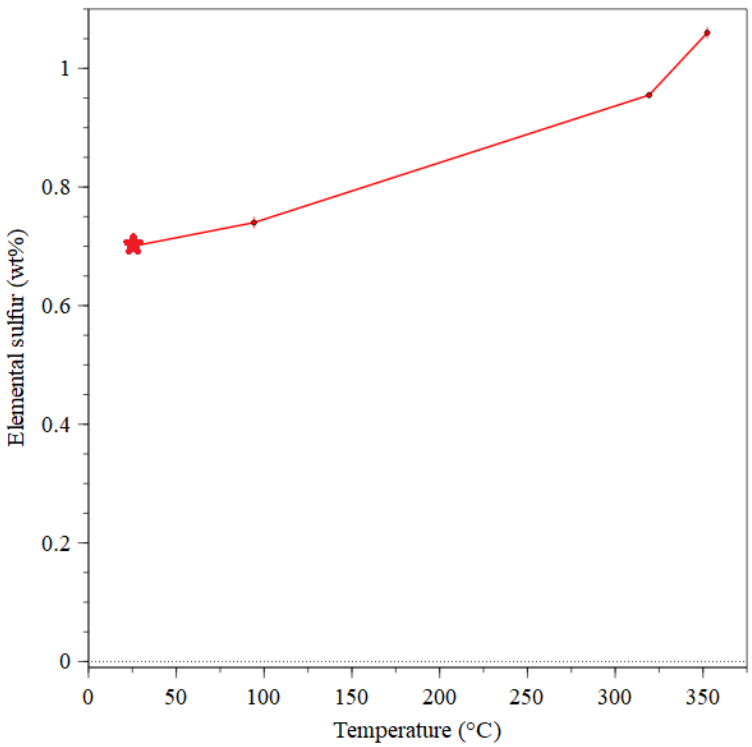
Improvement of thermal stability

Results


Elemental sulfur (wt%)
Temperature (°C)
0
0.2
0.4
0.6
0.8
1
0
50
100
150
200
250
300
350


OSO3H
C6
C4
C5
O
C3
C2
C1
O
HO
HO
CNC-H surface

Results


Elemental sulfur (wt%)
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0
0.2
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300
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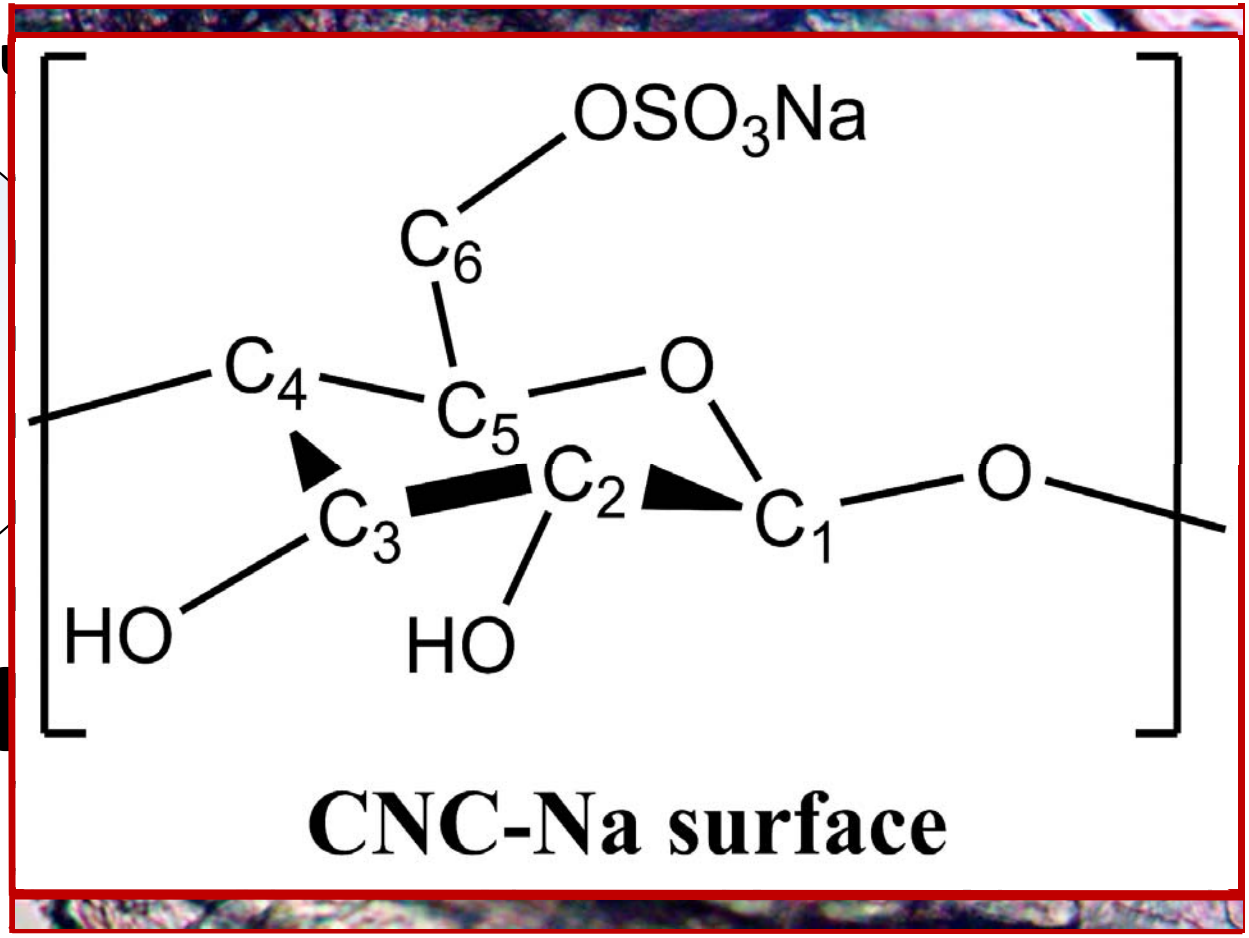
OSO3Na
C6
C4
C5
O
C3
C2
C1
O
HO
HO
CNC-Na surface

Results

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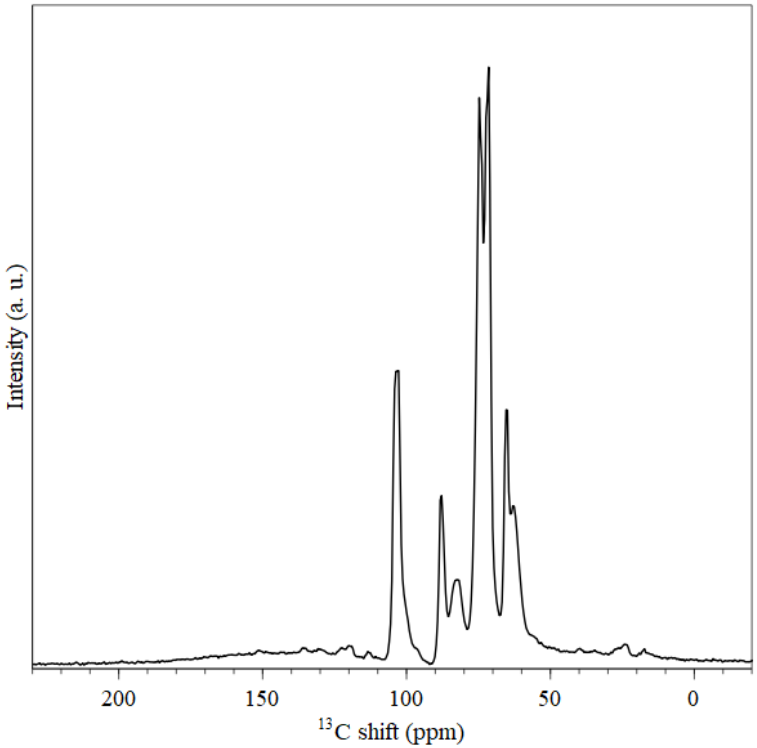

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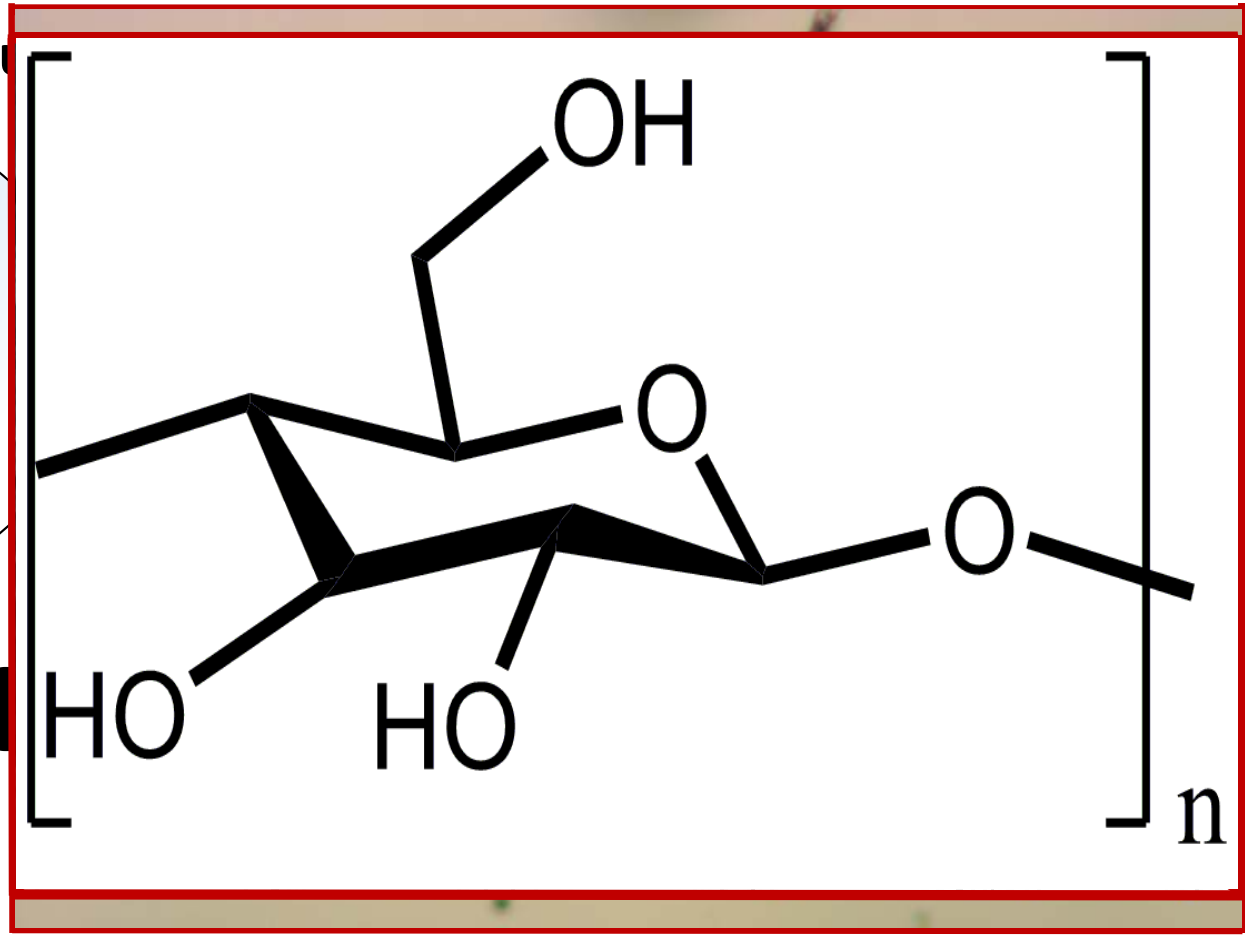

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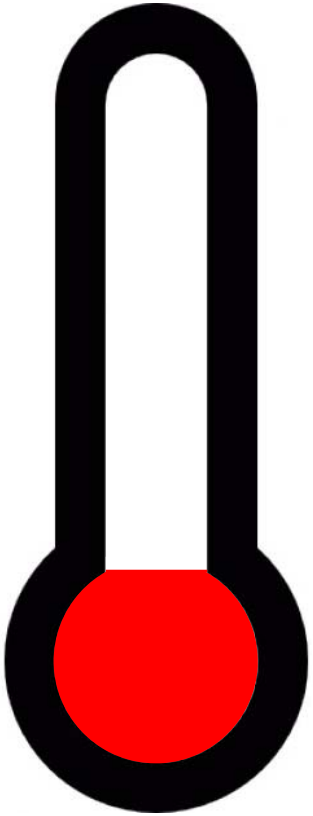
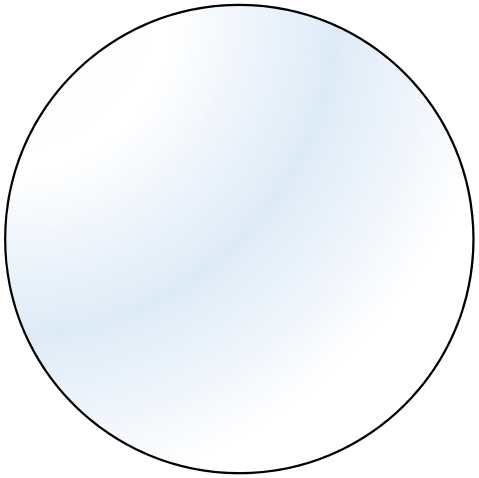
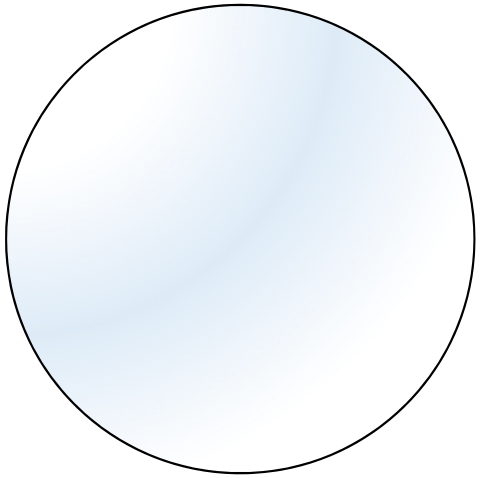


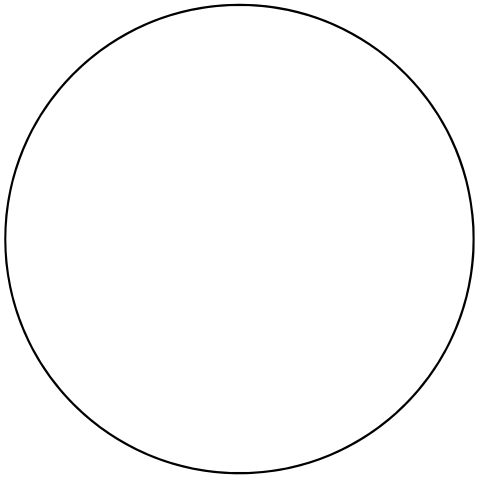
26 °C



CNC-H



CNC-Na



CF

1 cm

Results

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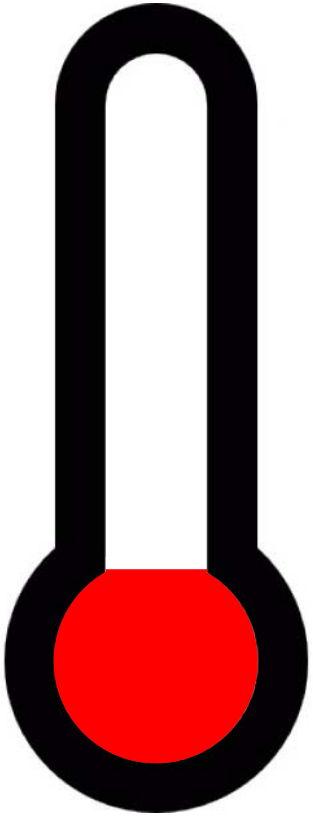
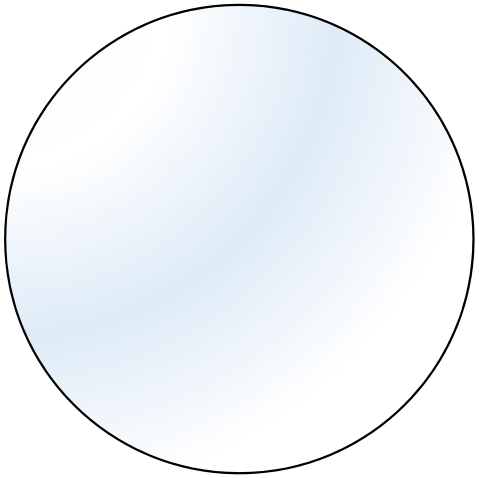


27 °C



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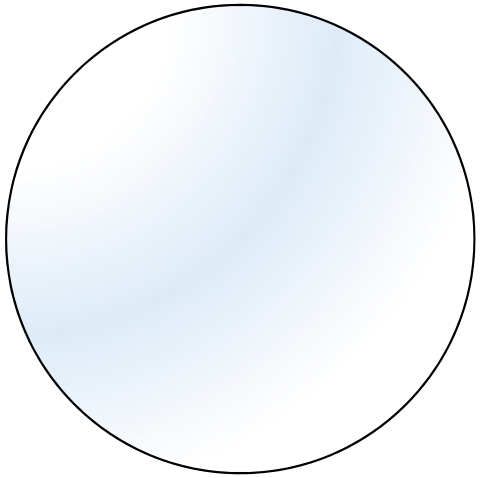
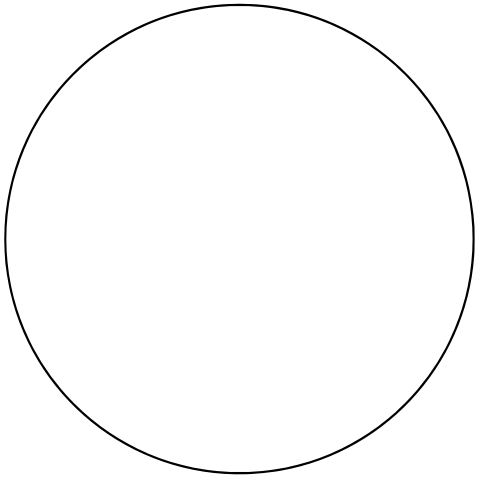


CNC-Na



CF

1 cm

Results

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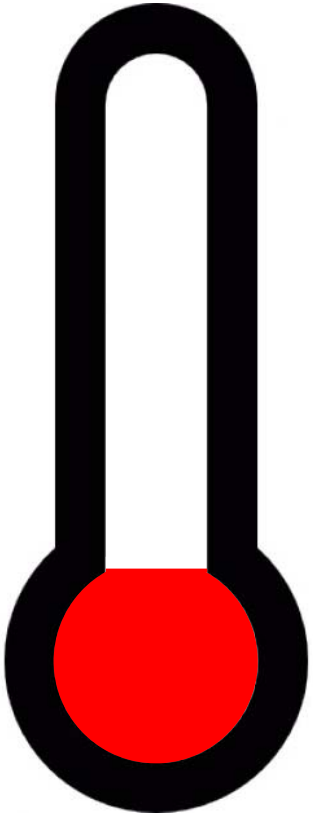
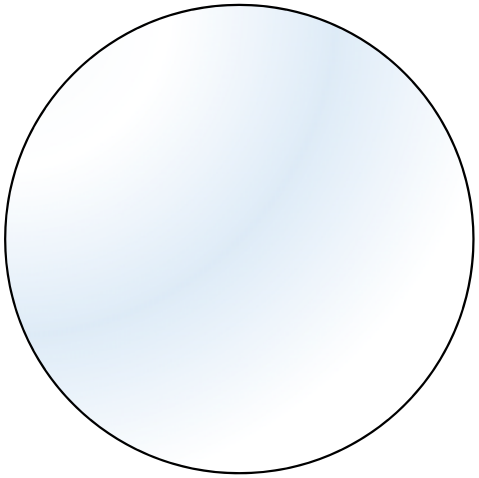


28 °C



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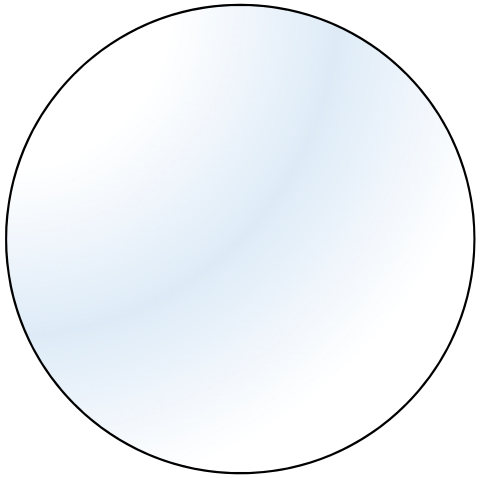

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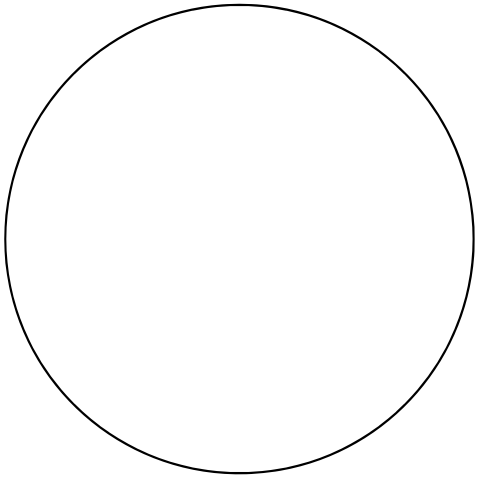

CF

1 cm

Results

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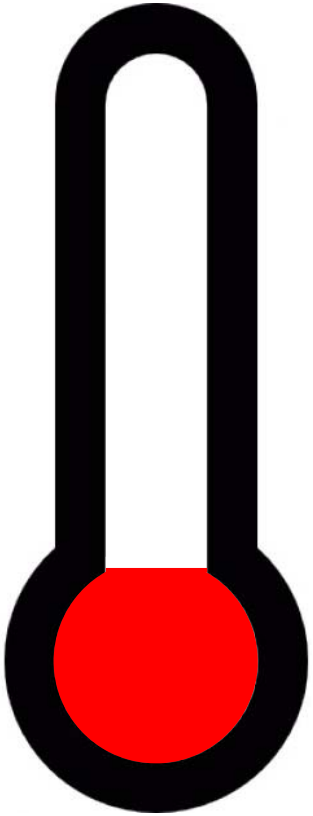
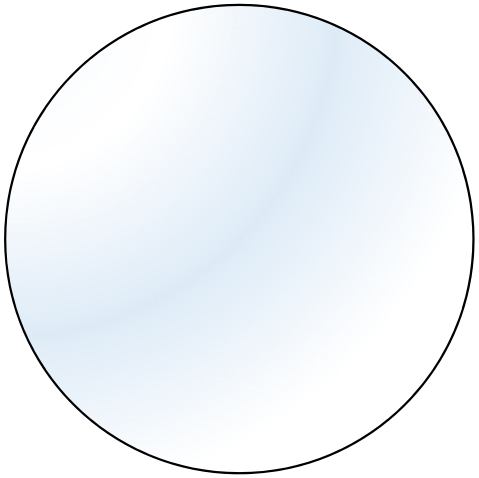


29 °C



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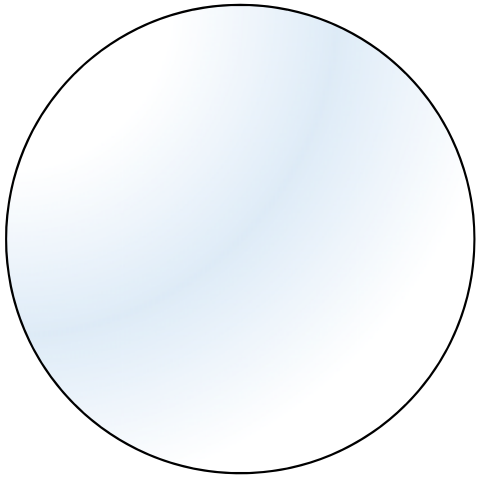

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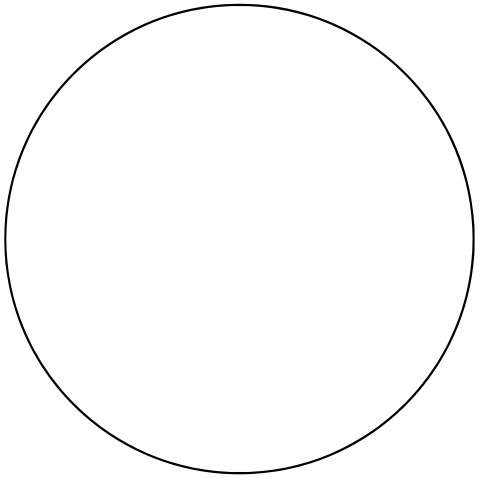

CF

1 cm

Results

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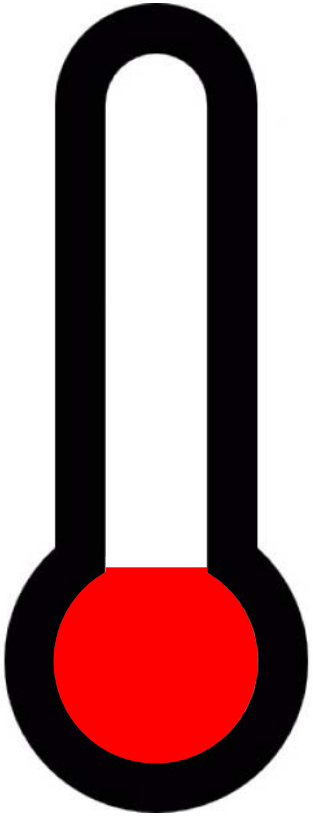
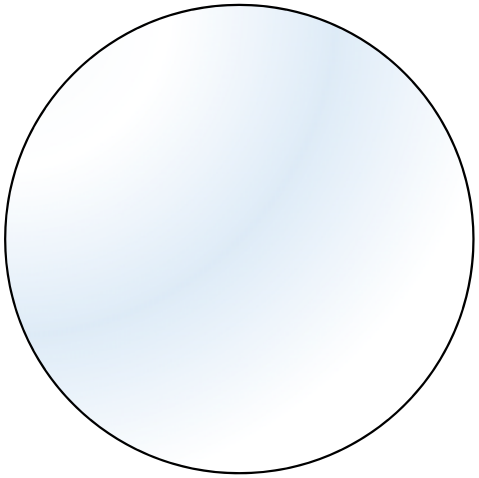


30 °C



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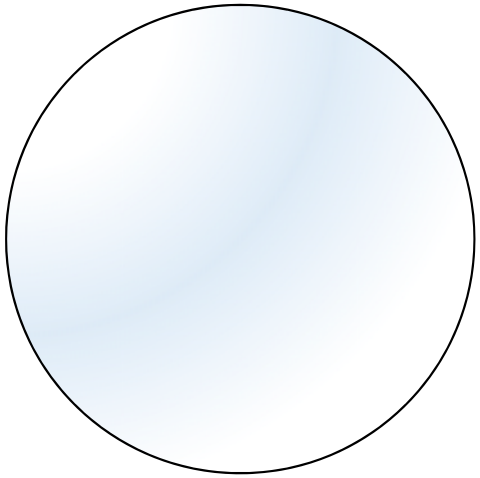

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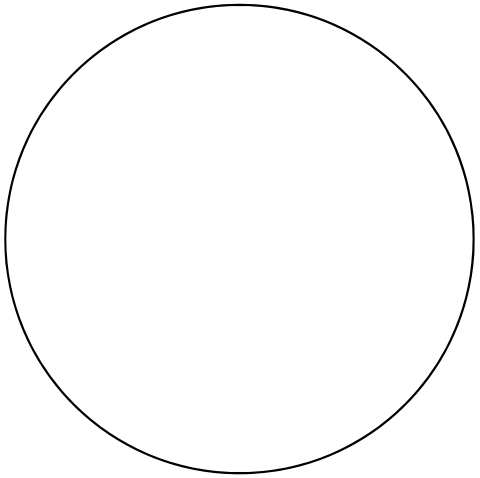

CF

1 cm

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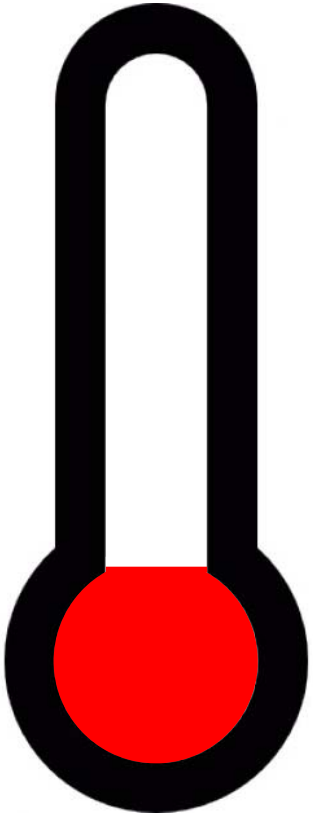
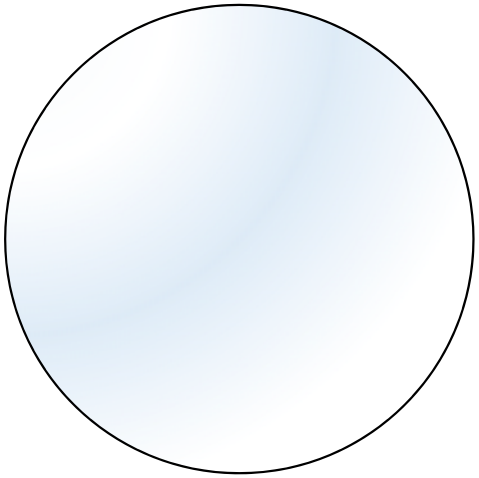


31 °C



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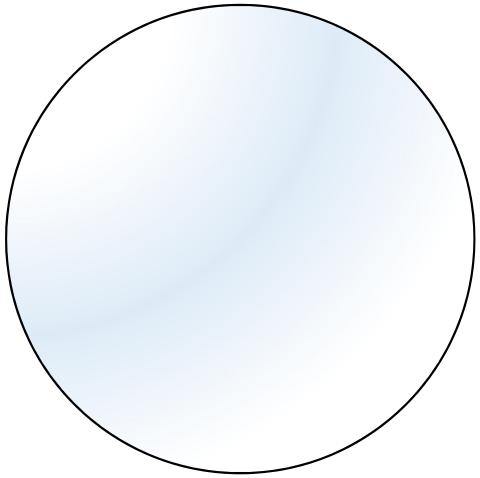

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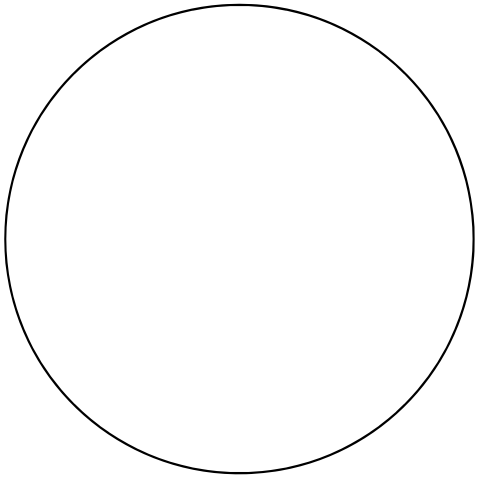

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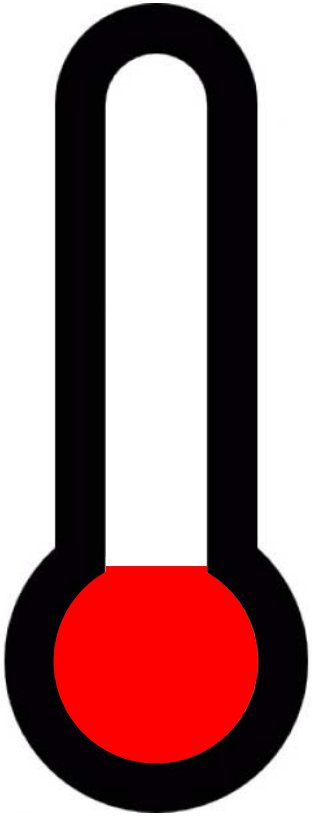
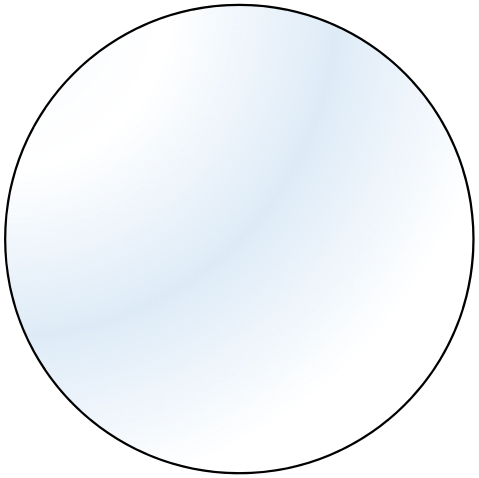


32 °C



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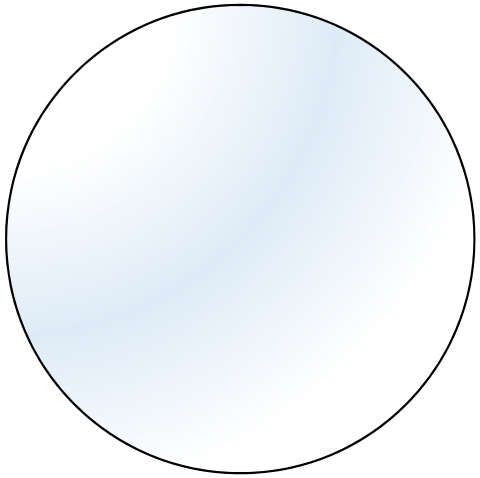

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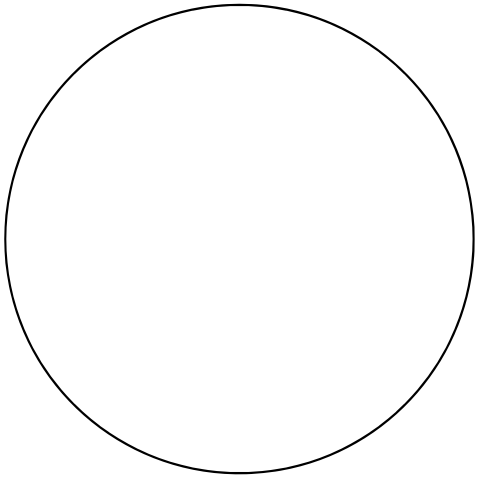

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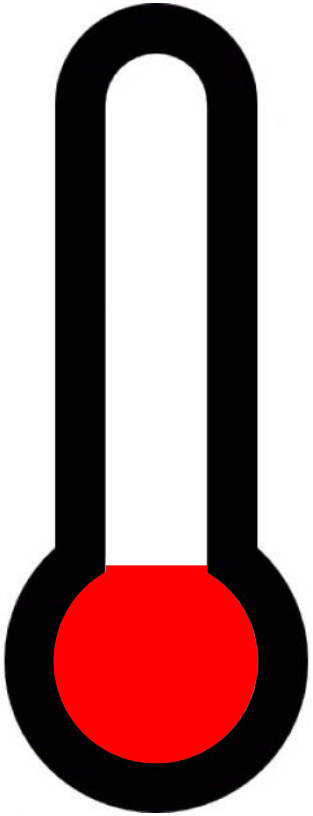

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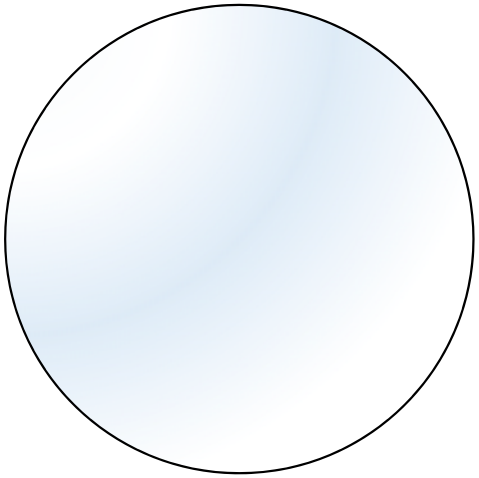

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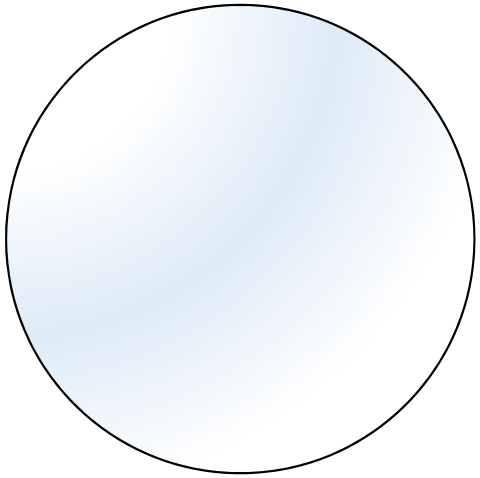

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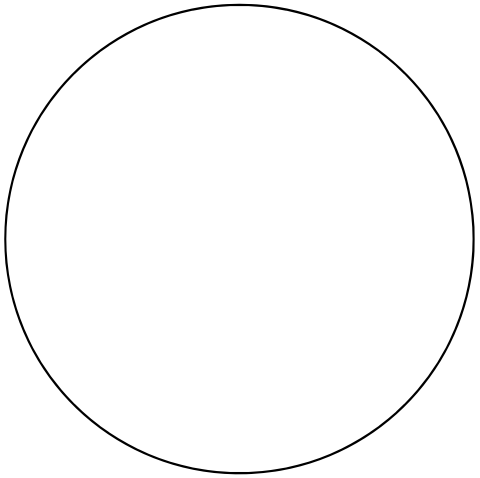

CF

1 cm

Results

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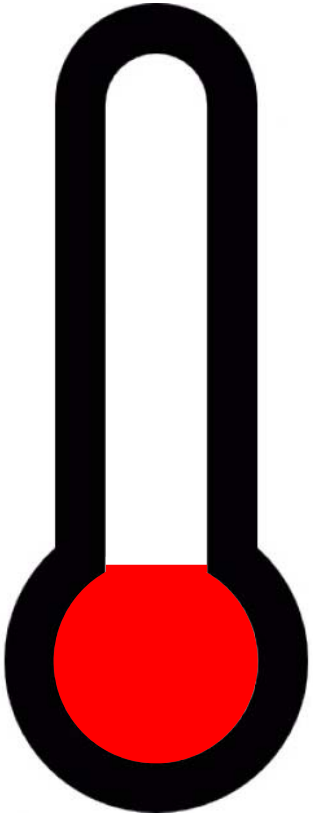
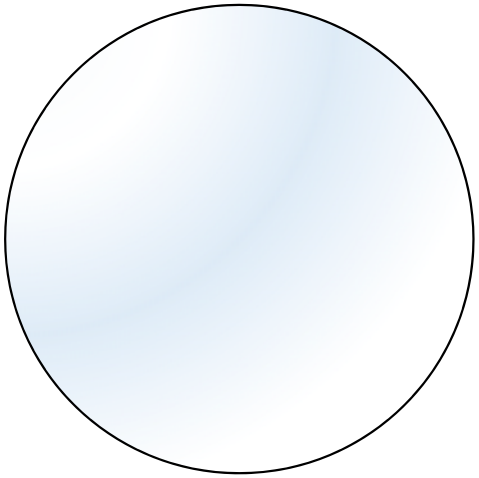


34 °C



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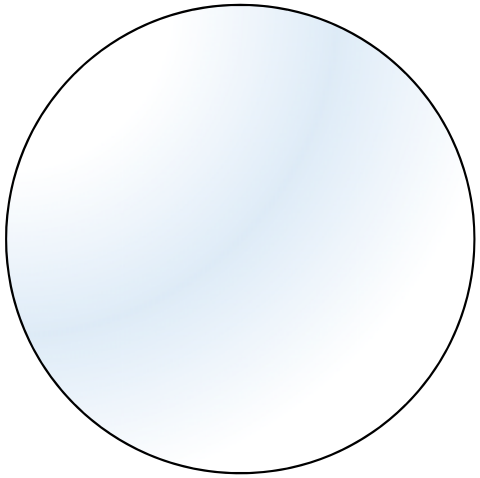

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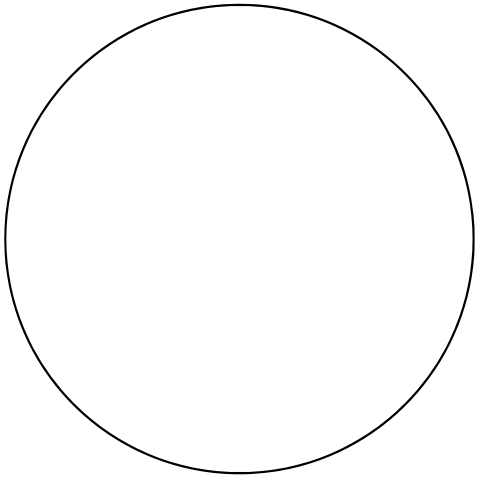

CF

1 cm

Results

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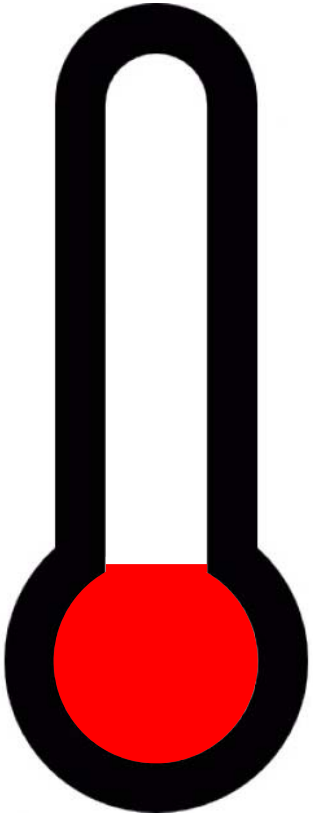
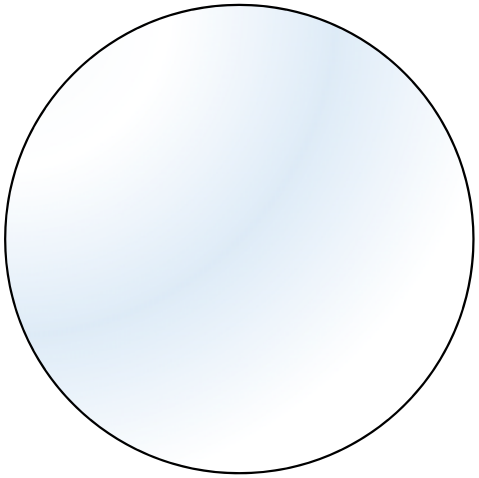


35 °C



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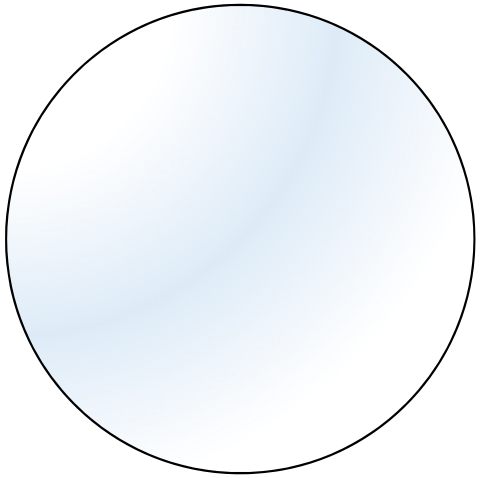
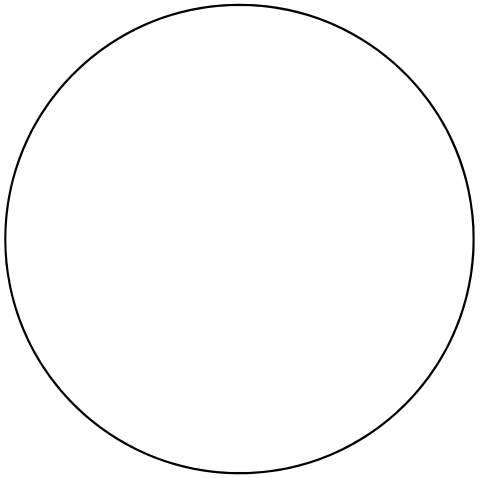


CNC-Na



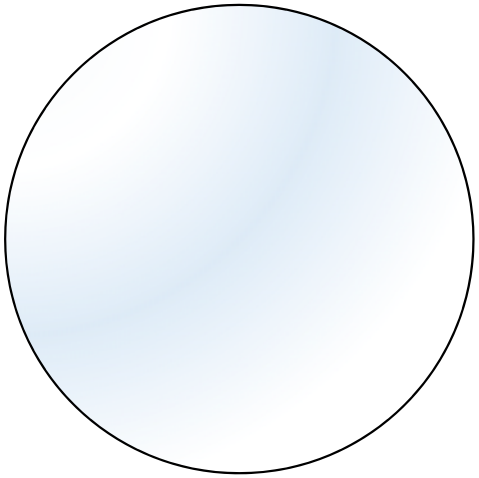
CF

1 cm

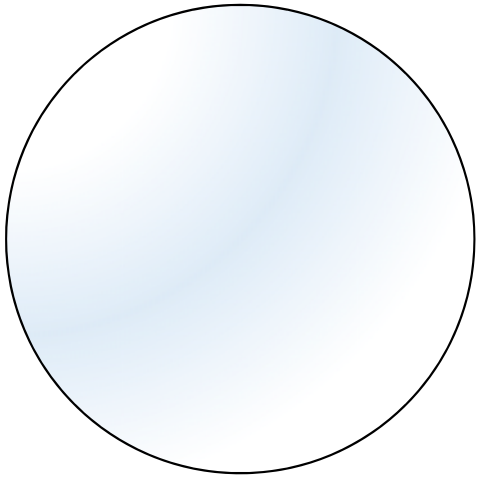
Results

THE UNIVERSITY OF BRITISH COLUMBIA

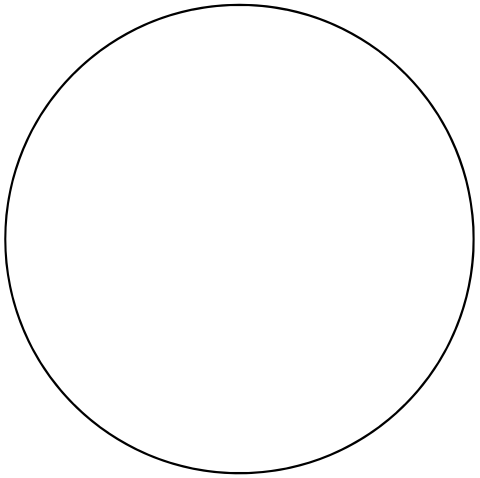
36 °C



CNC-H



CNC-Na

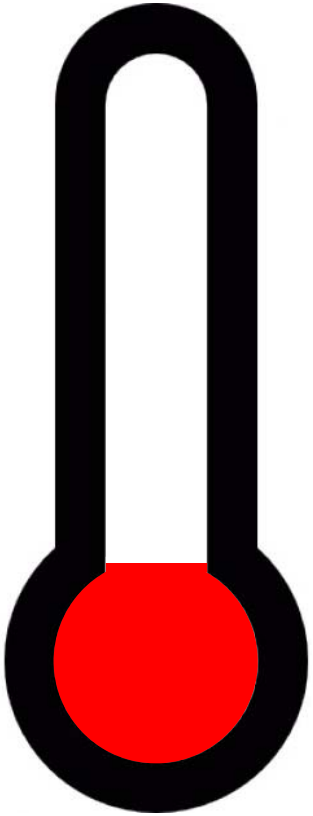


CF

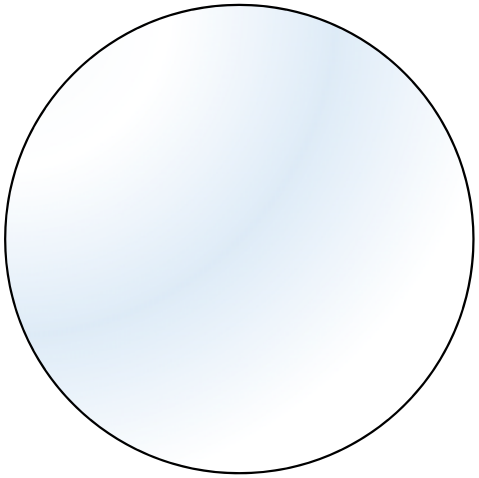
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



37 °C



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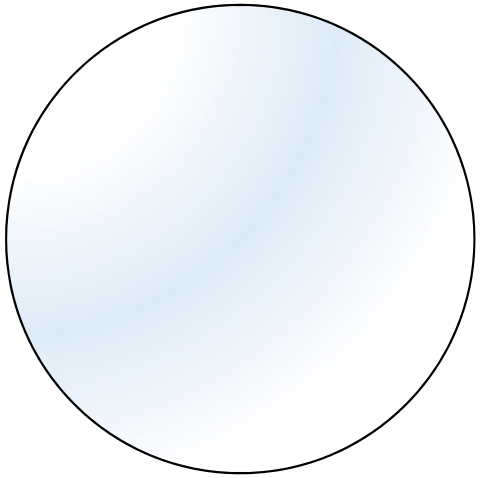

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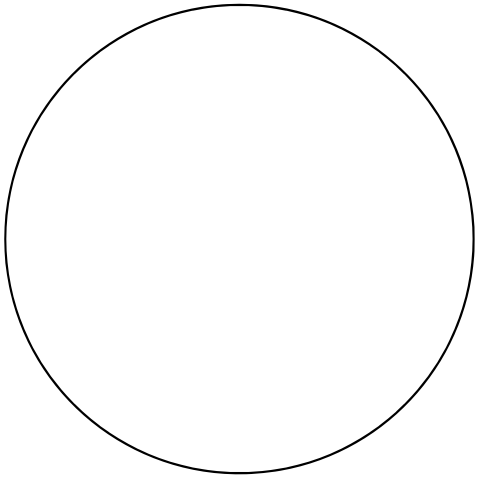
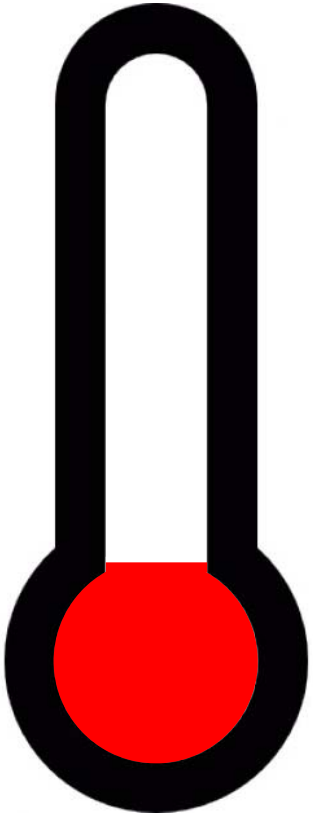


CF

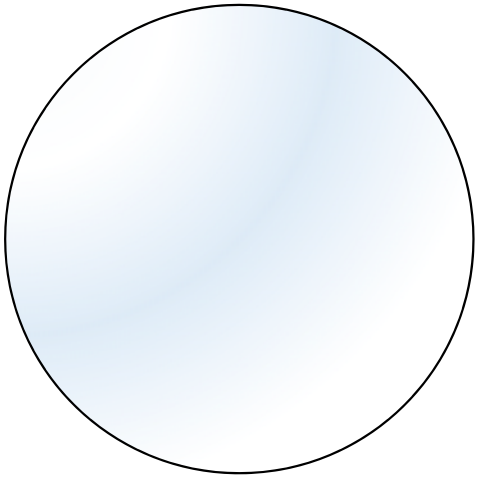
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



38 °C



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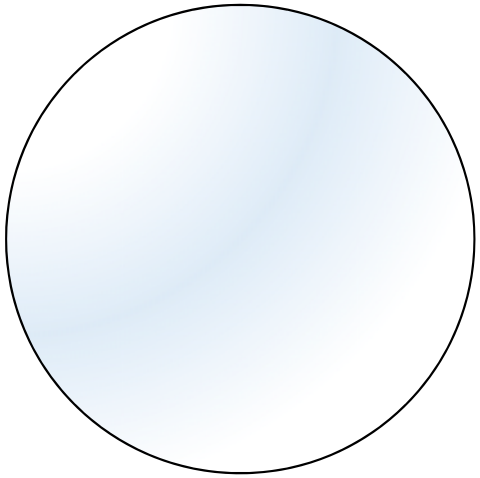

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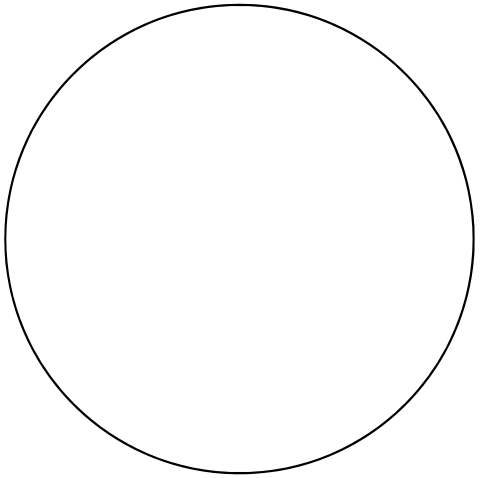
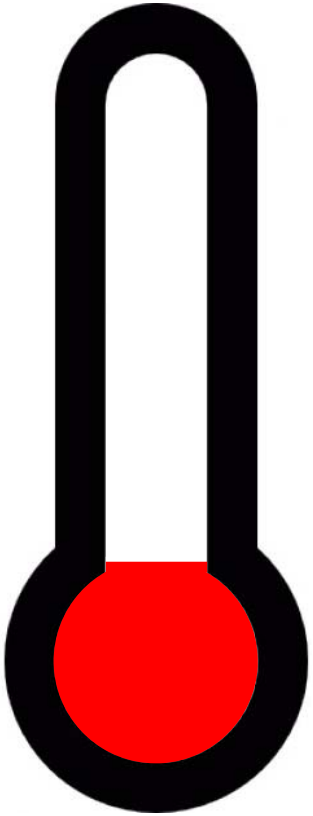


CF

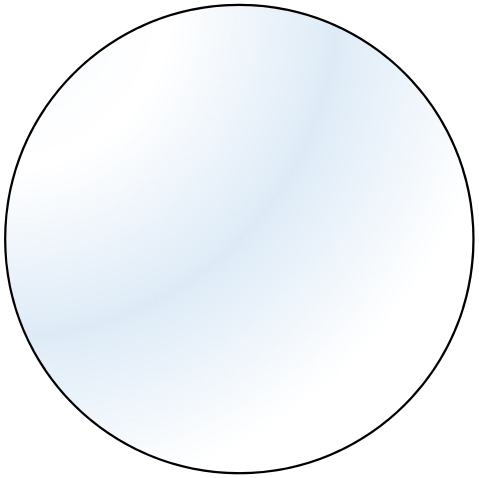
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



39 °C



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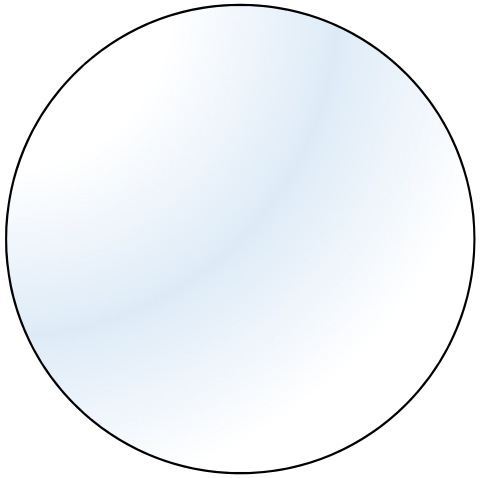
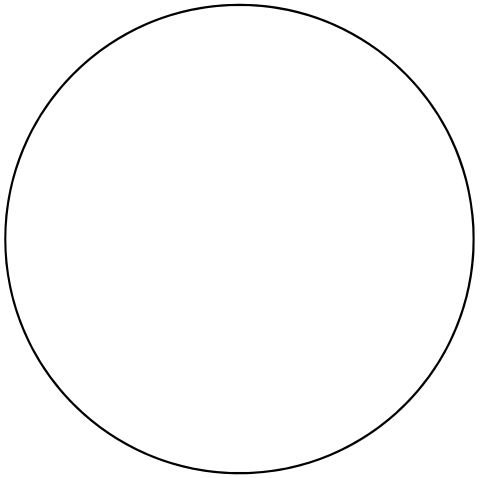


CNC-Na

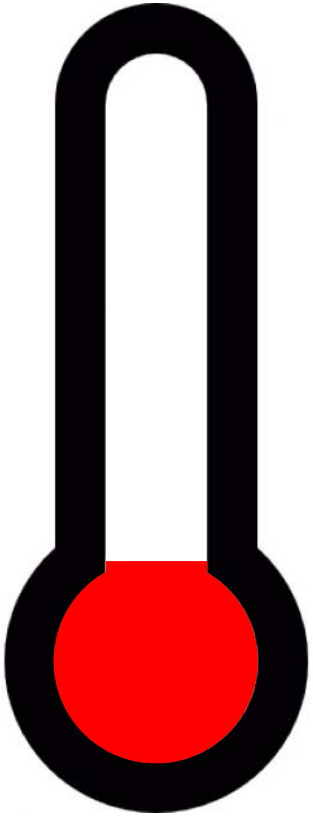


CF

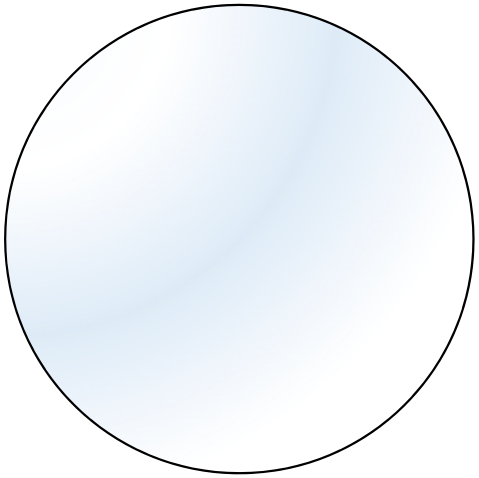
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



40 °C



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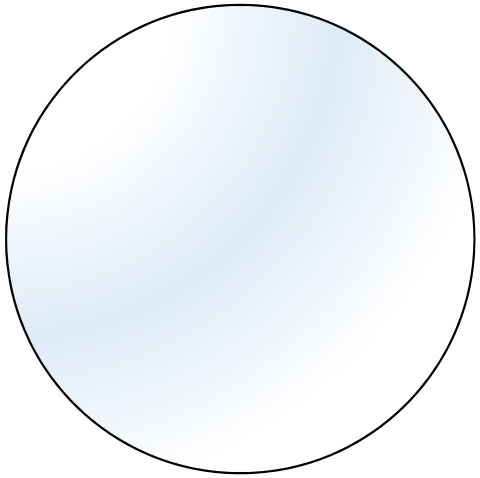

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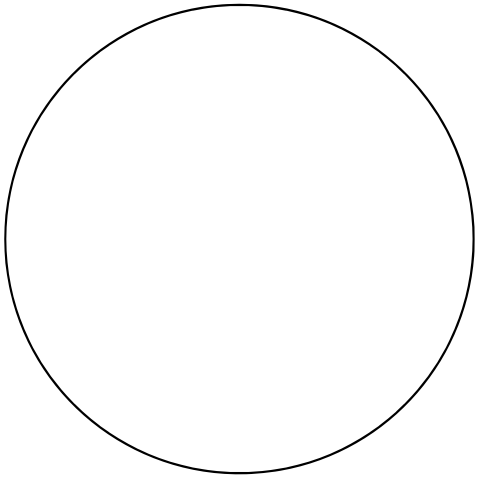
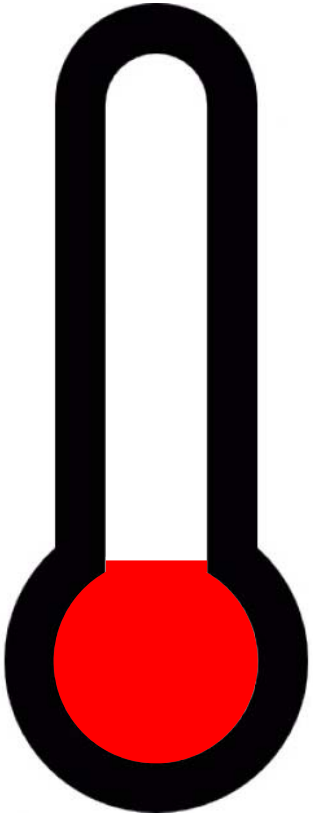


CF

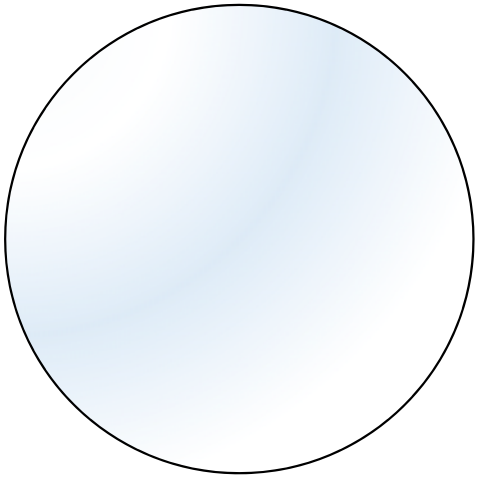
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



41 °C



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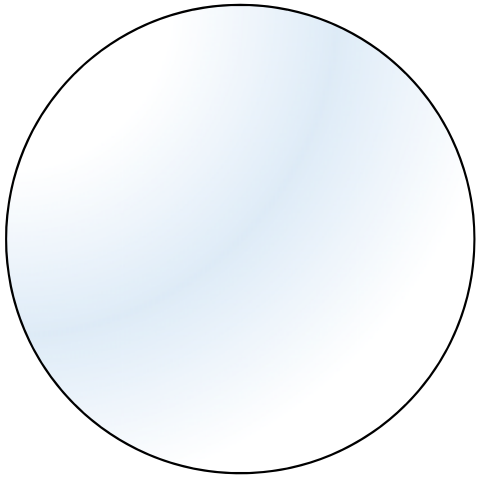

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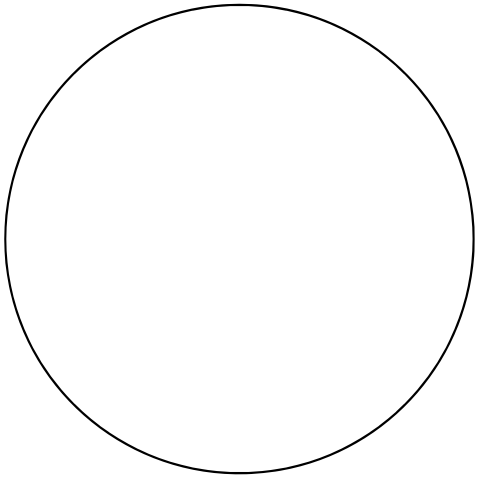
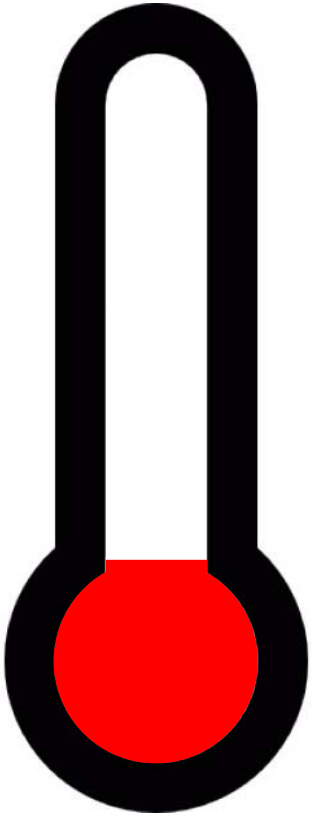


CF

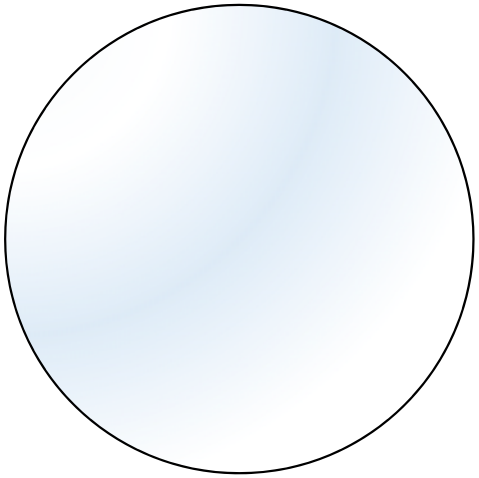
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



42 °C



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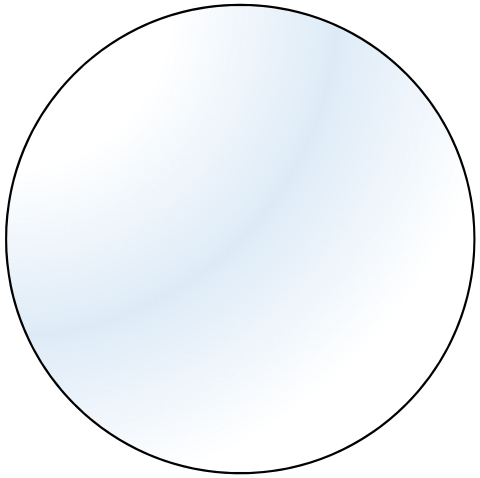

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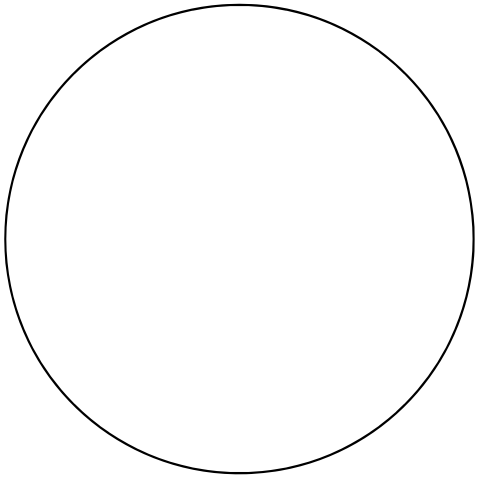
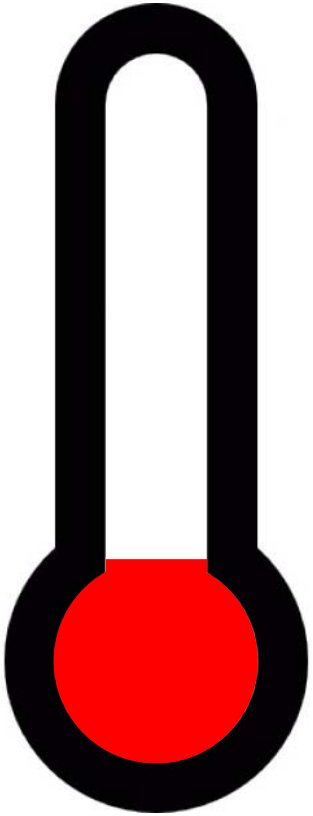


CF

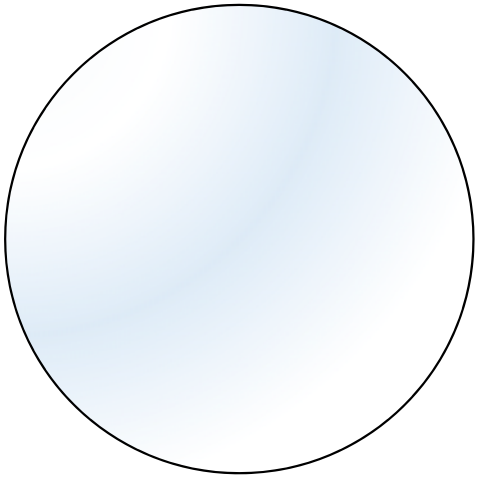
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



43 °C



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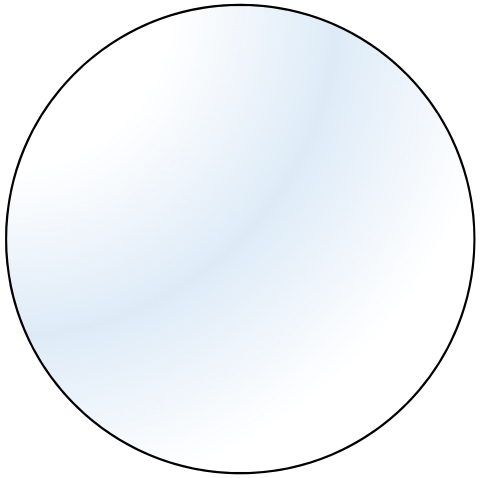

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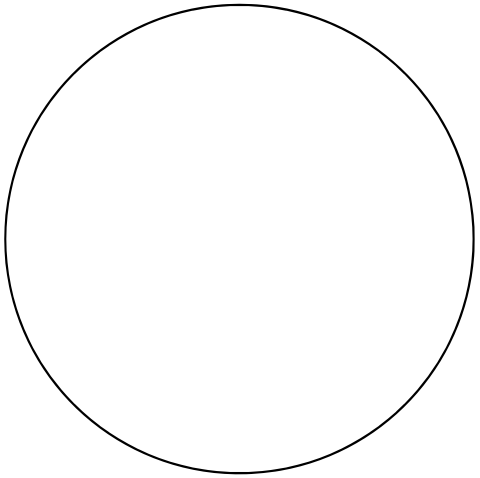
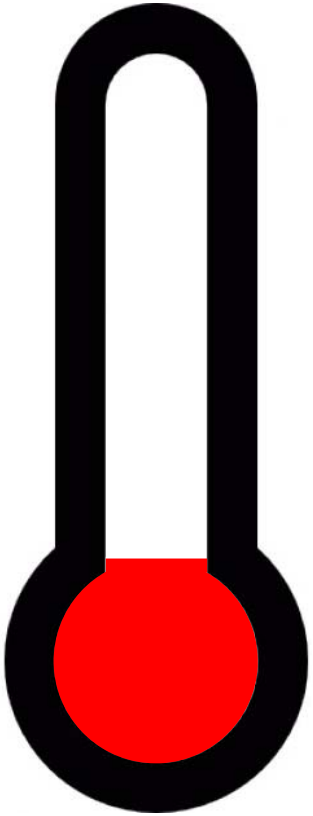


CF

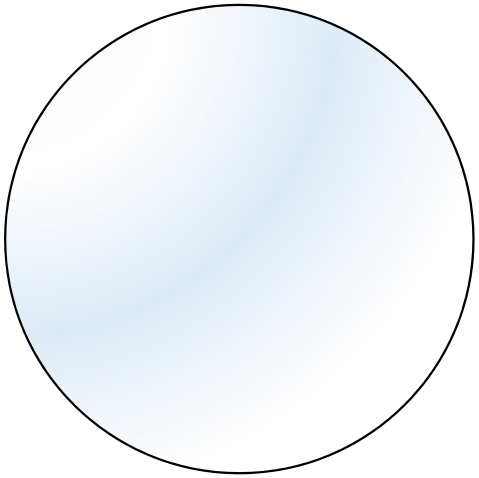
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



44 °C



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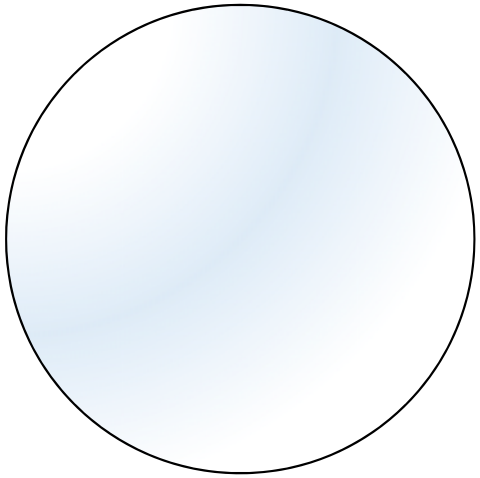

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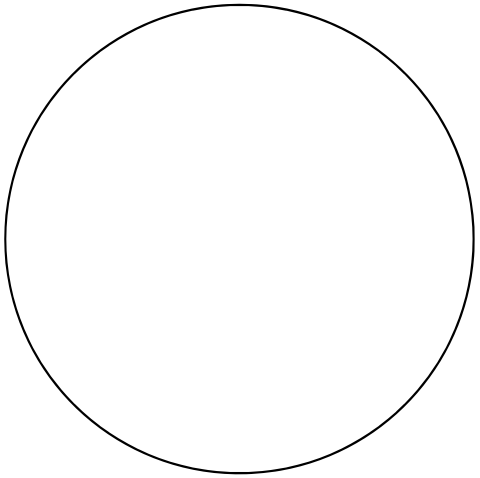
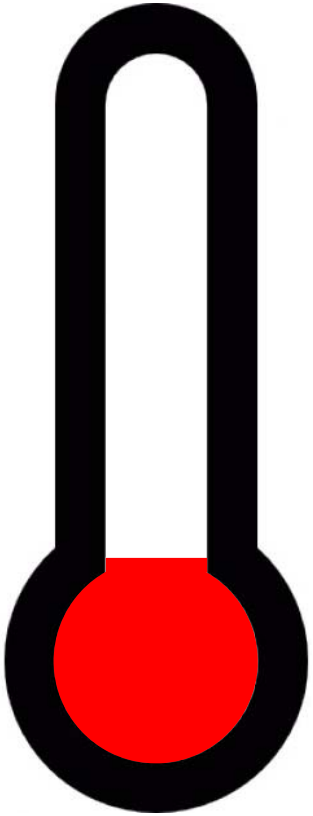


CF

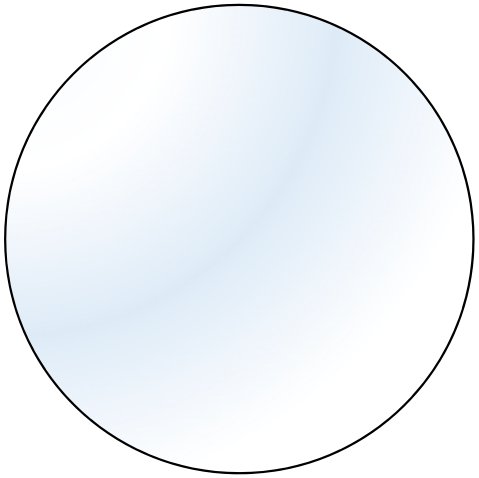
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



45 °C



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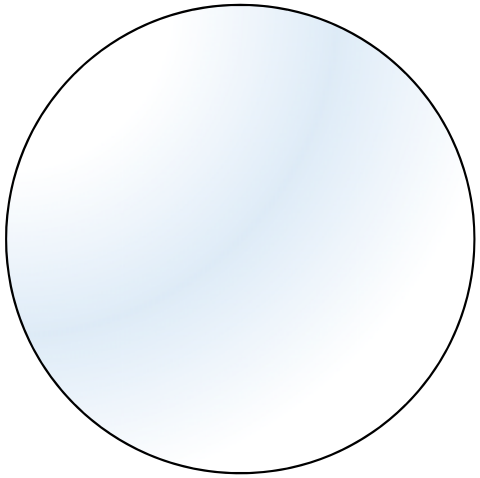

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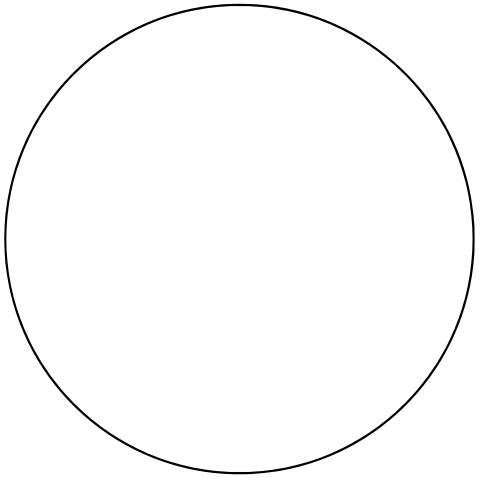
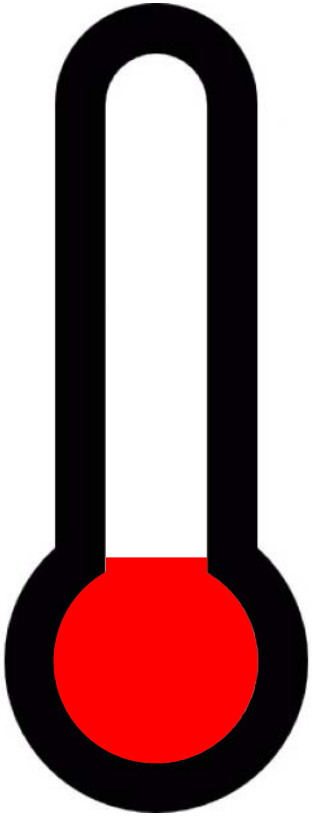


CF

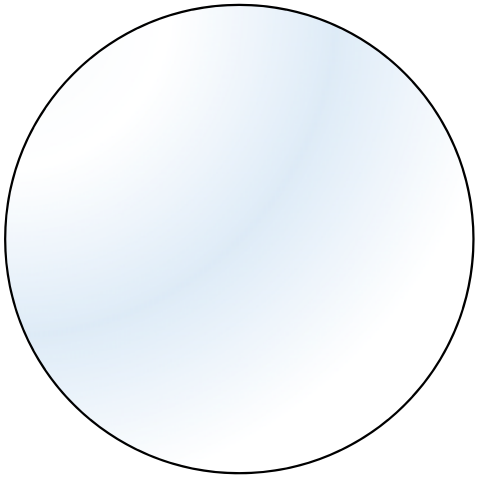
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



46 °C



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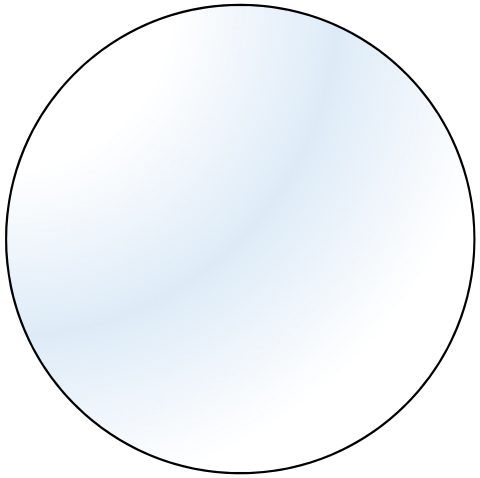

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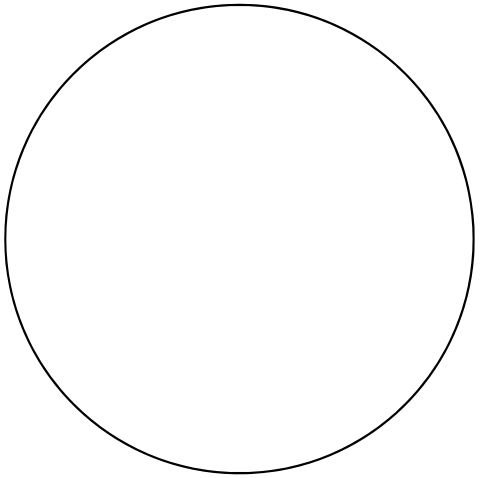
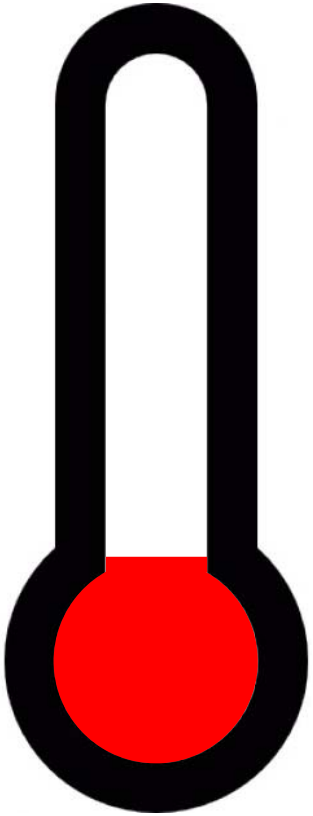


CF

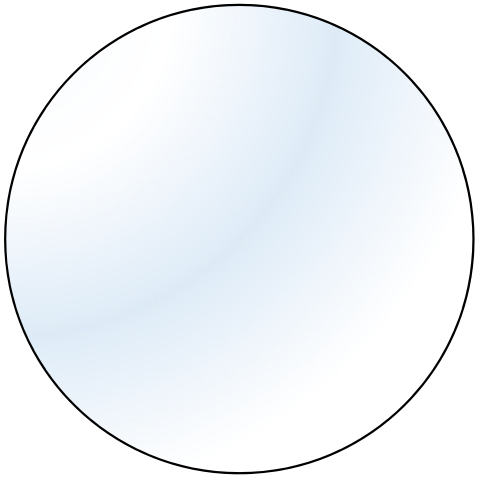
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



47 °C



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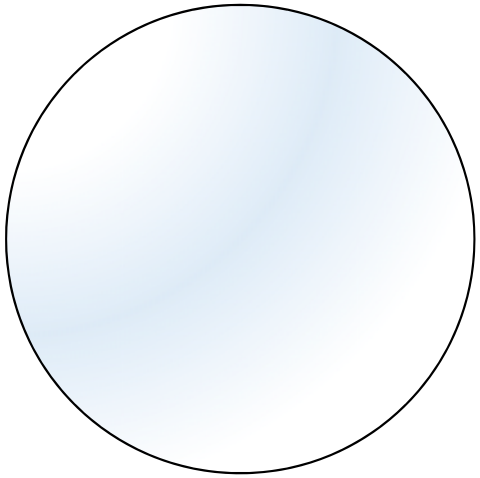

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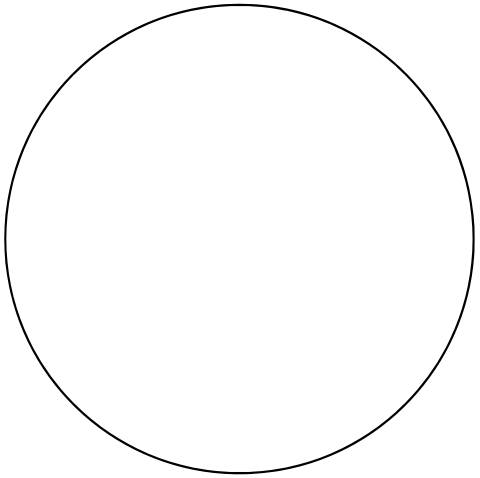
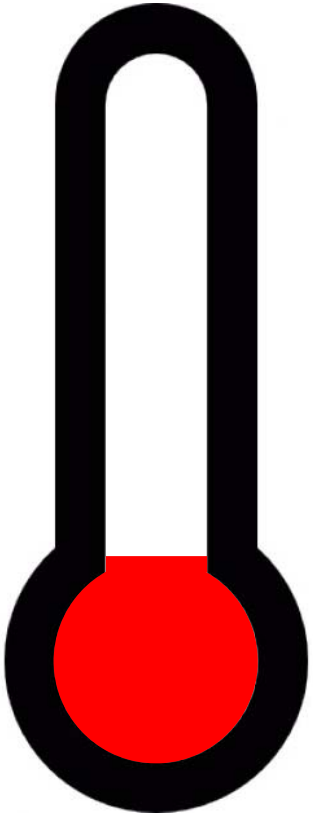


CF

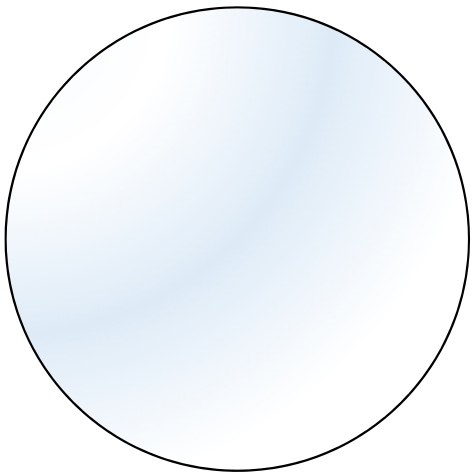
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



48 °C



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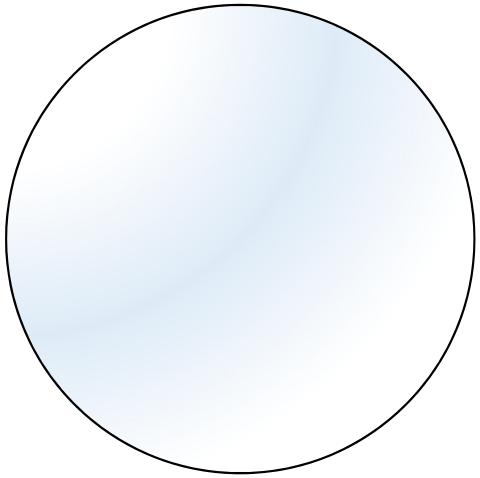

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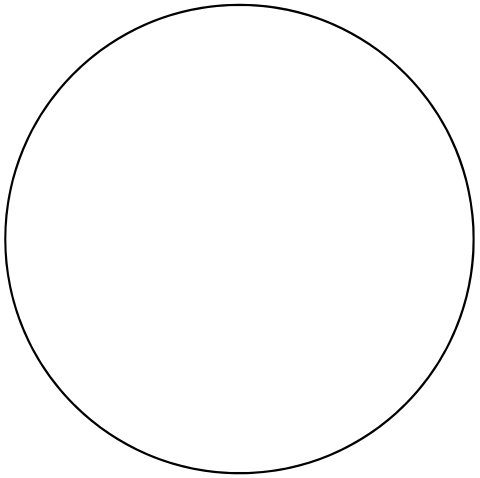
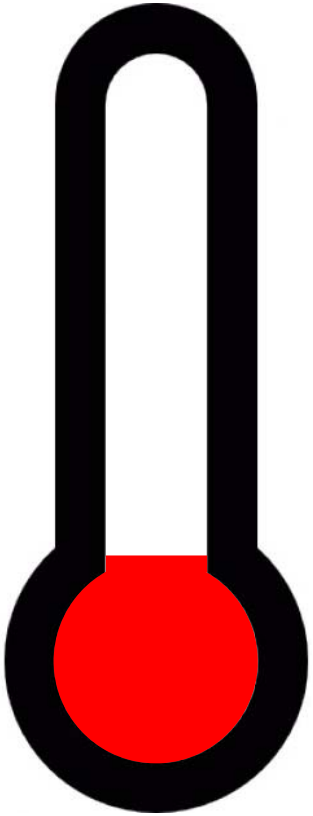


CF

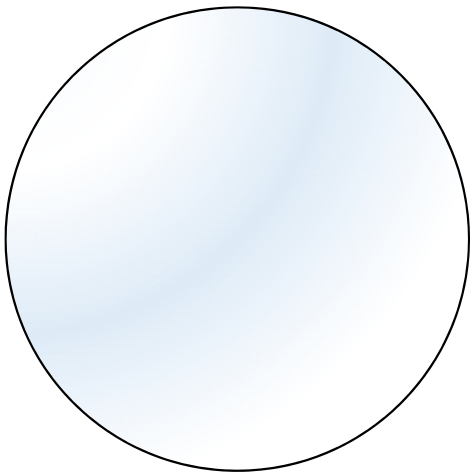
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



49 °C



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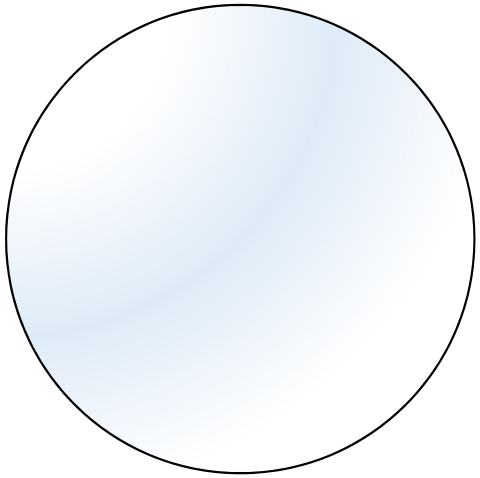

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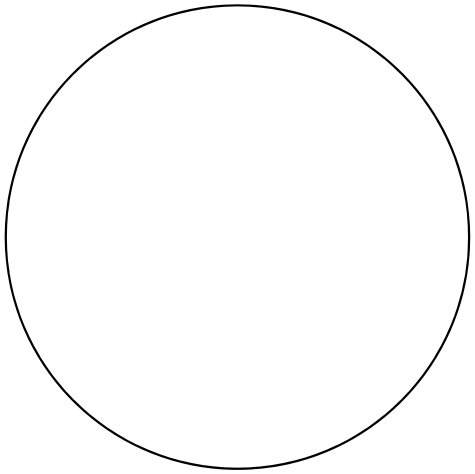
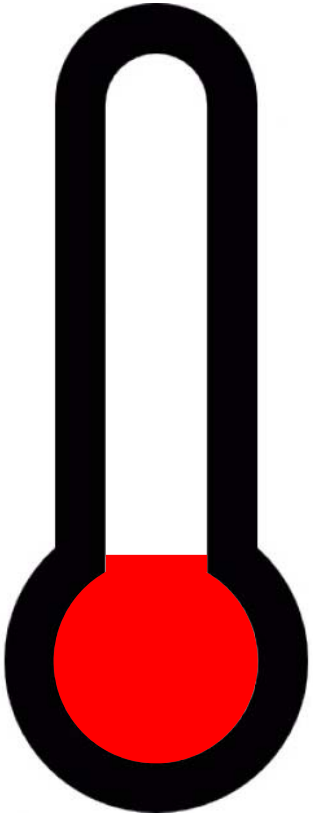


CF

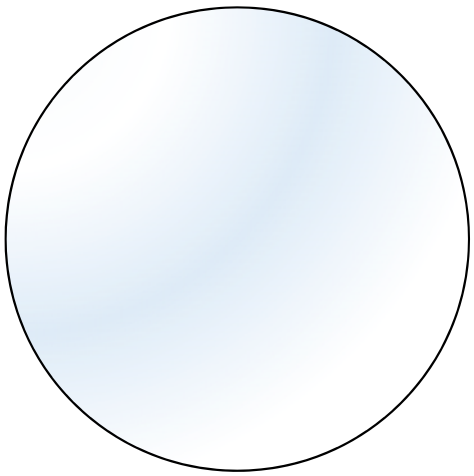
1 cm

Results

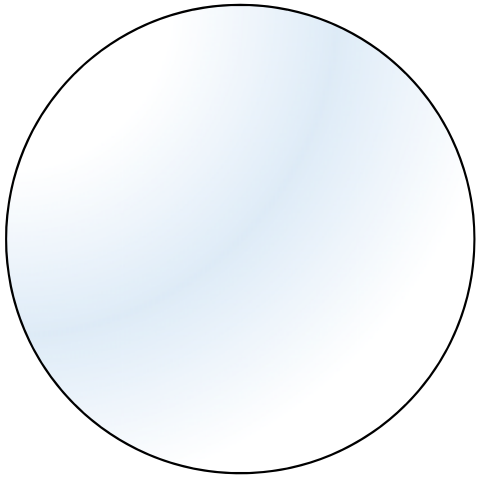
THE UNIVERSITY OF BRITISH COLUMBIA



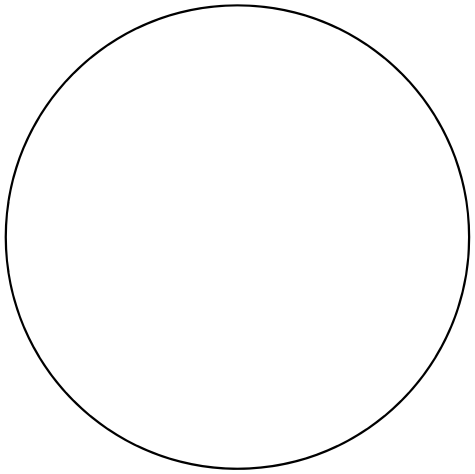
50 °C



CNC-H



CNC-Na

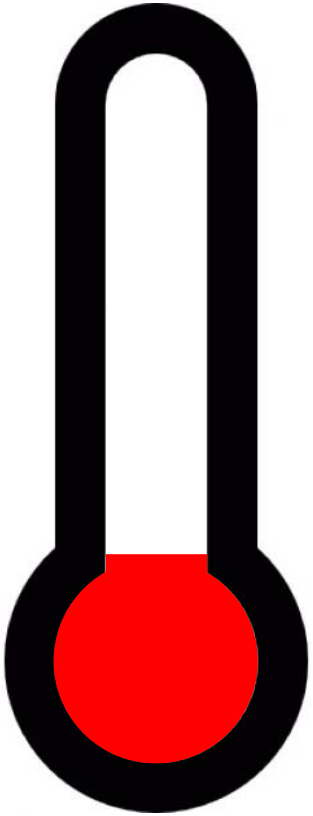


CF

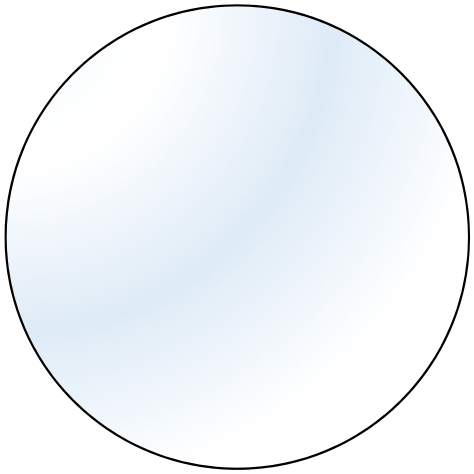
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



51 °C



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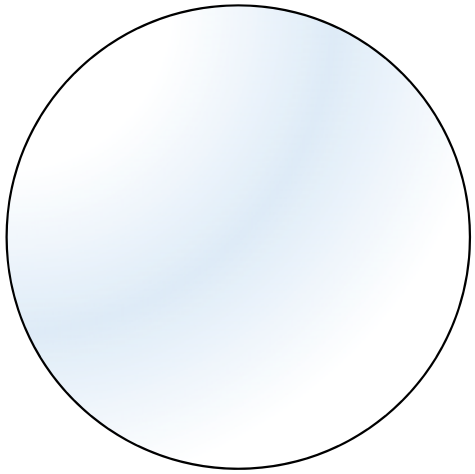

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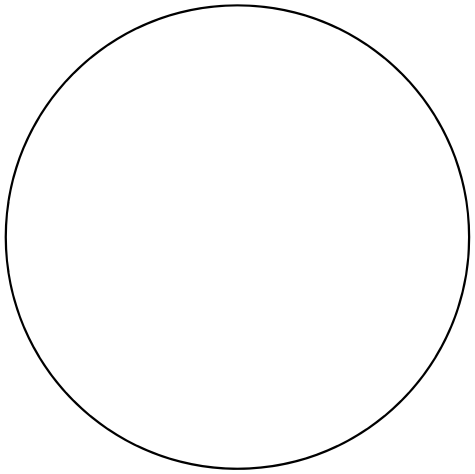
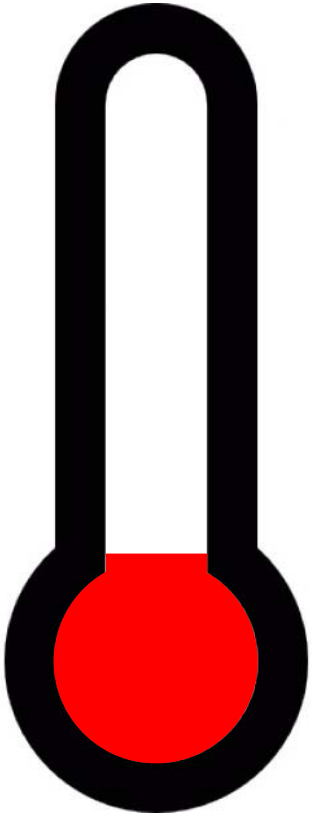


CF

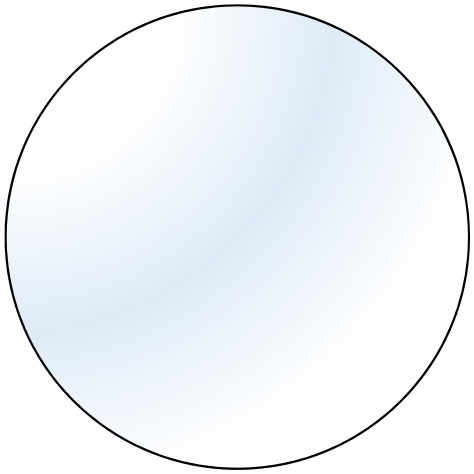
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



52 °C



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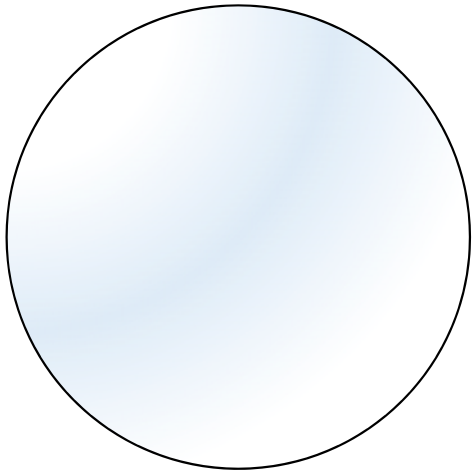

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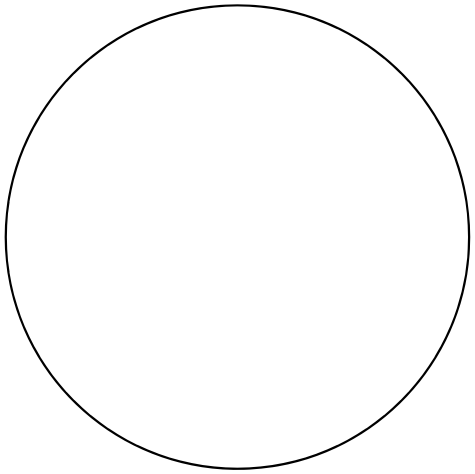
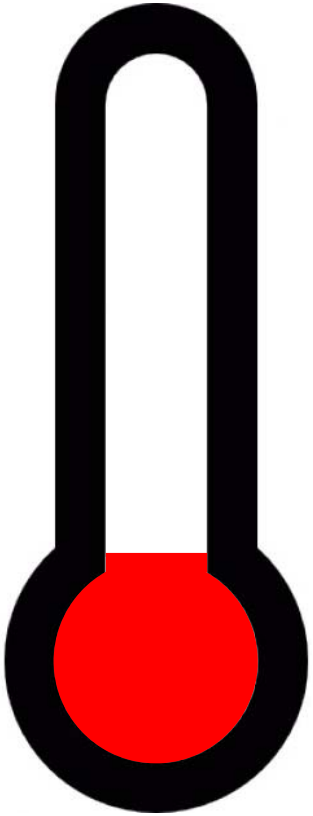


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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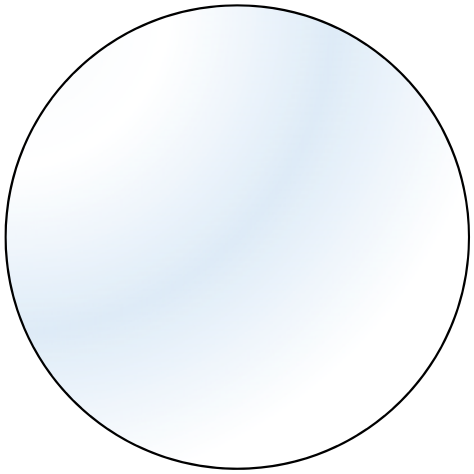

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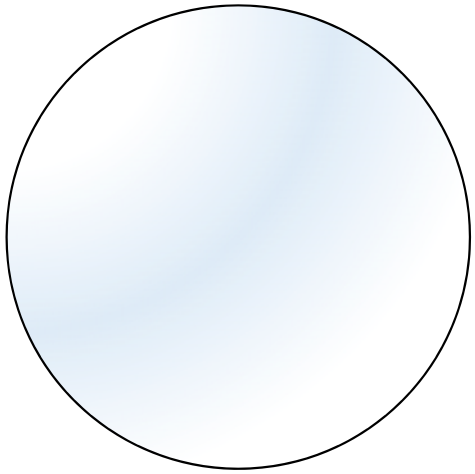

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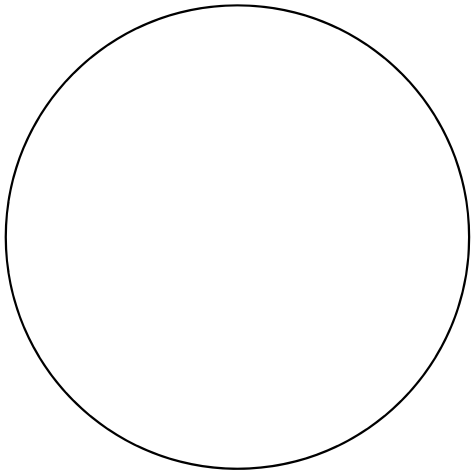
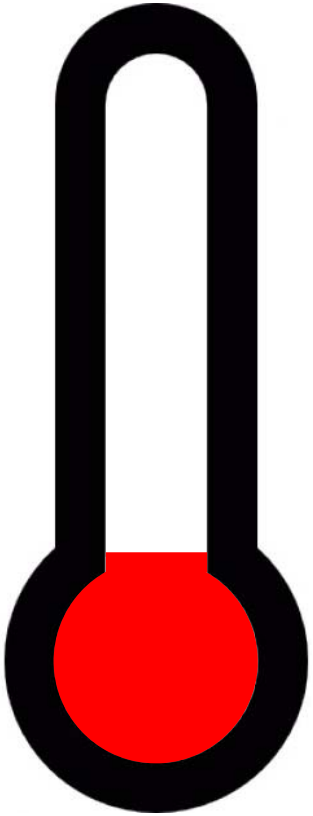


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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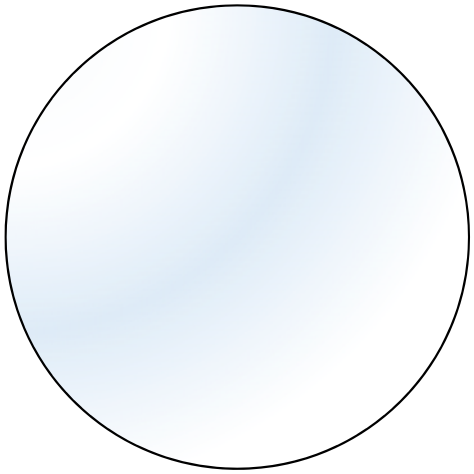

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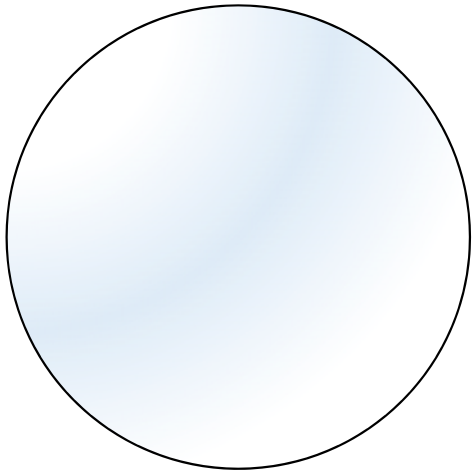

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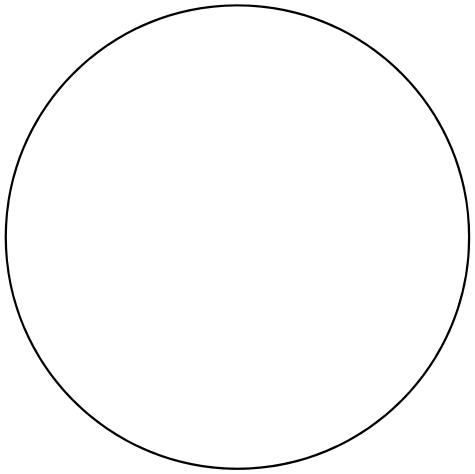
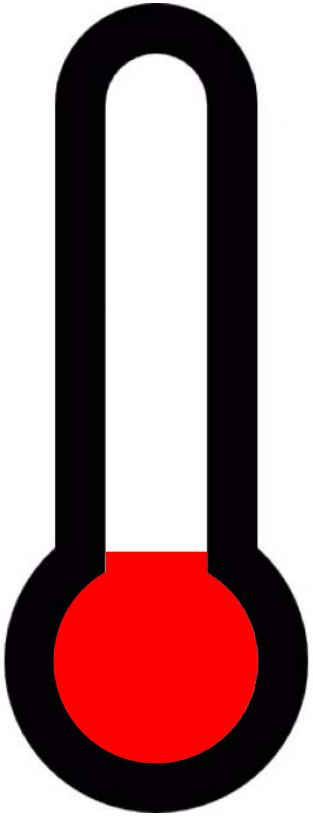


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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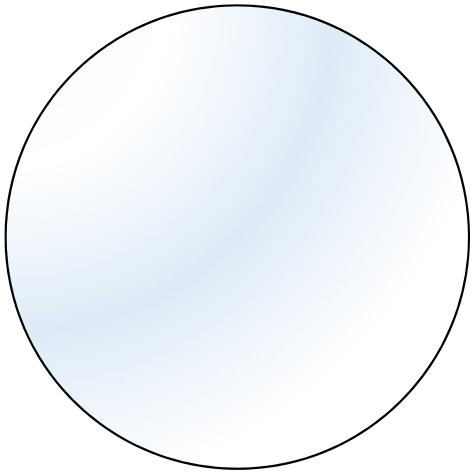

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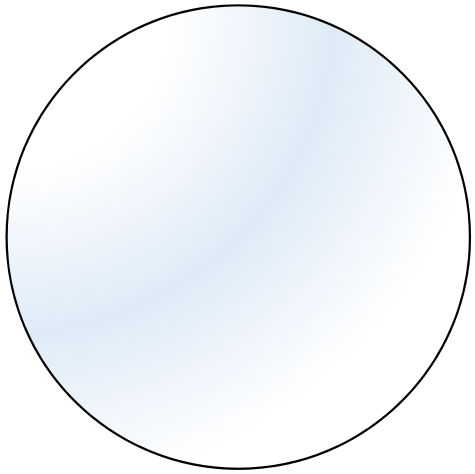

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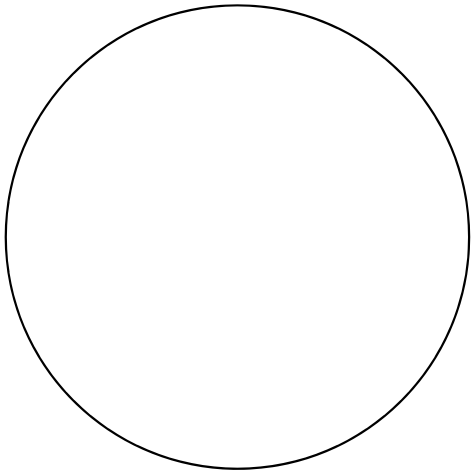

CF

1 cm

Results

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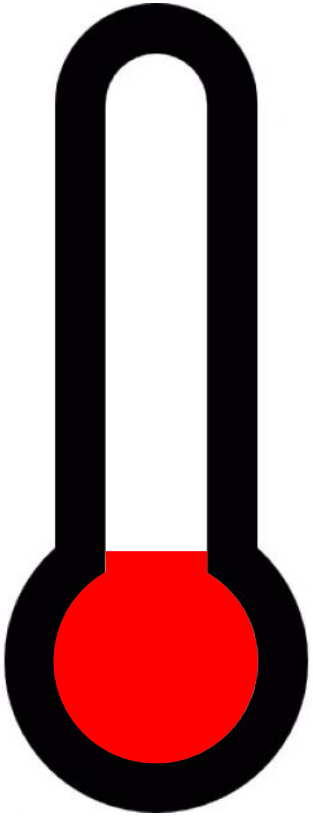
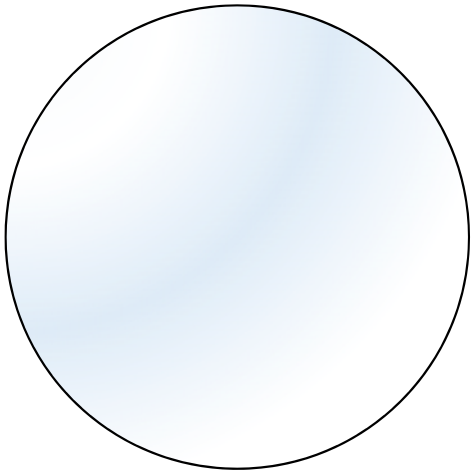


56 °C



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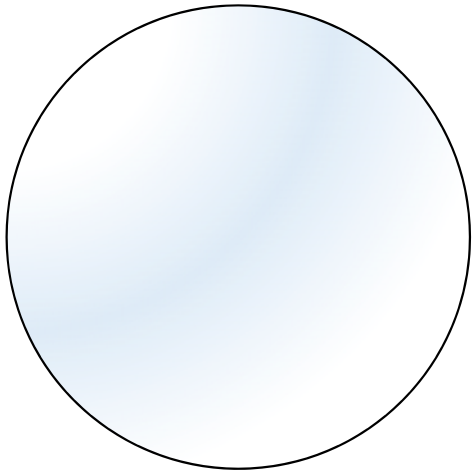

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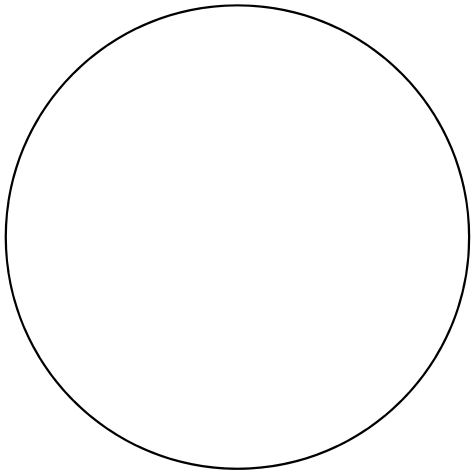
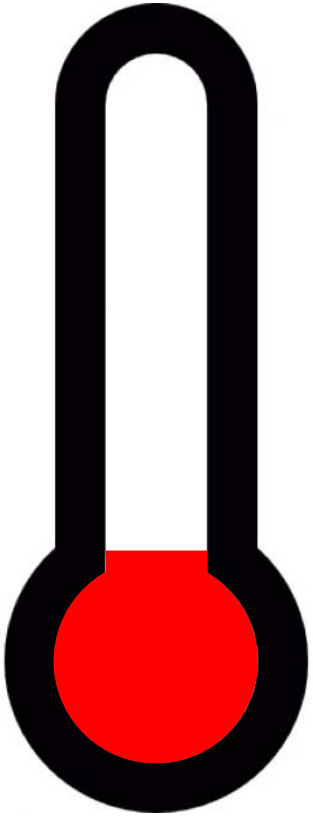


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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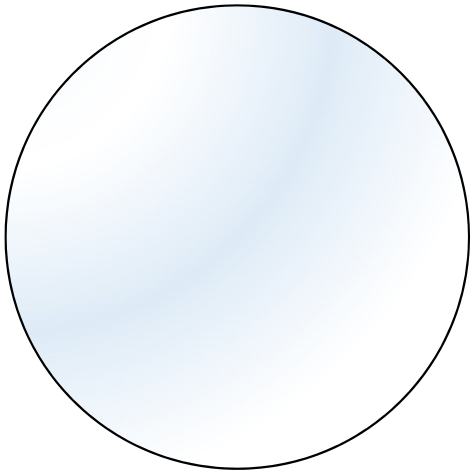

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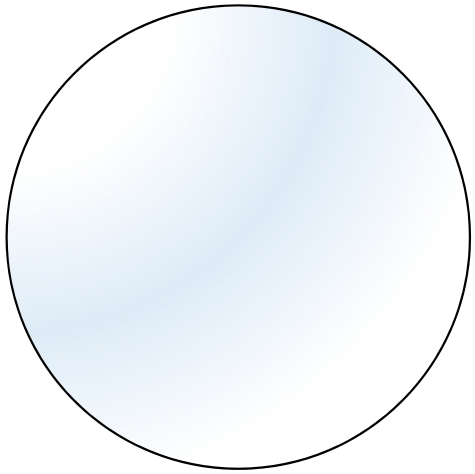

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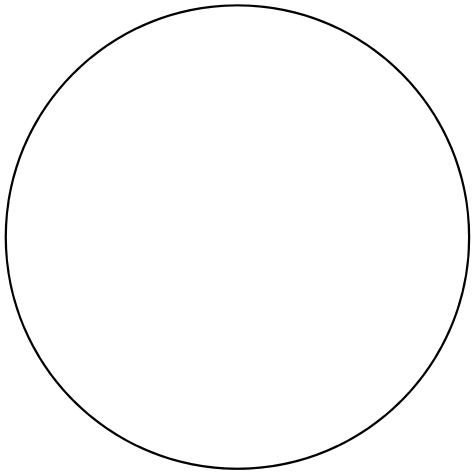

CF

1 cm

Results

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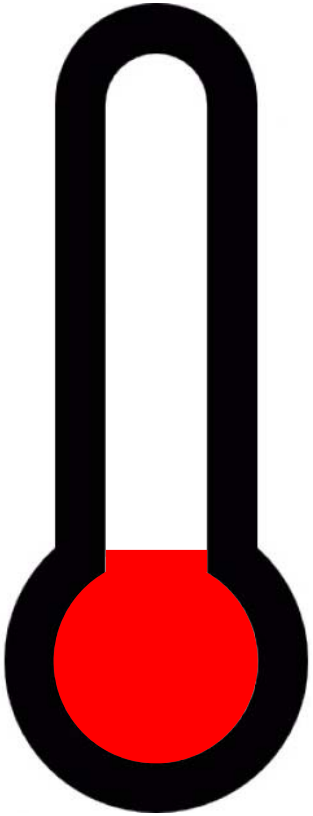

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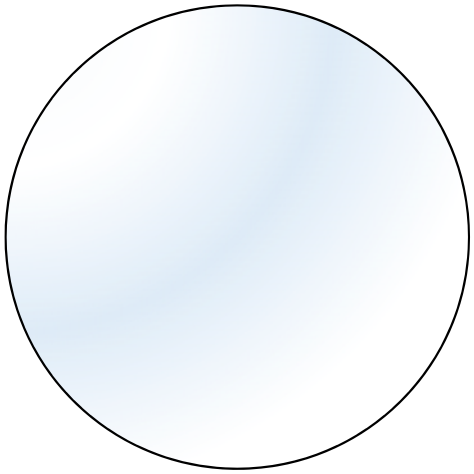

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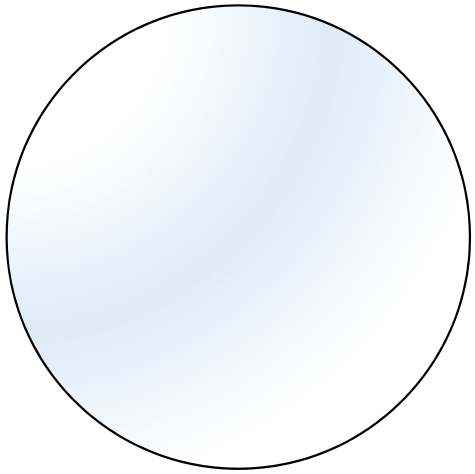

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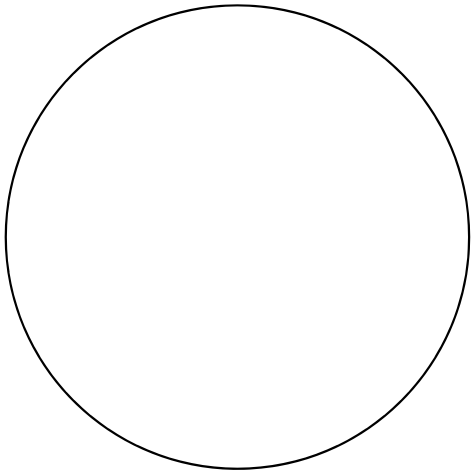
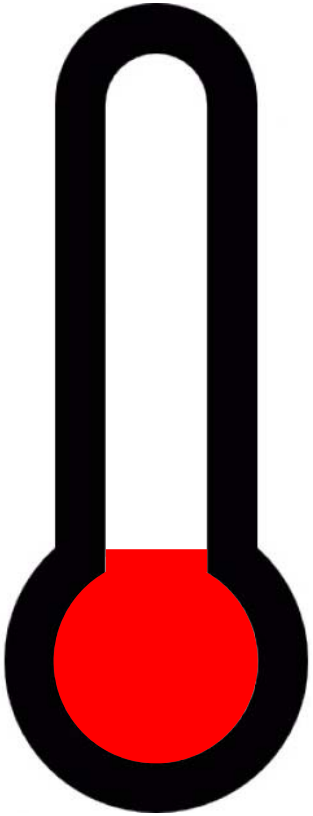


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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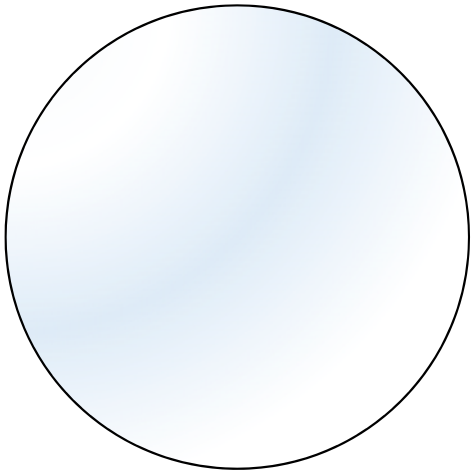

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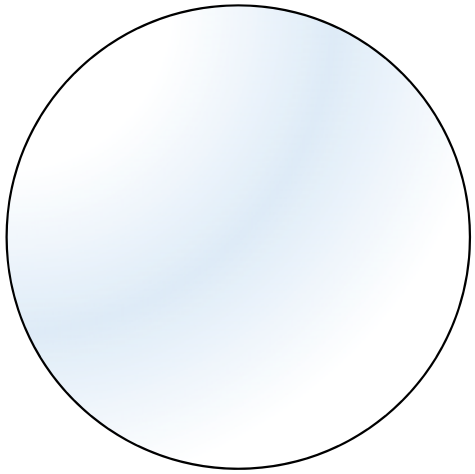

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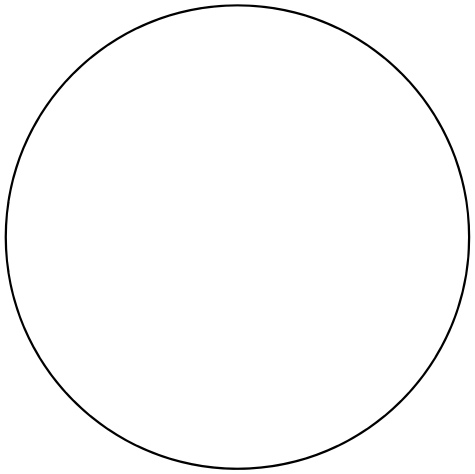

CF

1 cm

Results

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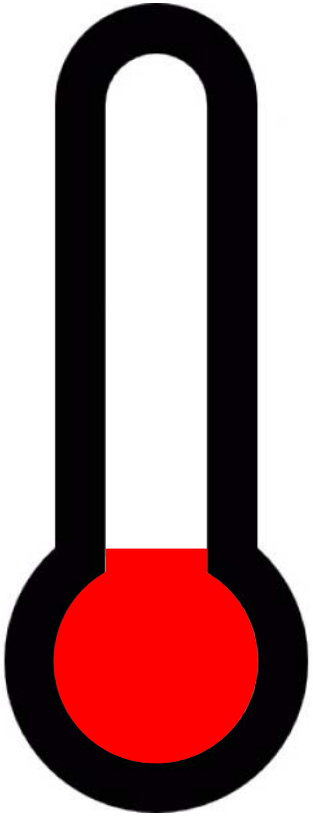

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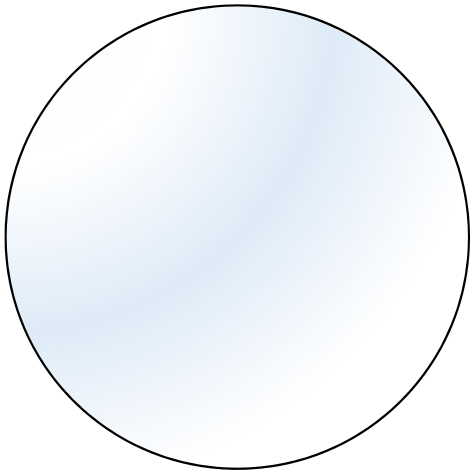

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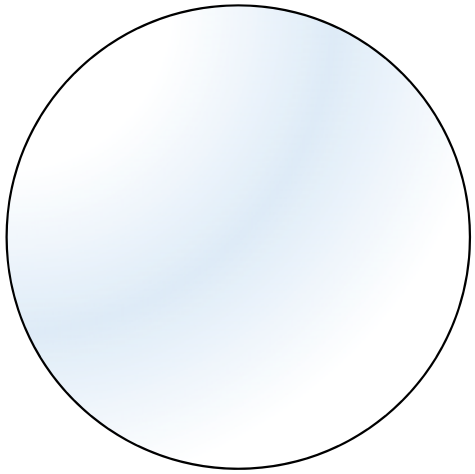

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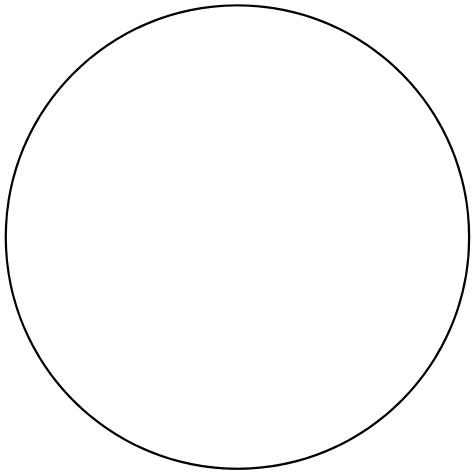

CF

1 cm

Results

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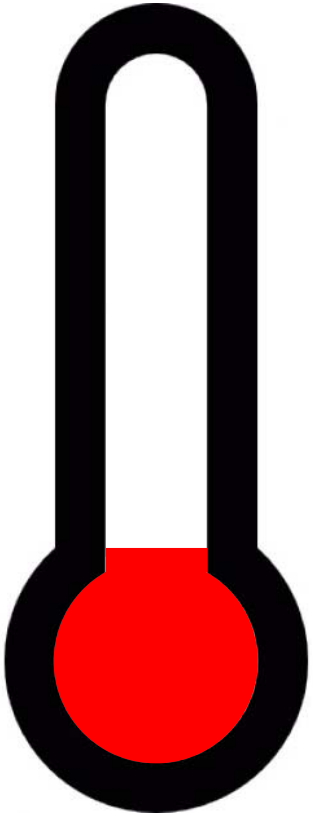
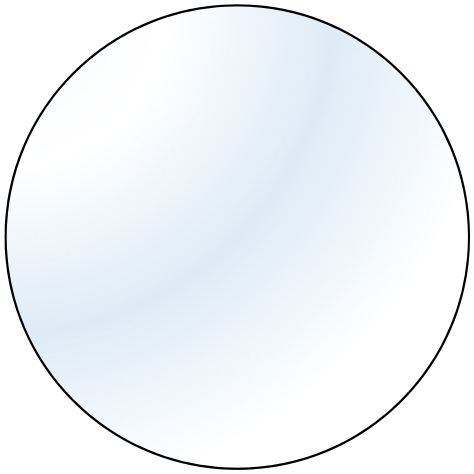


61 °C



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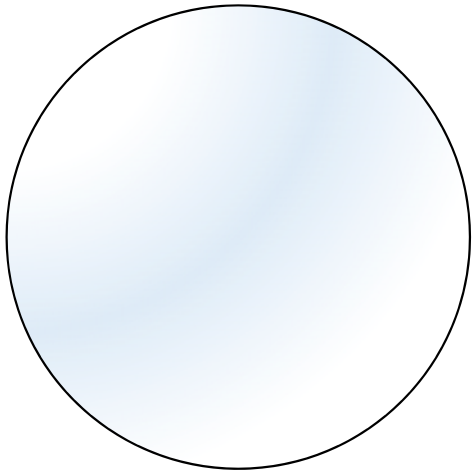

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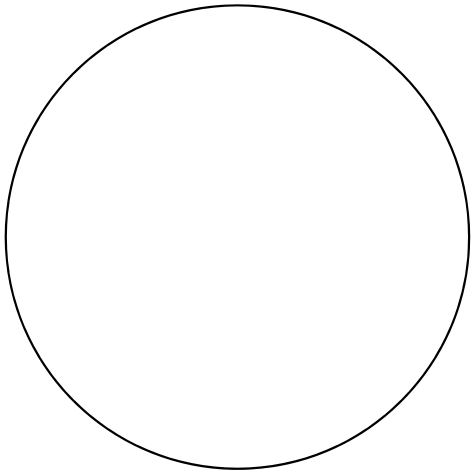

CF

1 cm

Results

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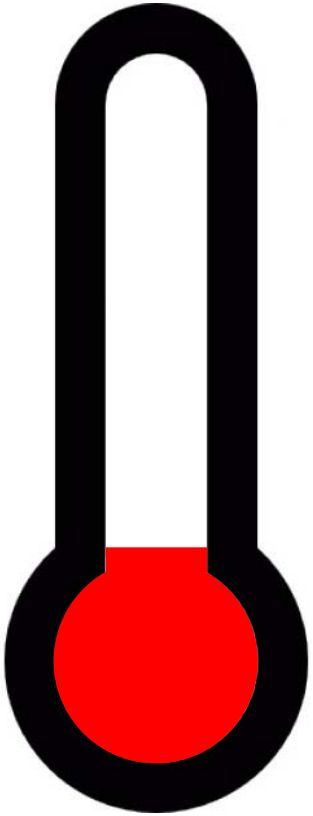

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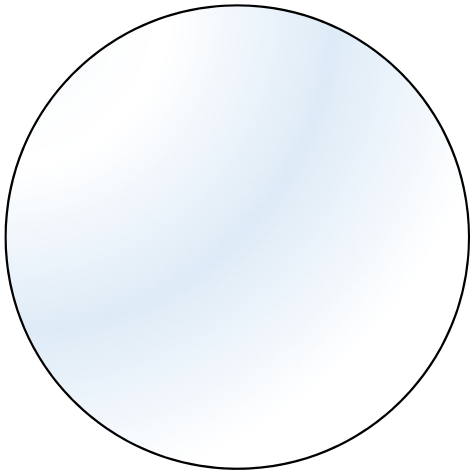

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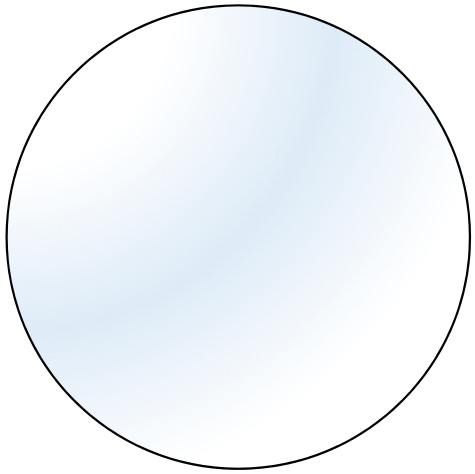

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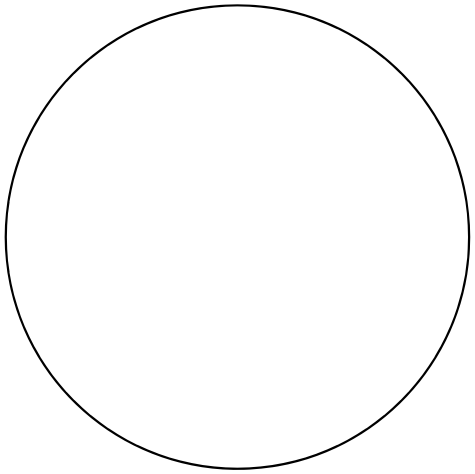
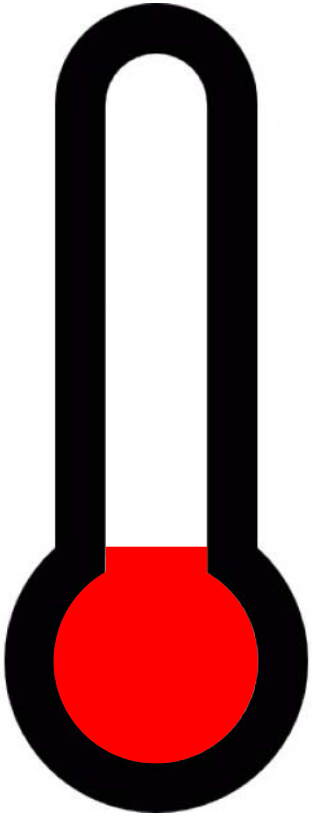


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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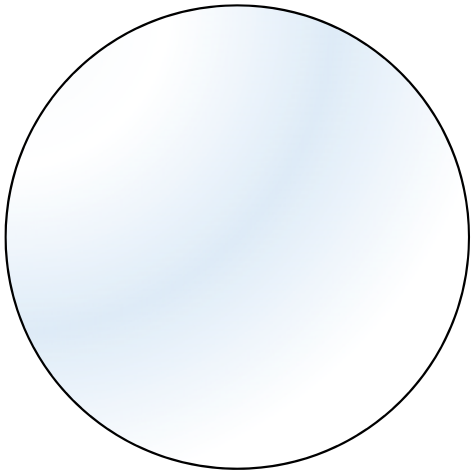

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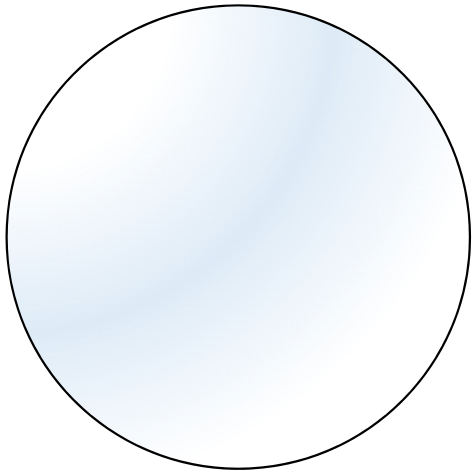

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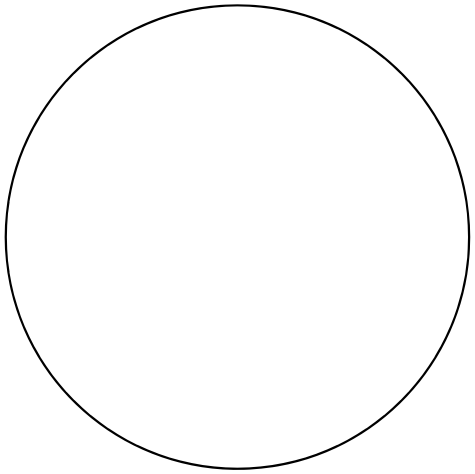

CF

1 cm

Results

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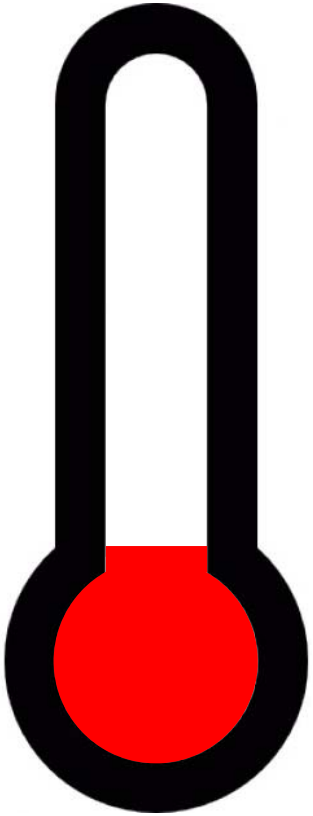
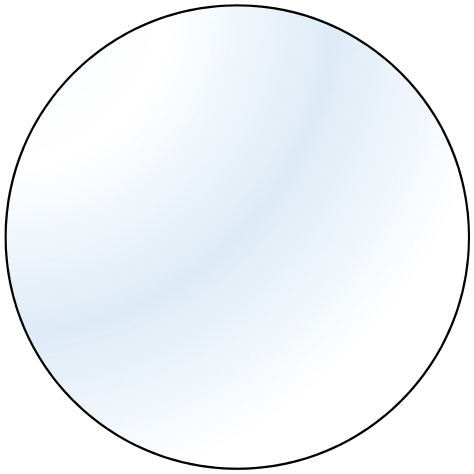


64 °C



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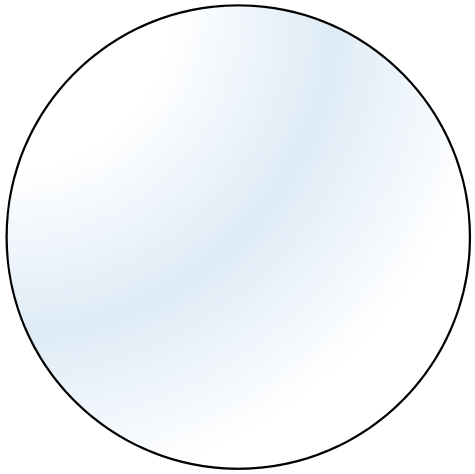

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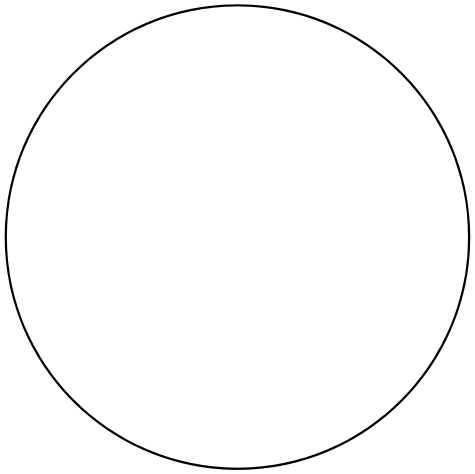
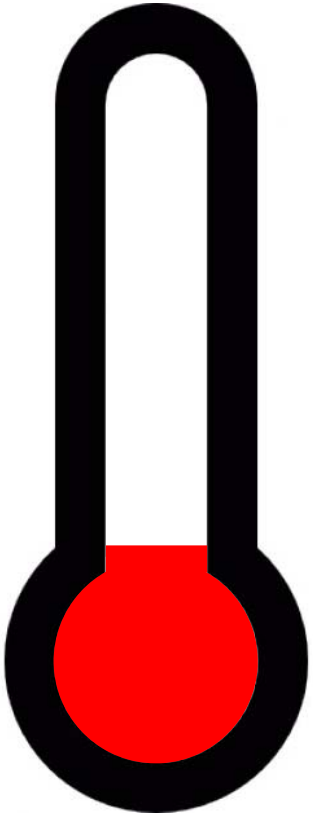


CF

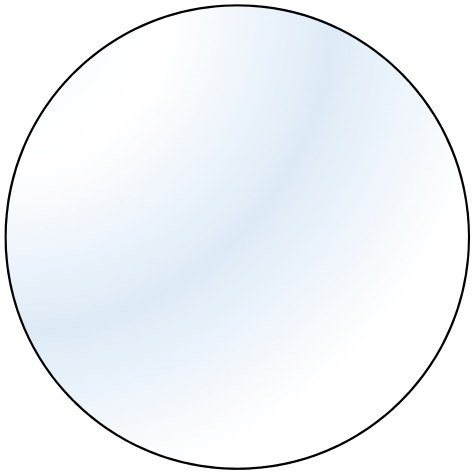
1 cm

Results

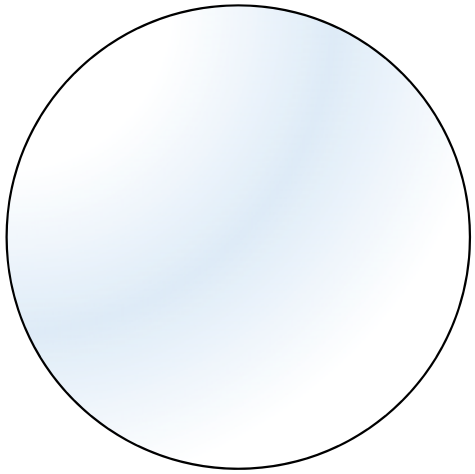
THE UNIVERSITY OF BRITISH COLUMBIA



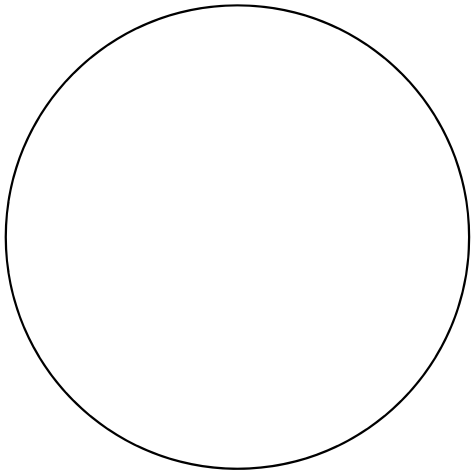
65 °C



CNC-H



CNC-Na

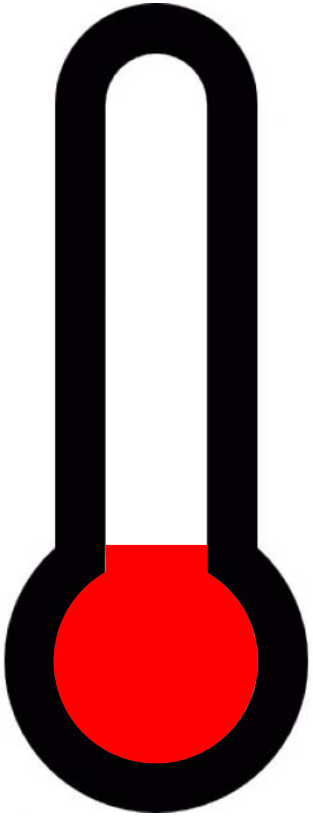


CF

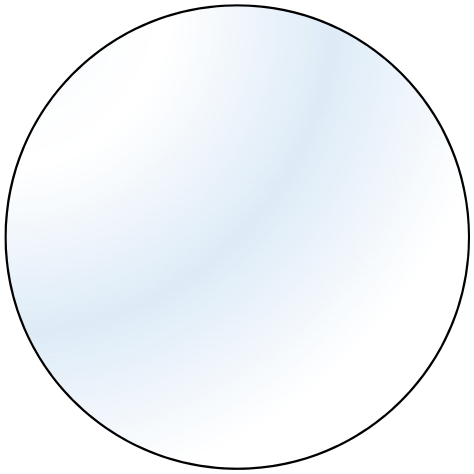
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



66 °C



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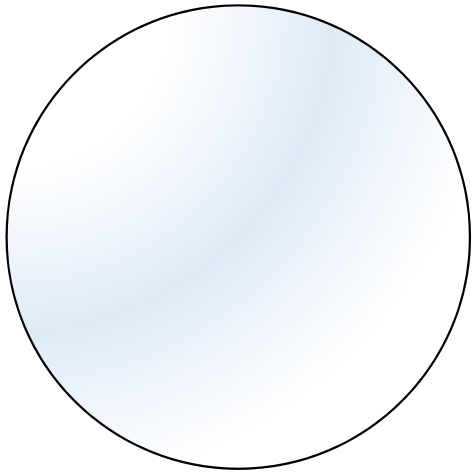

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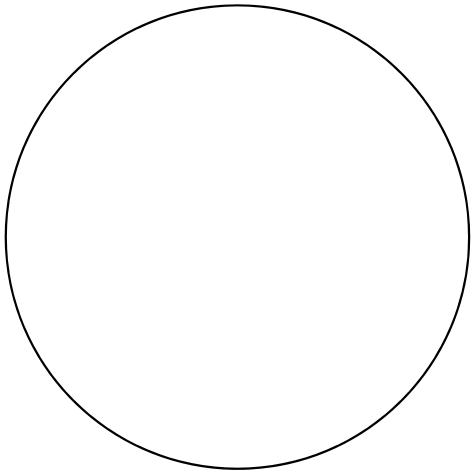
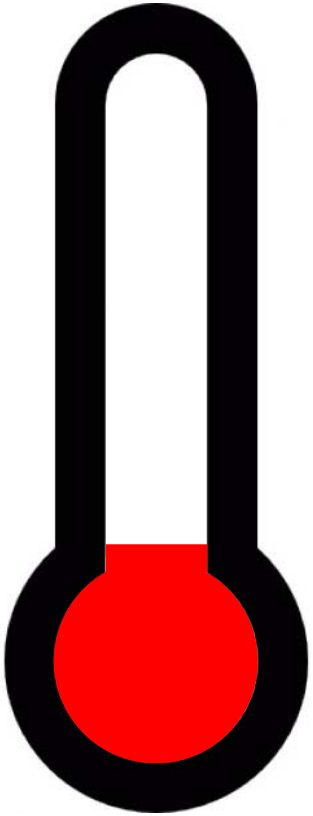


CF

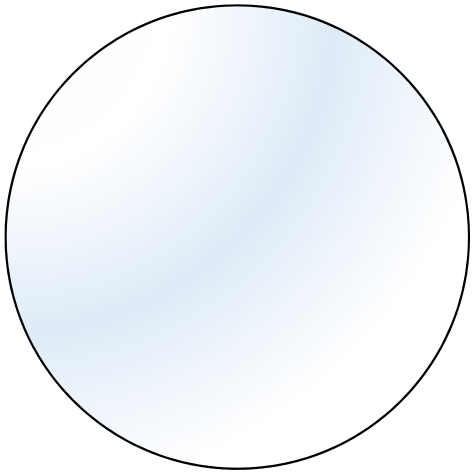
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



67 °C



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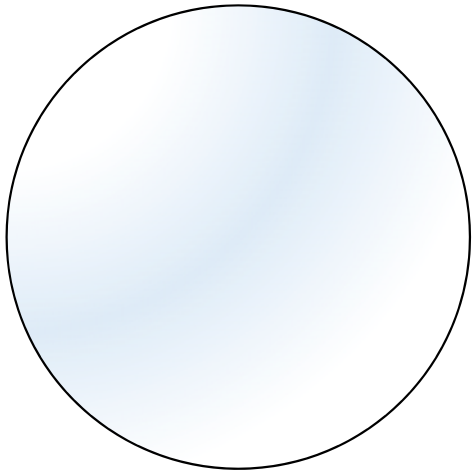

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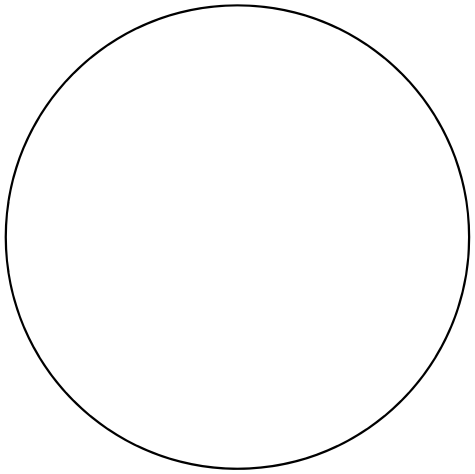
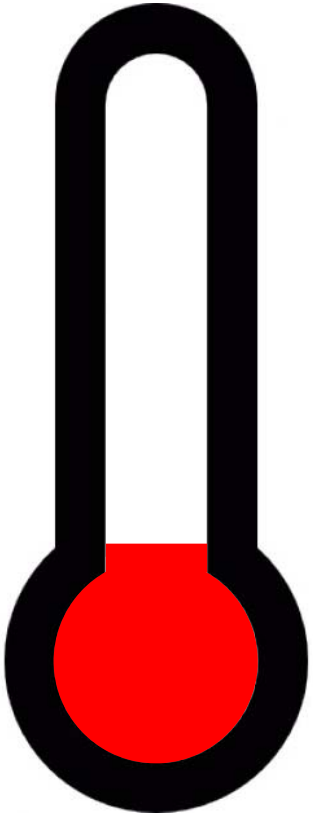


CF

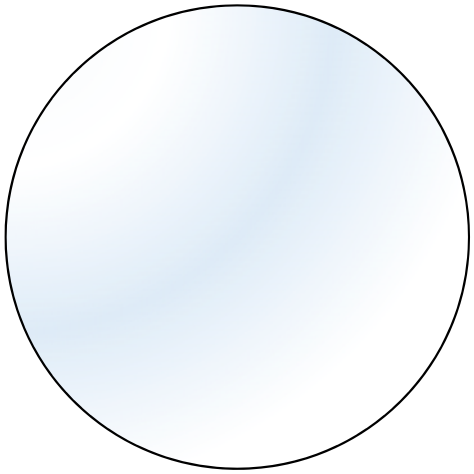
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



68 °C



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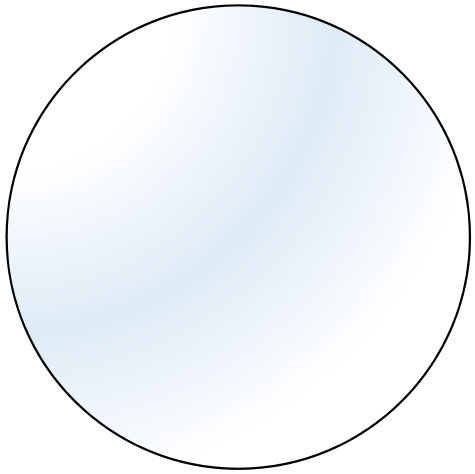

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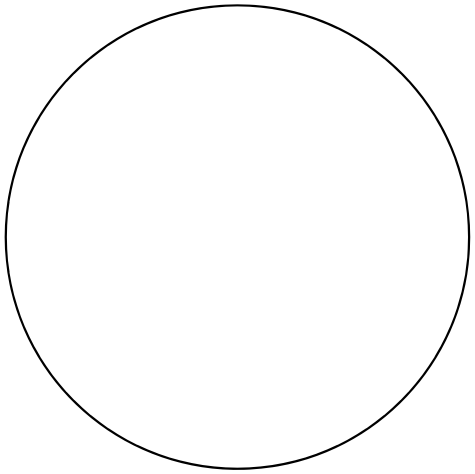
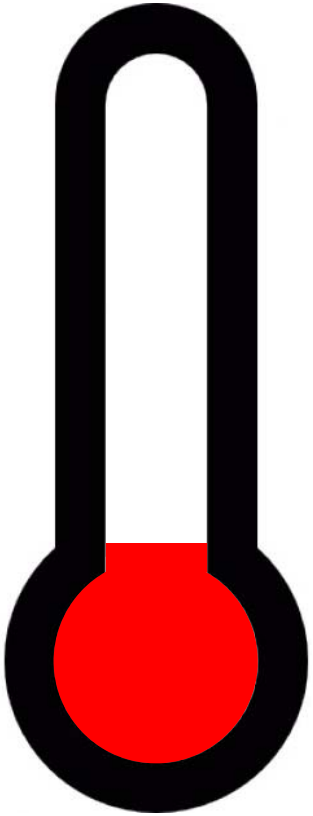


CF

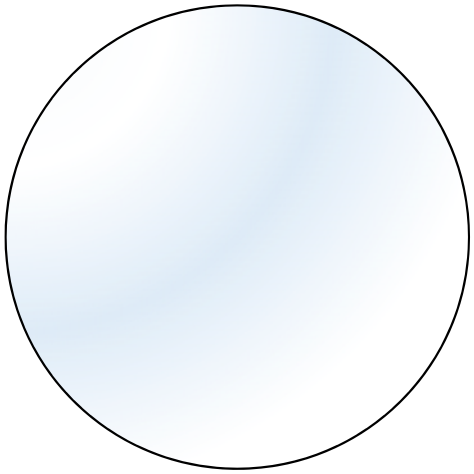
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



69 °C



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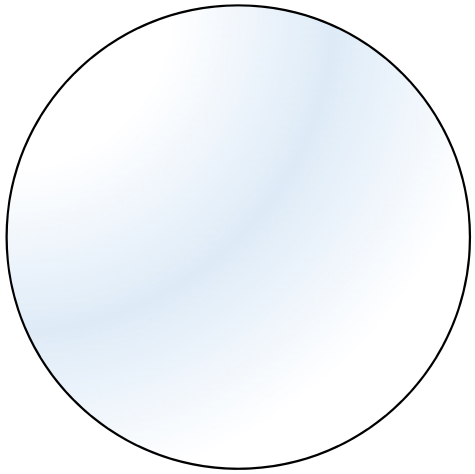

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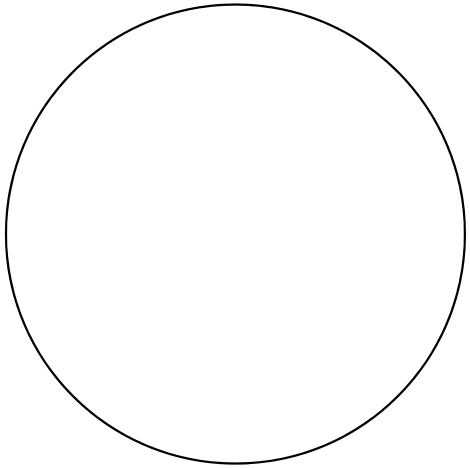
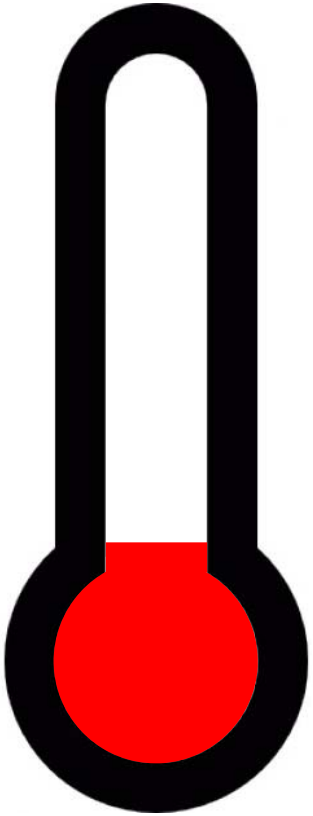


CF

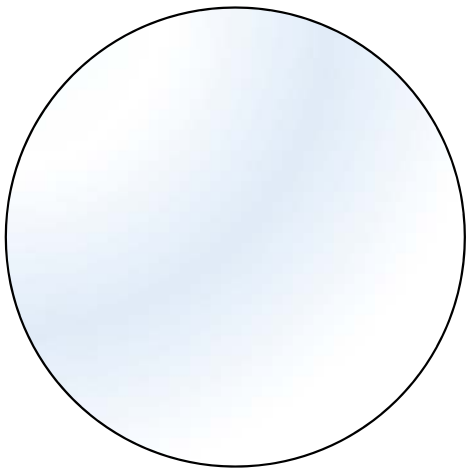
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



70 °C



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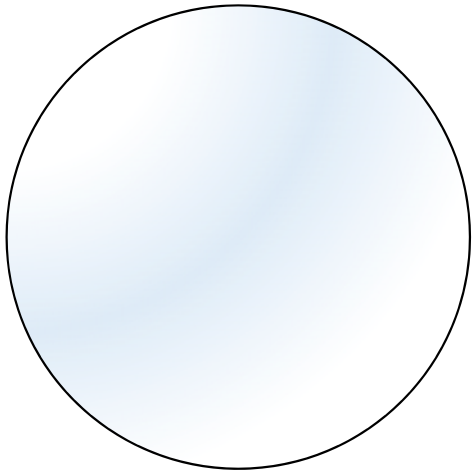

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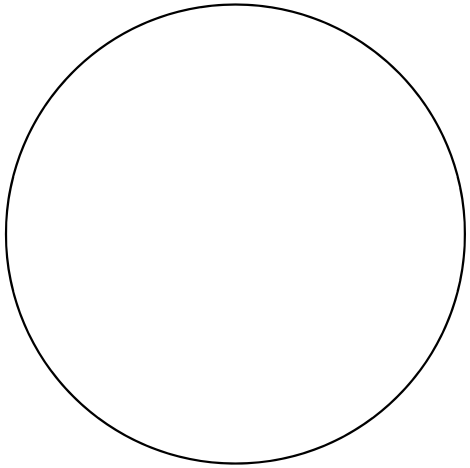
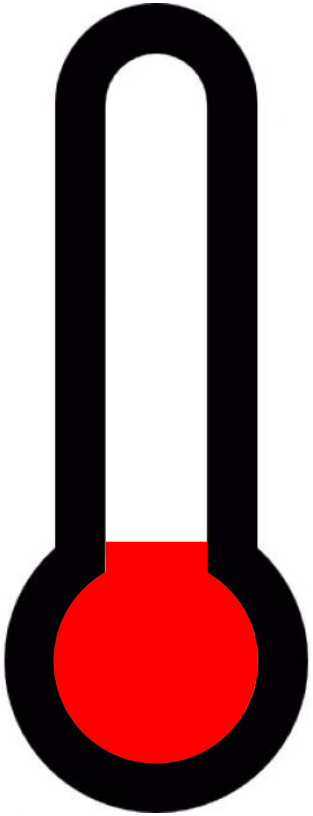


CF

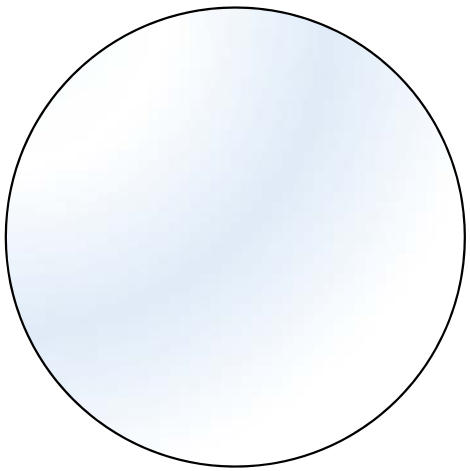
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



71 °C



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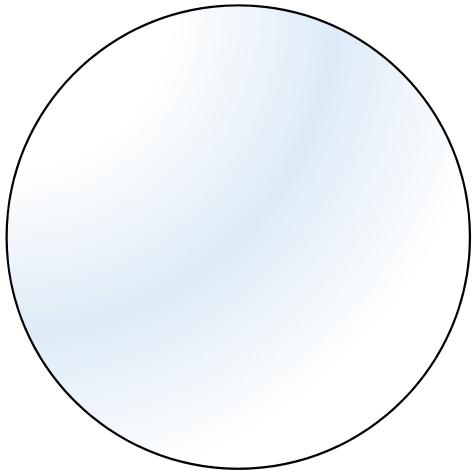

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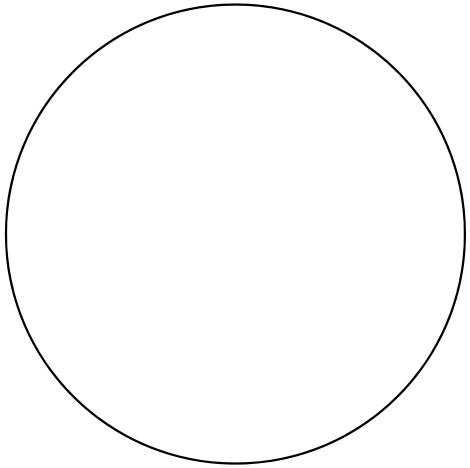
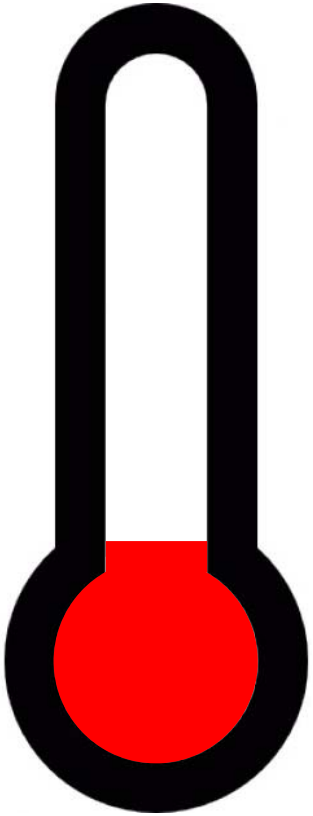


CF

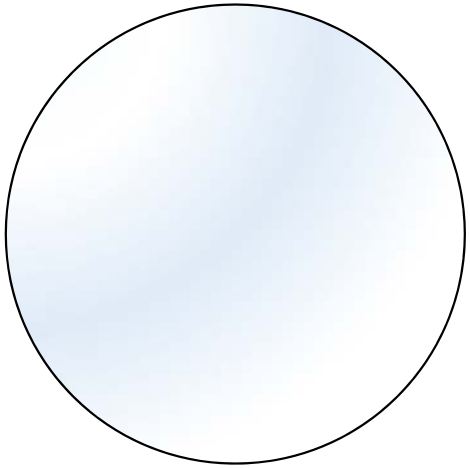
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



72 °C



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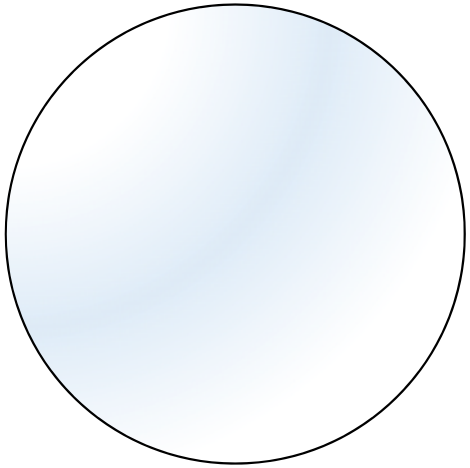

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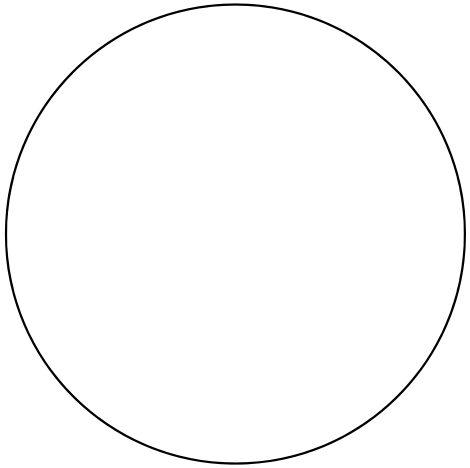

CF

1 cm

Results

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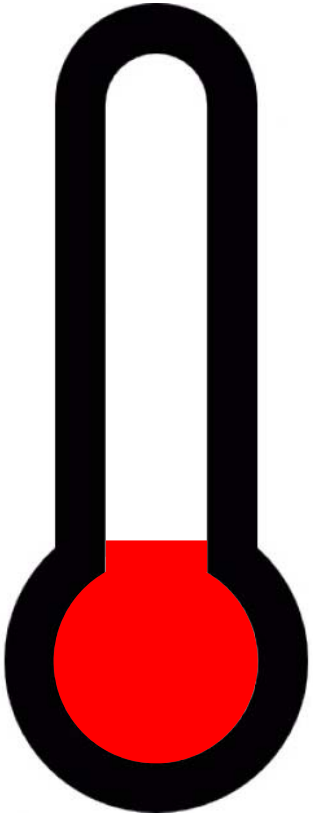
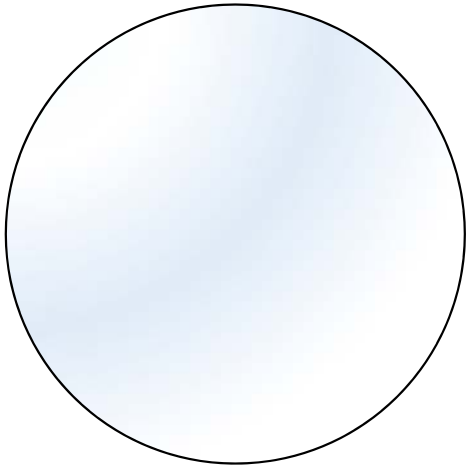


73 °C



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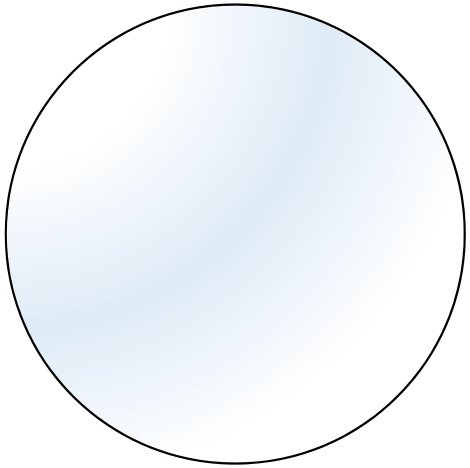

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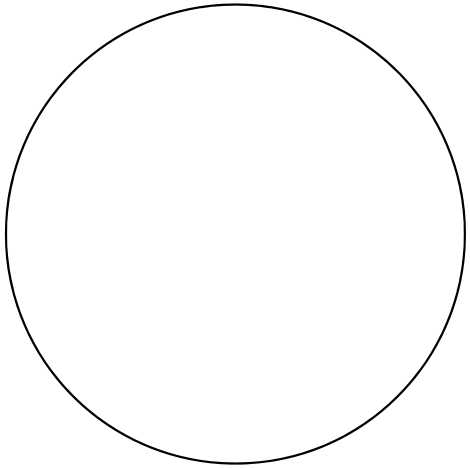
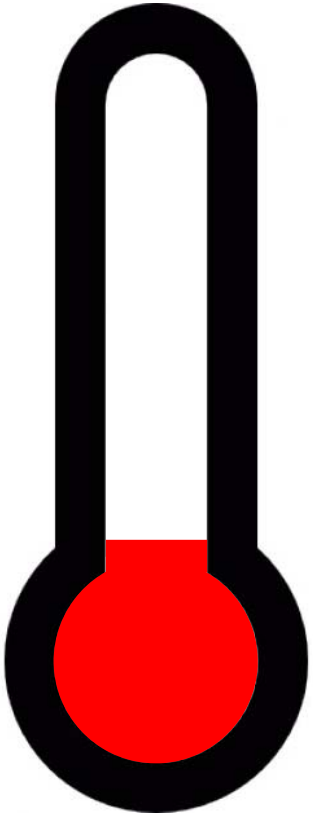


CF

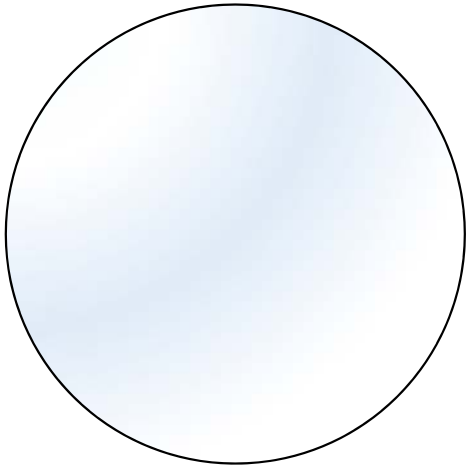
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



74 °C



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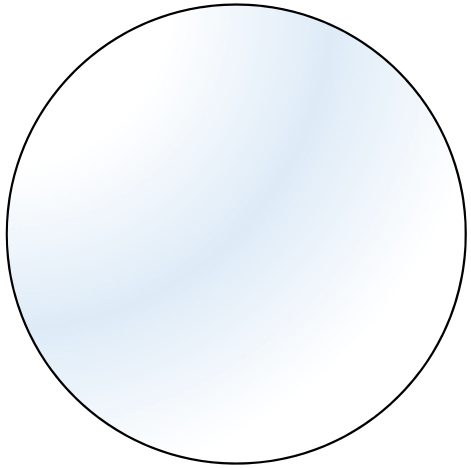

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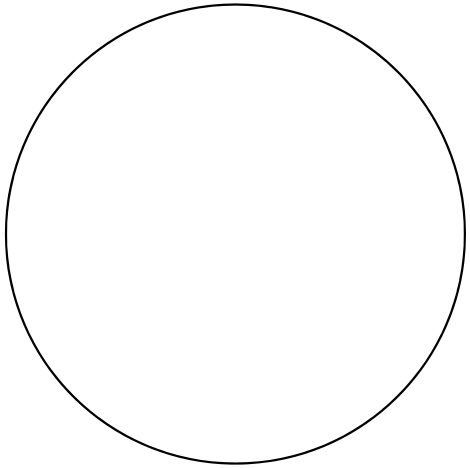
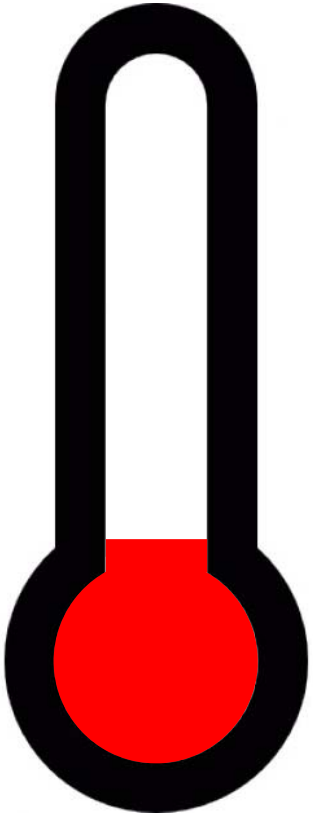


CF

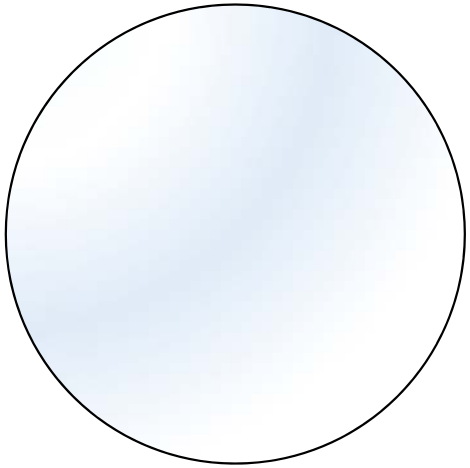
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



75 °C



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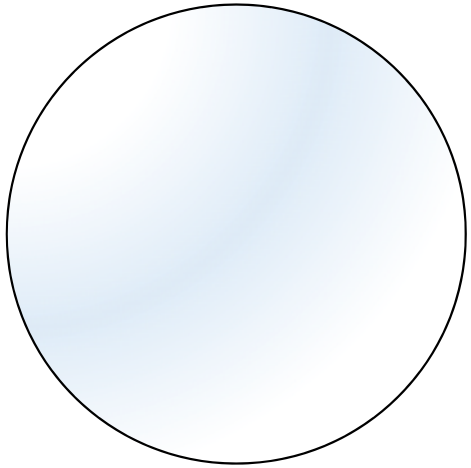

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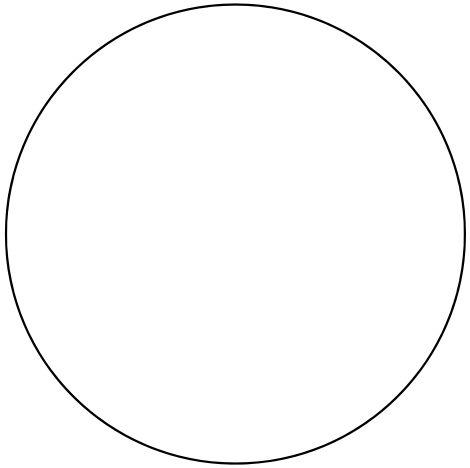
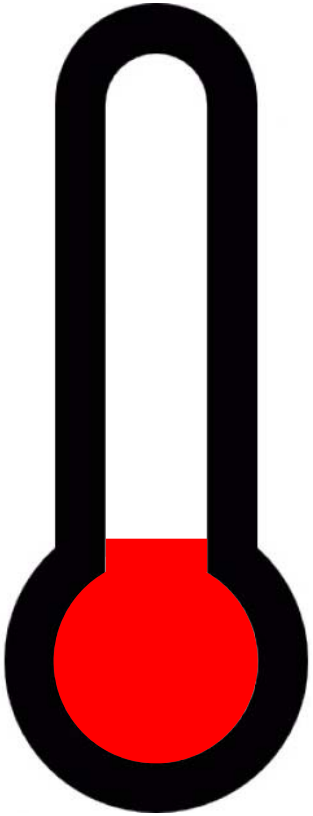


CF

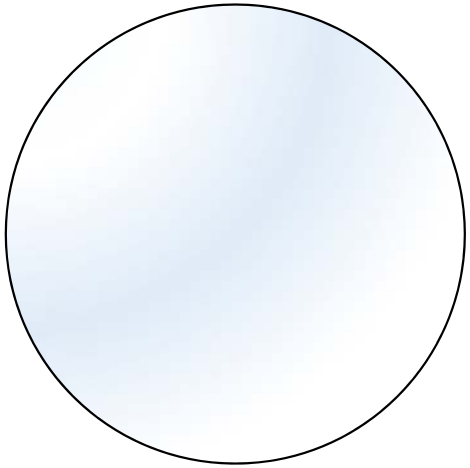
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



76 °C



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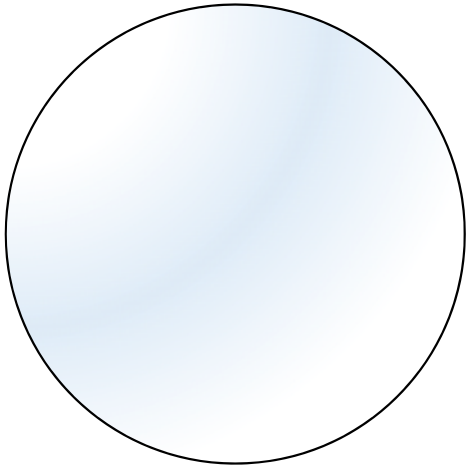

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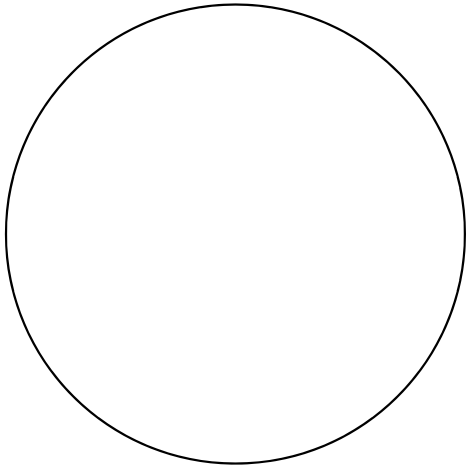
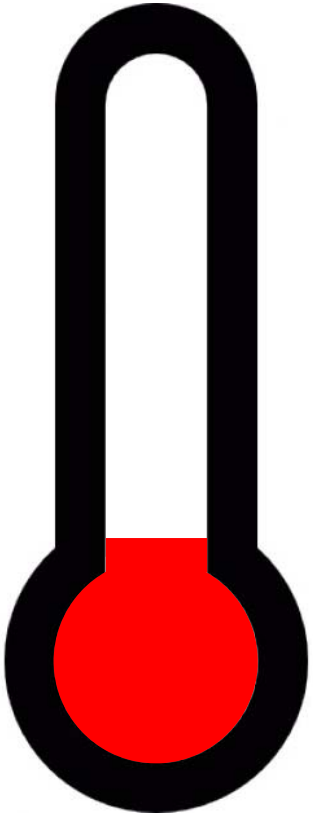


CF

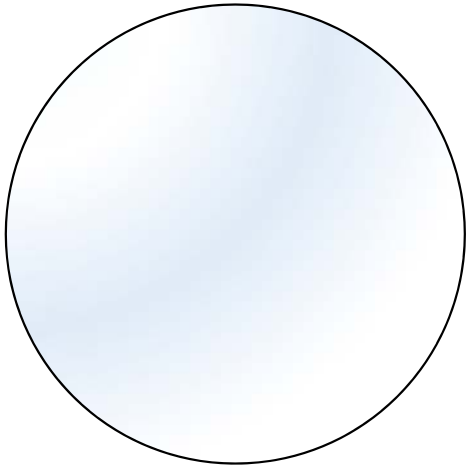
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



77 °C



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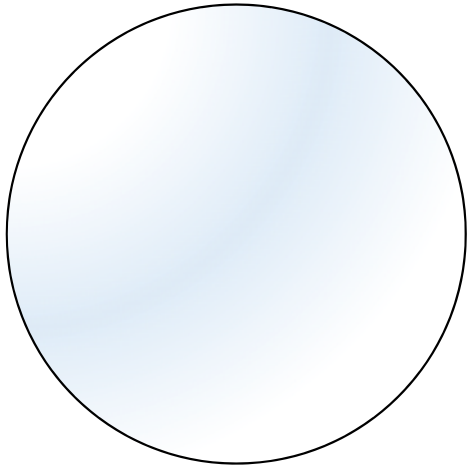

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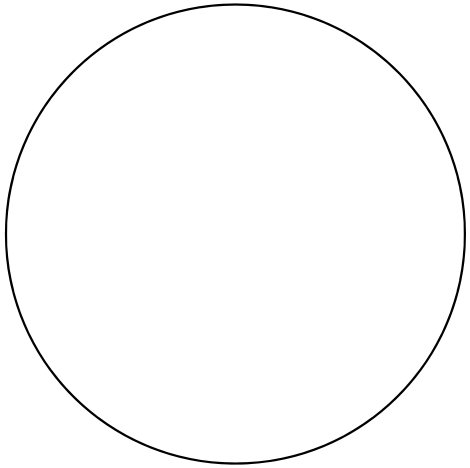
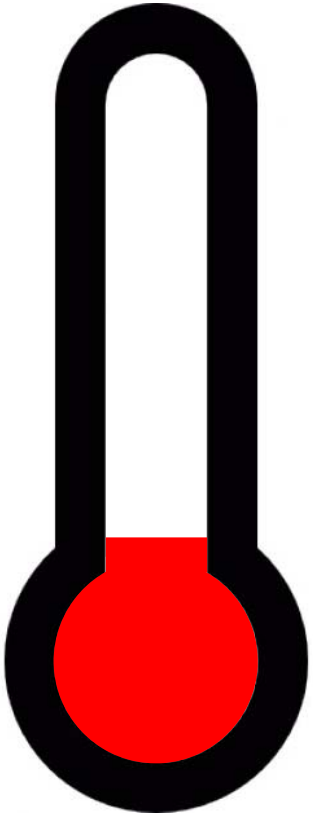


CF

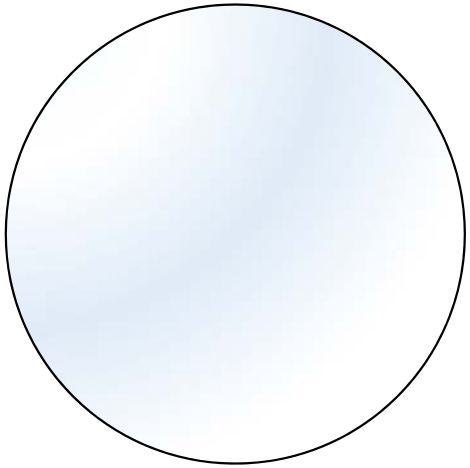
1 cm

Results

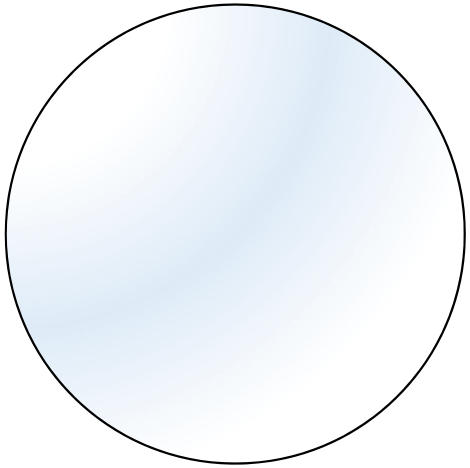
THE UNIVERSITY OF BRITISH COLUMBIA



78 °C



CNC-H



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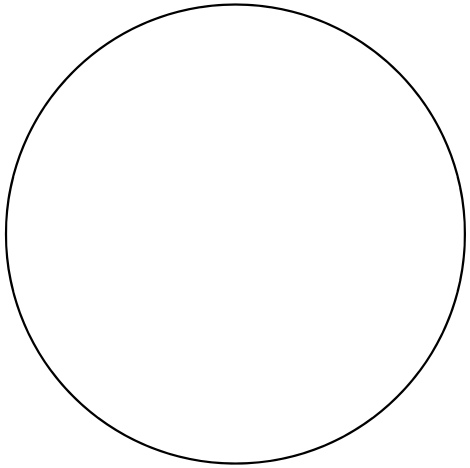
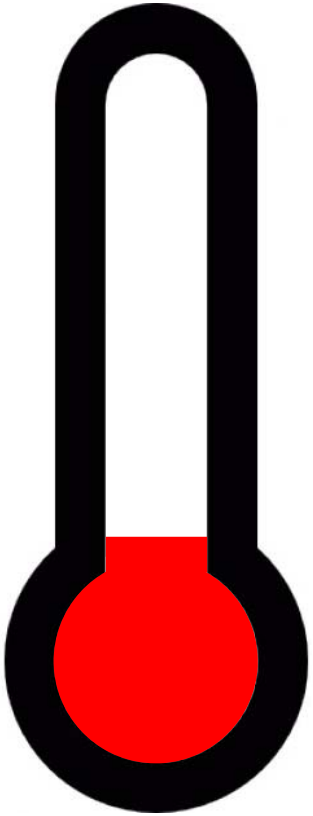


CF

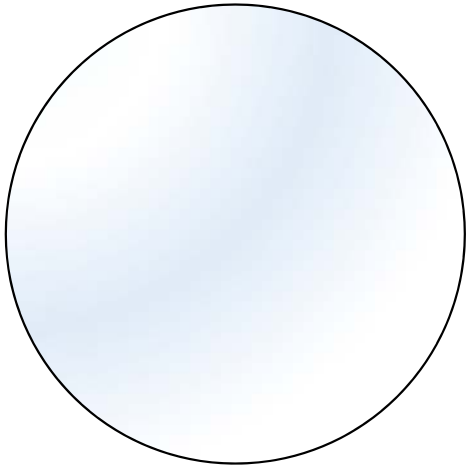
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



79 °C



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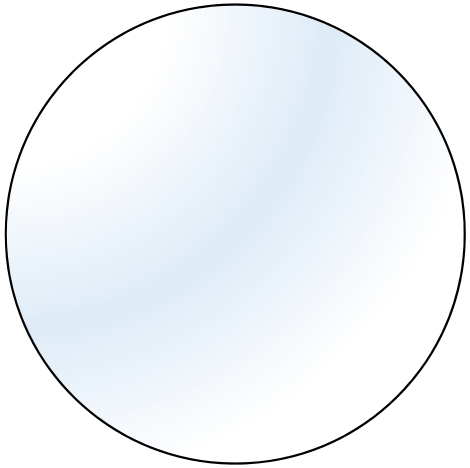
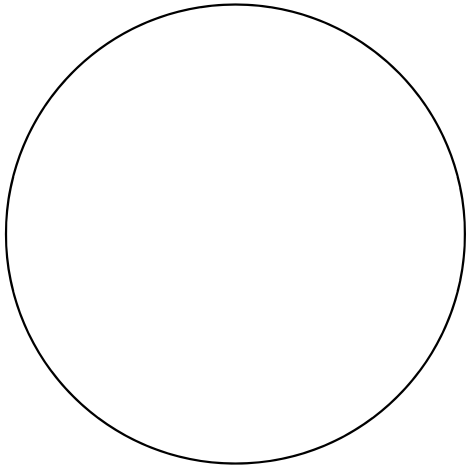


CNC-Na

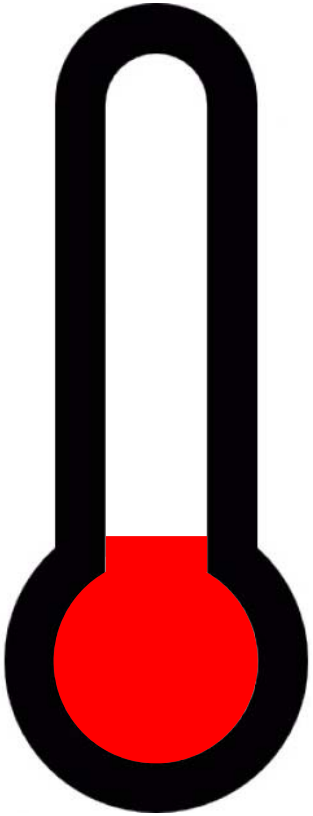


CF

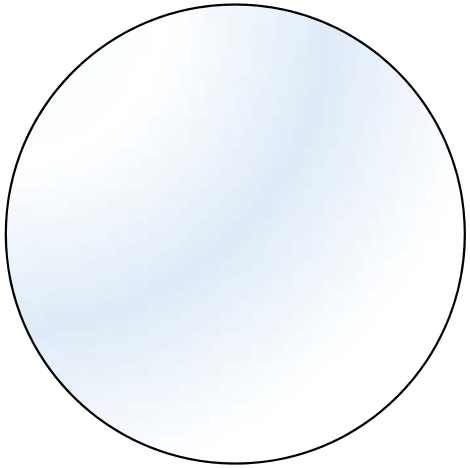
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



80 °C



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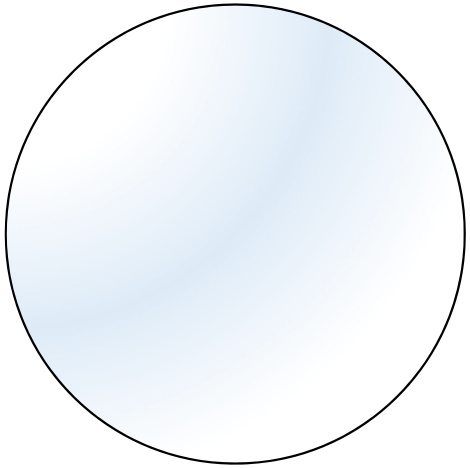

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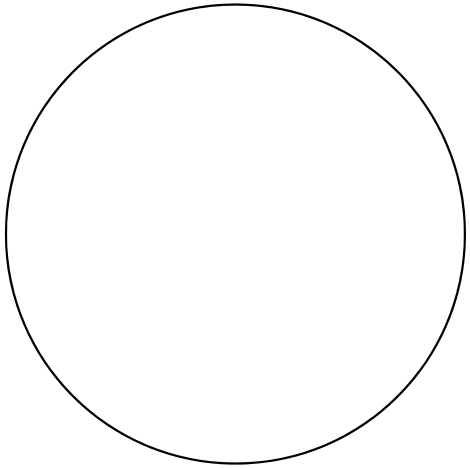
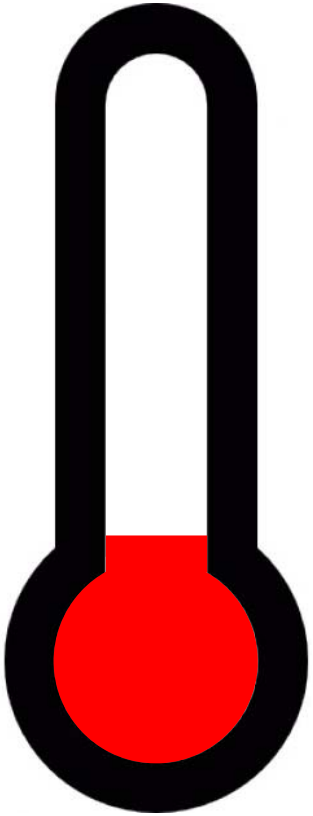


CF

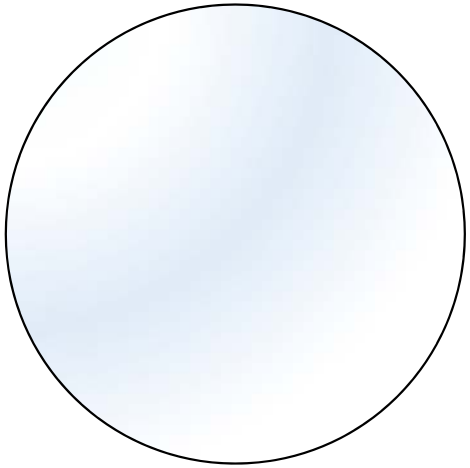
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



81 °C



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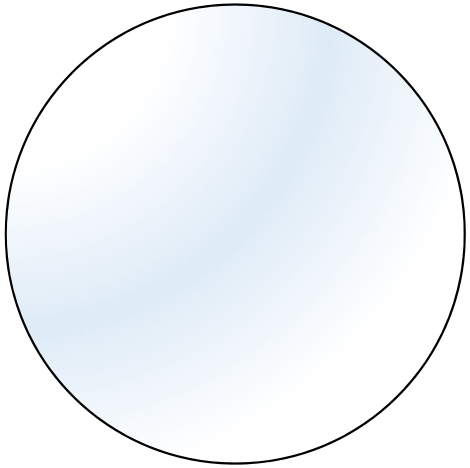

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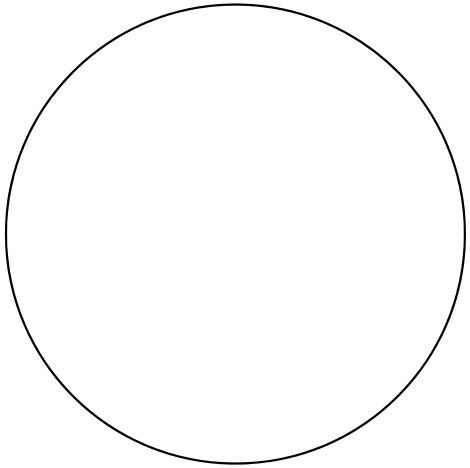
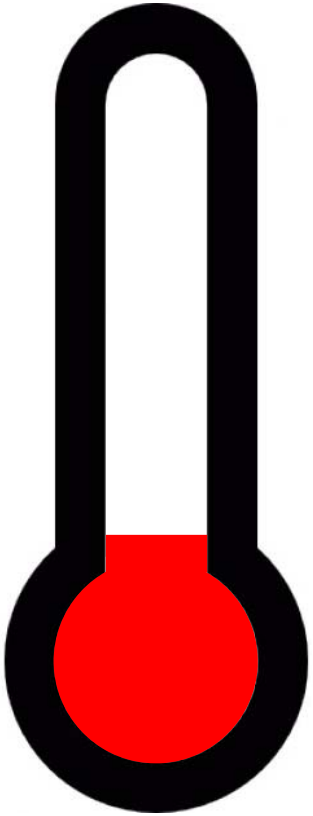


CF

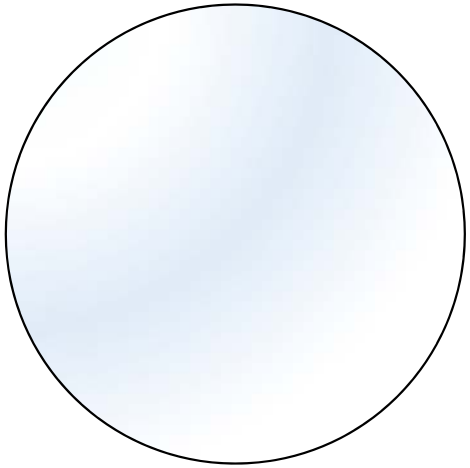
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



82 °C



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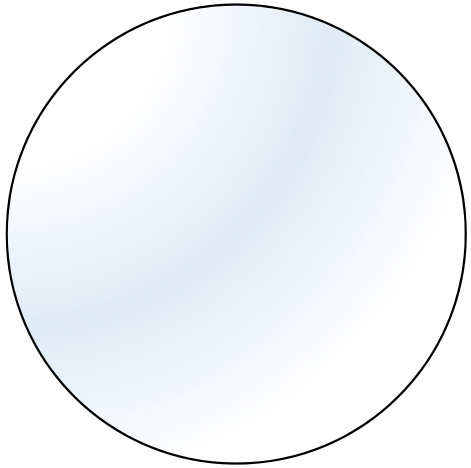

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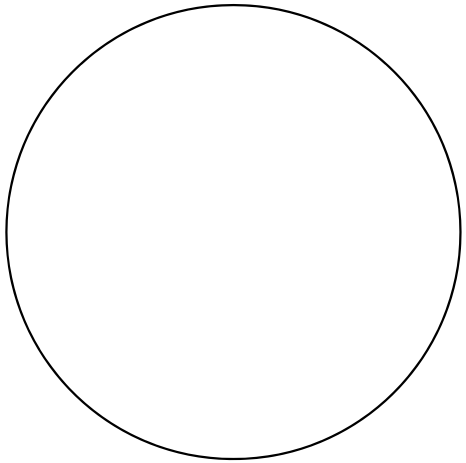
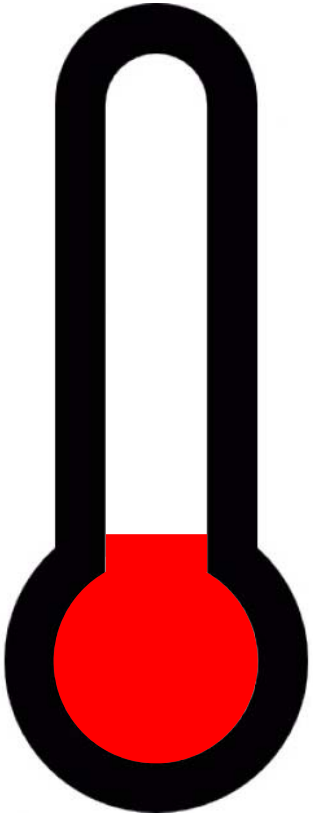


CF

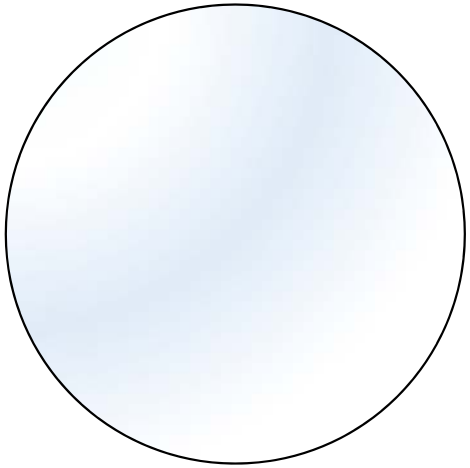
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



83 °C



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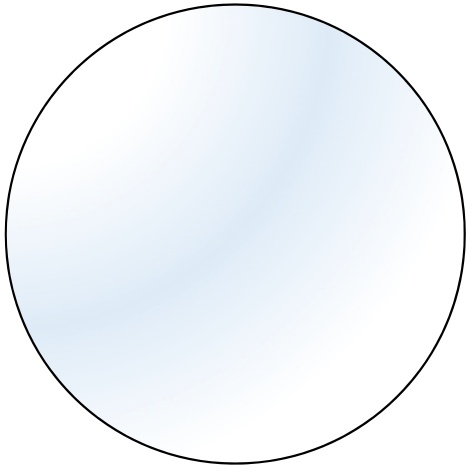

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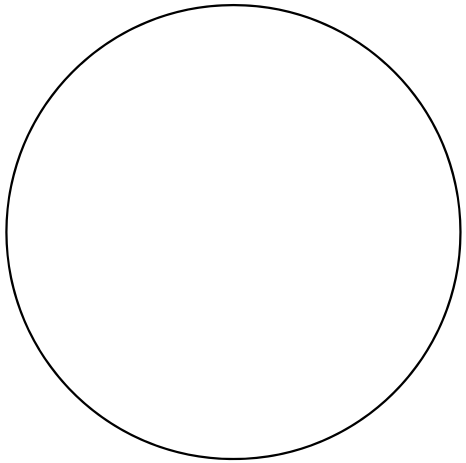
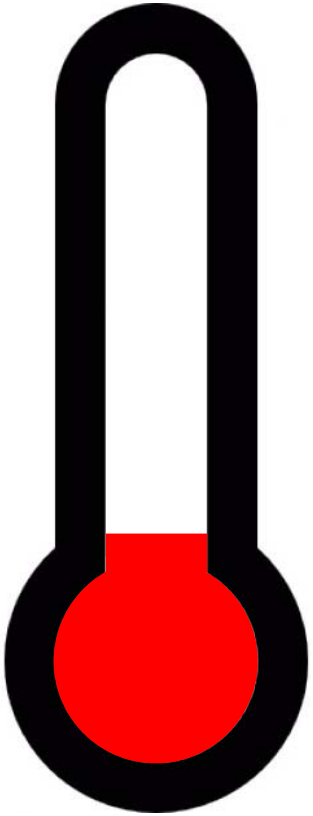


CF

1 cm

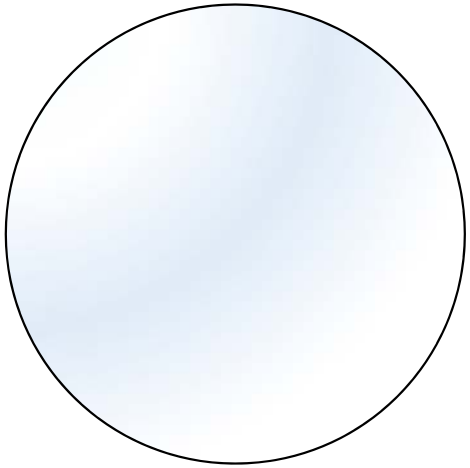
Results

THE UNIVERSITY OF BRITISH COLUMBIA



84 °C

Dehydration



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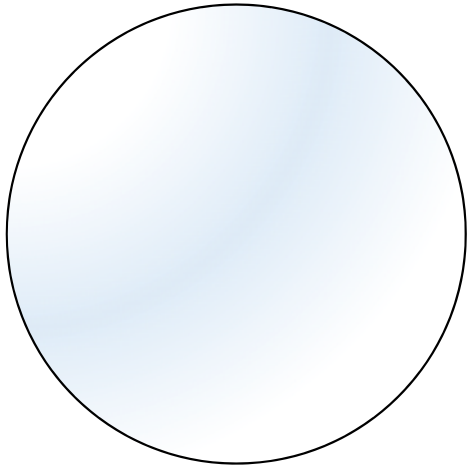
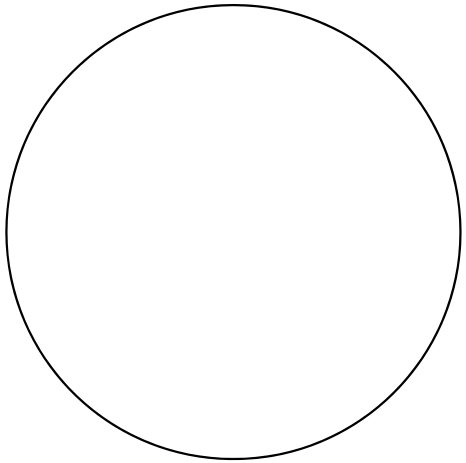


CNC-Na

Dehydration

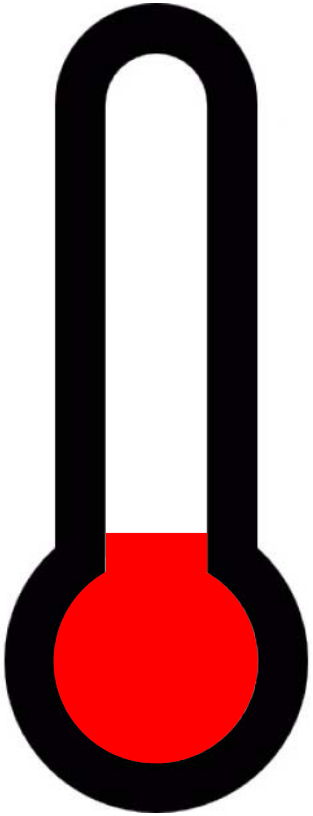


CF

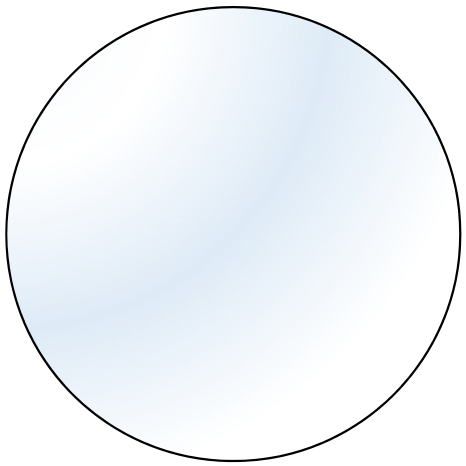
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



85 °C



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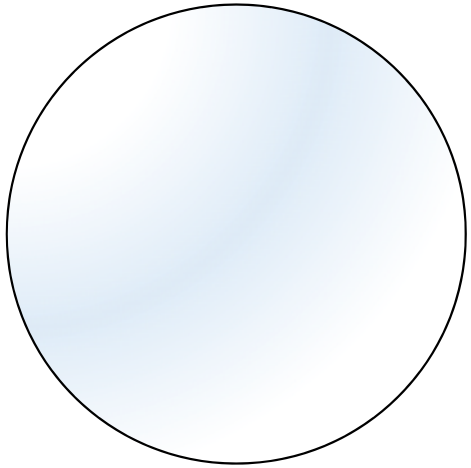

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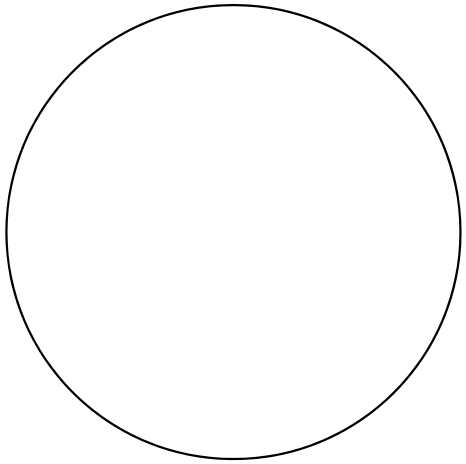
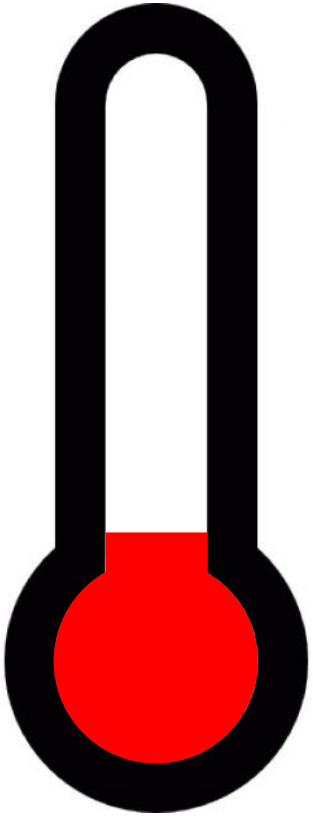


CF

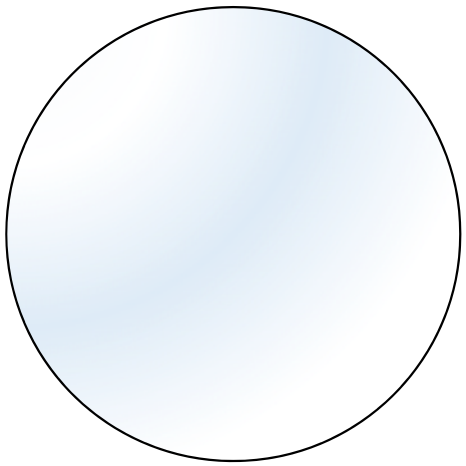
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



86 °C



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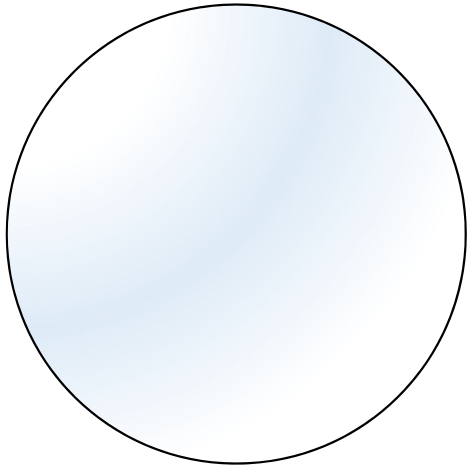

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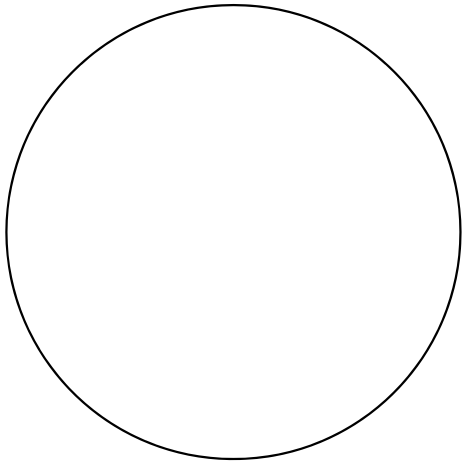
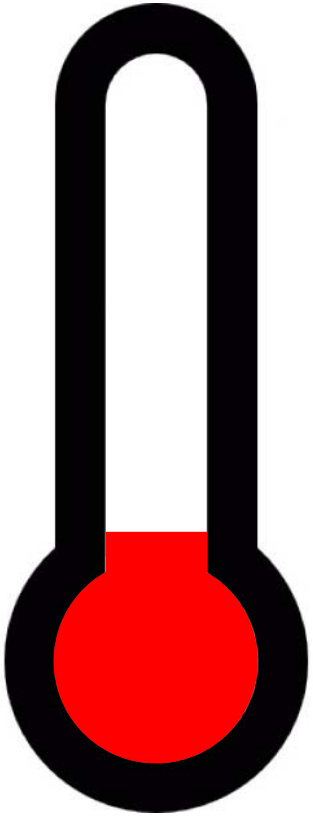


CF

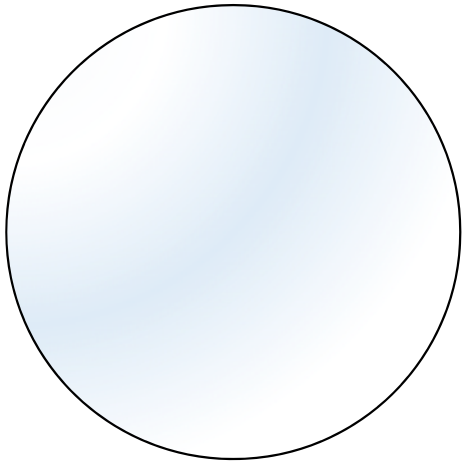
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



87 °C



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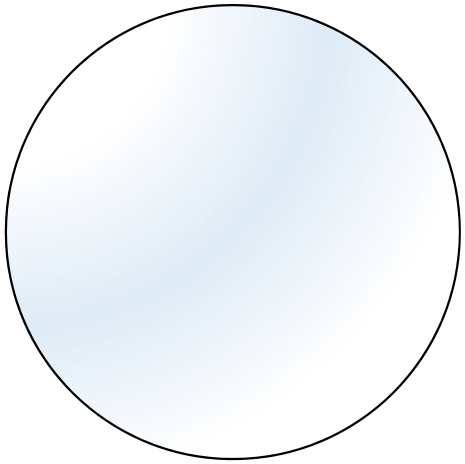

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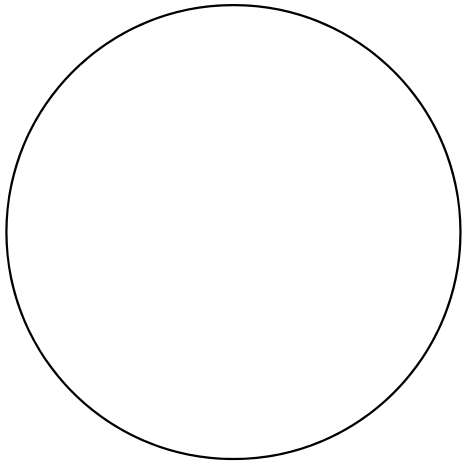
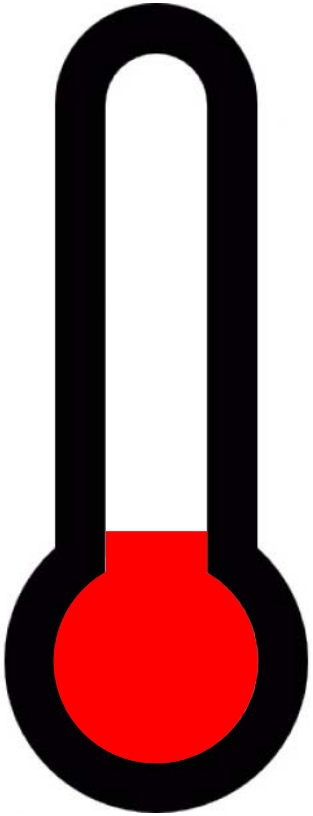


CF

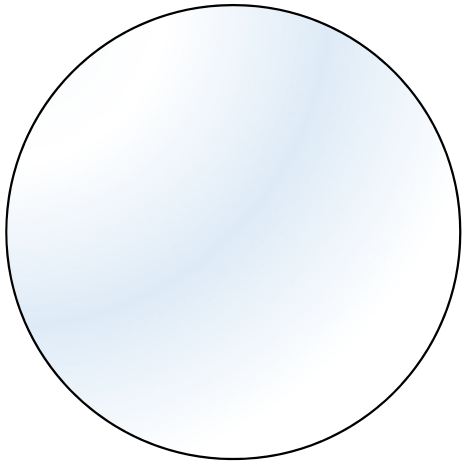
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



88 °C



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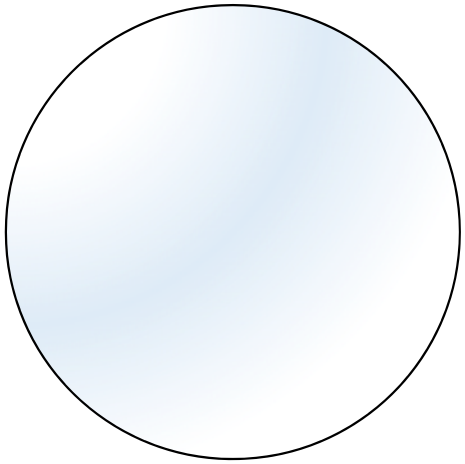

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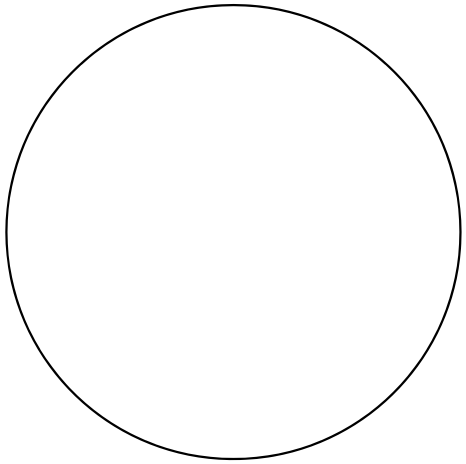
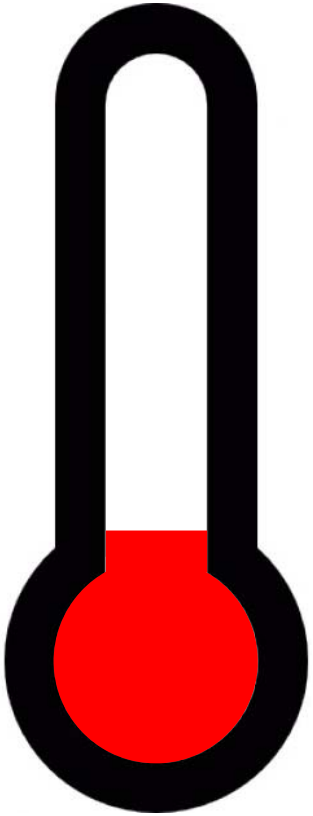


CF

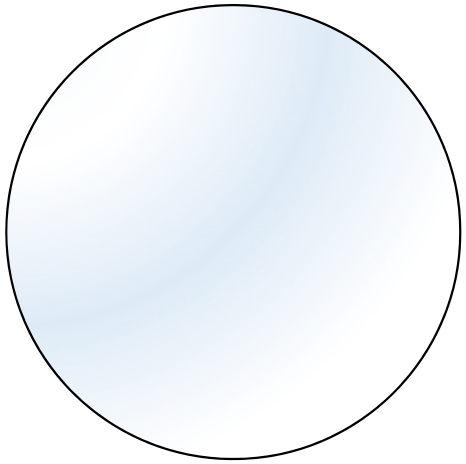
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



89 °C



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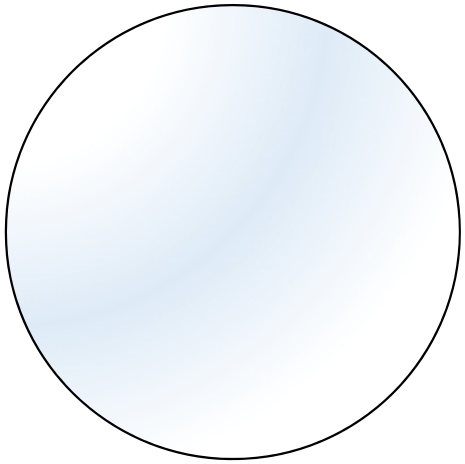

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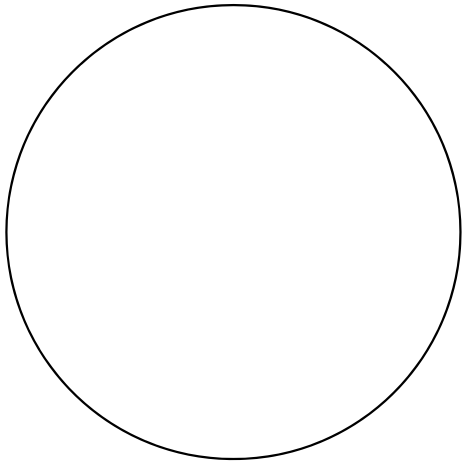
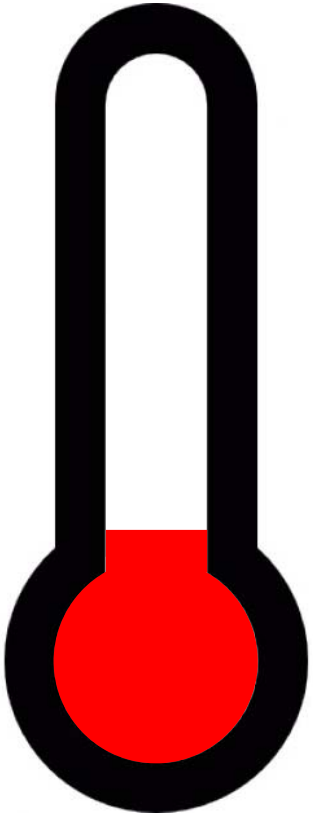


CF

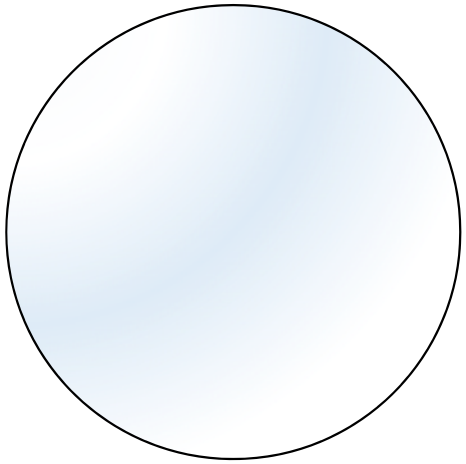
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



90 °C



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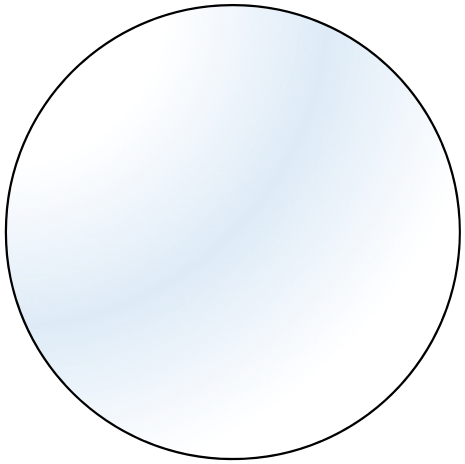

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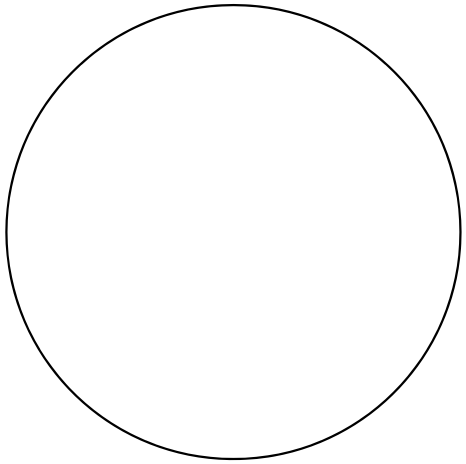
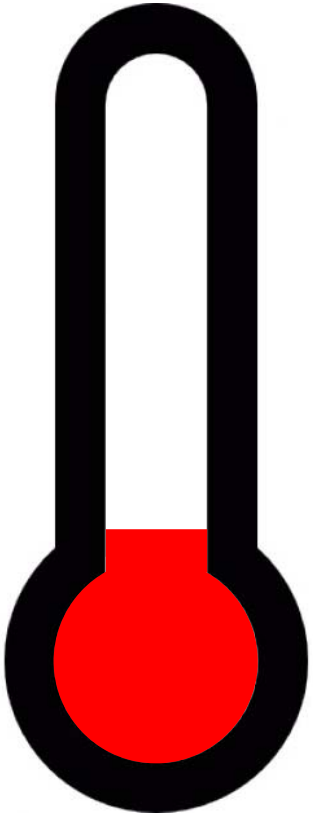


CF

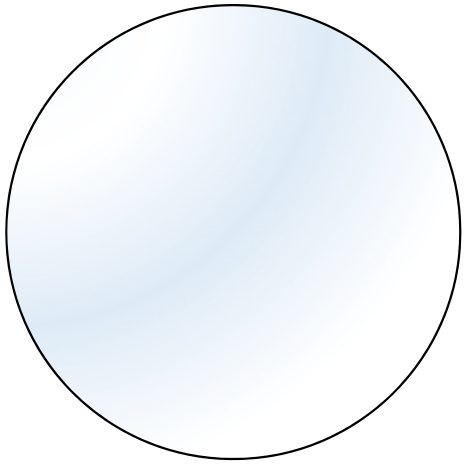
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



91 °C



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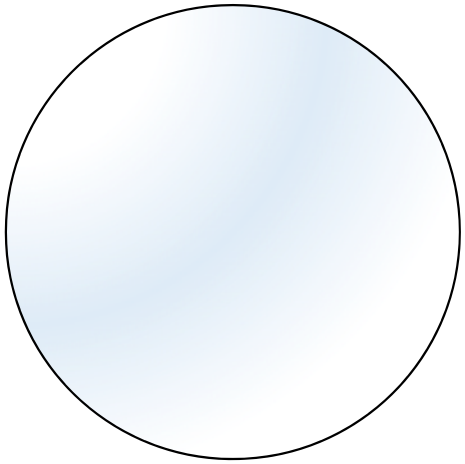
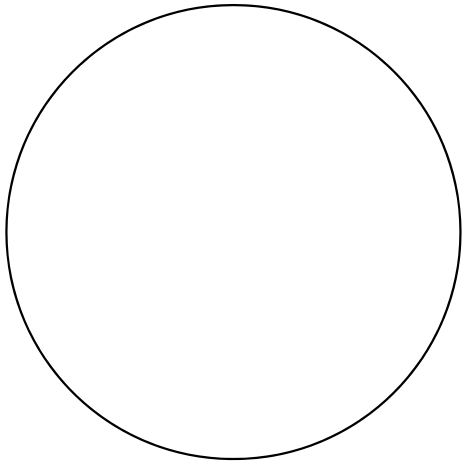


CNC-Na

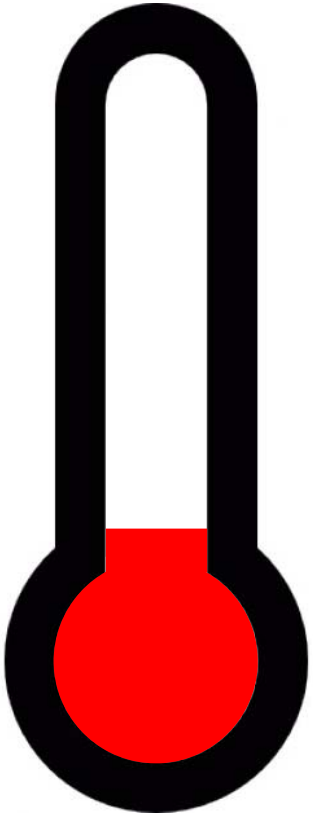


CF

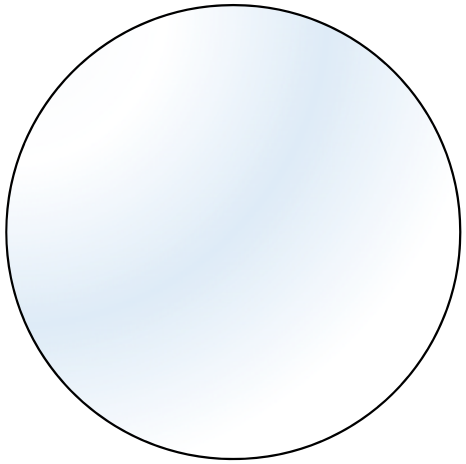
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



92 °C



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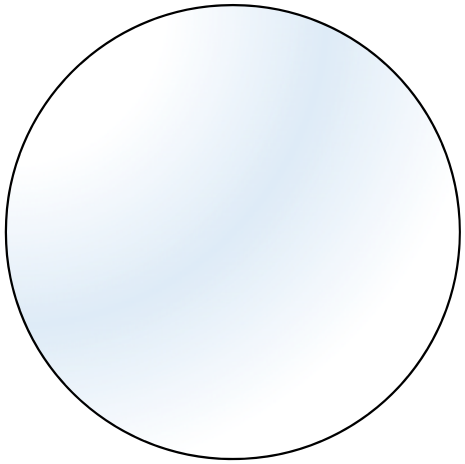

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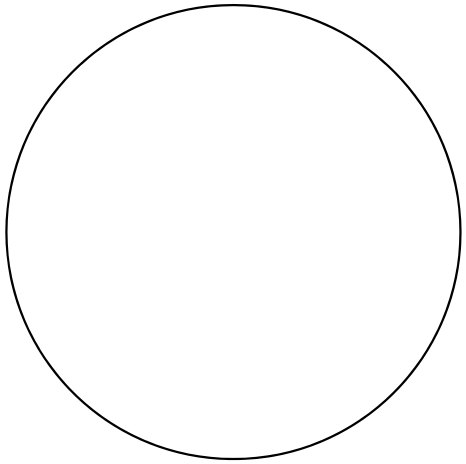
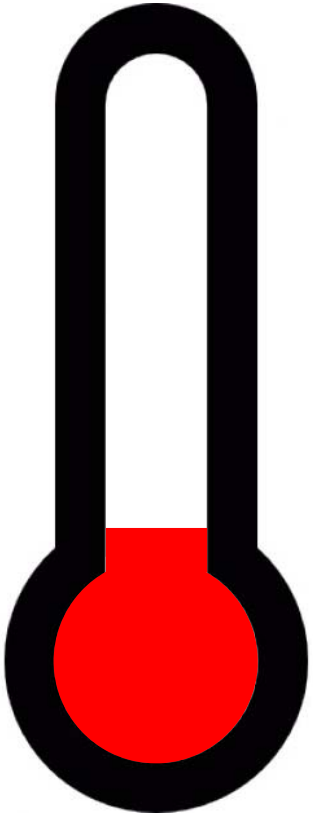


CF

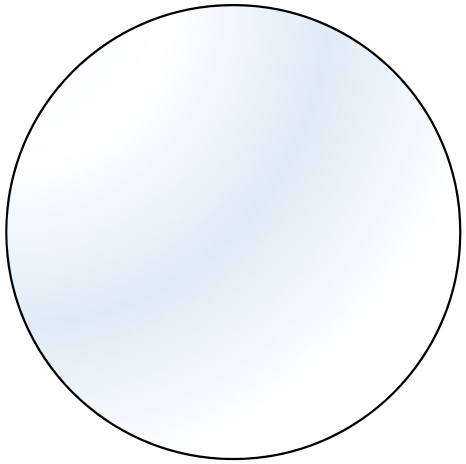
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



93 °C



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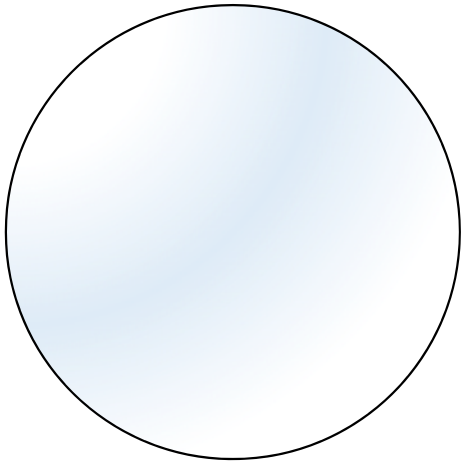
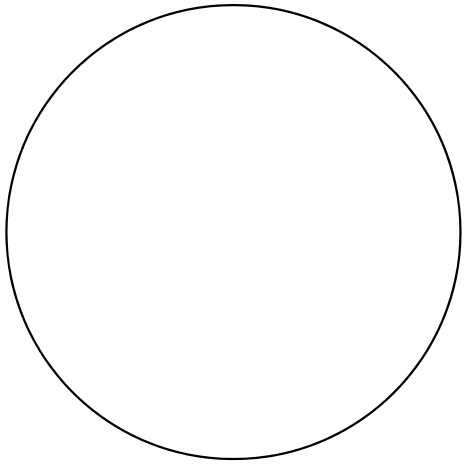


CNC-Na

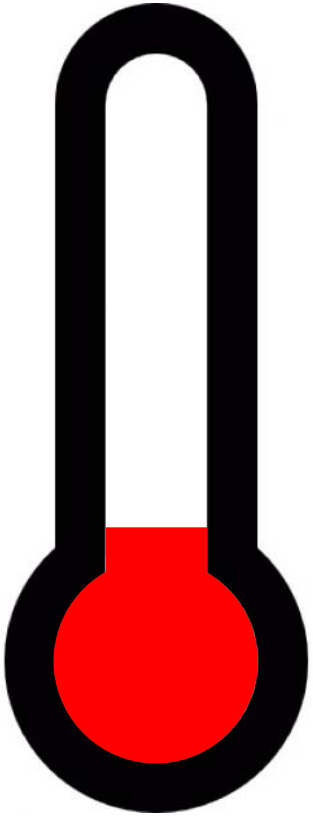


CF

1 cm

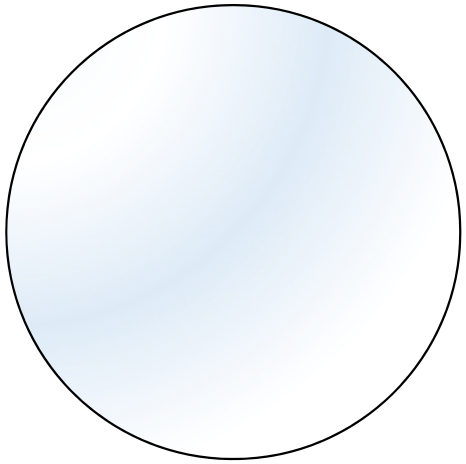
Results

THE UNIVERSITY OF BRITISH COLUMBIA

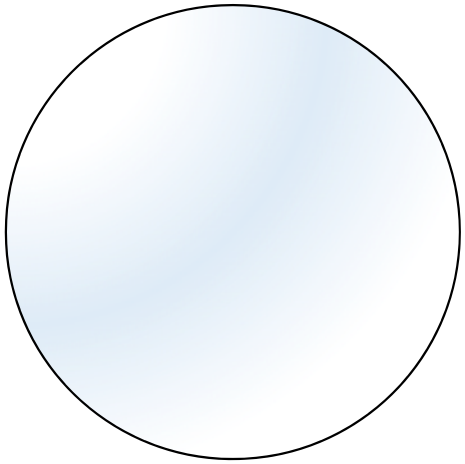


94 °C

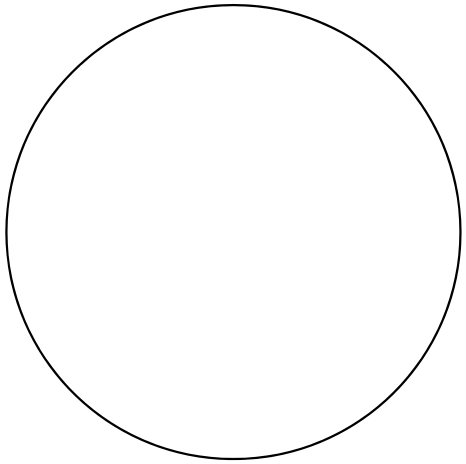
Dehydration



CNC-H



CNC-Na

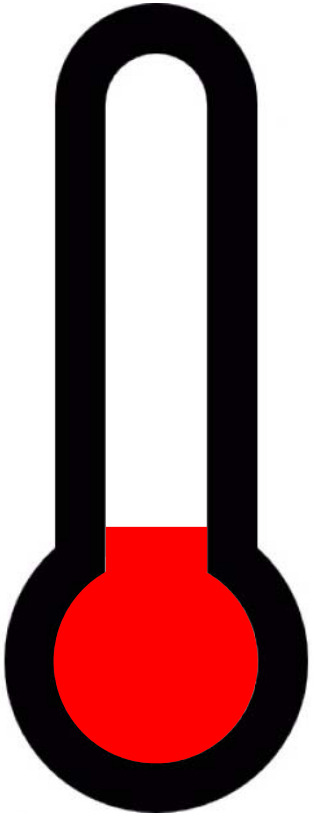


CF

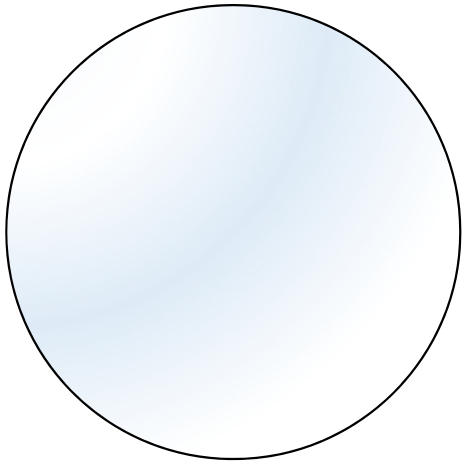
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



95 °C



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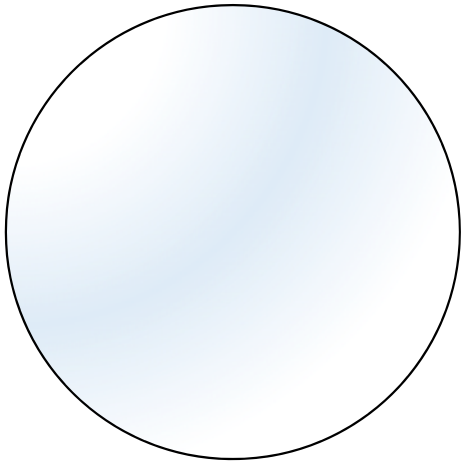

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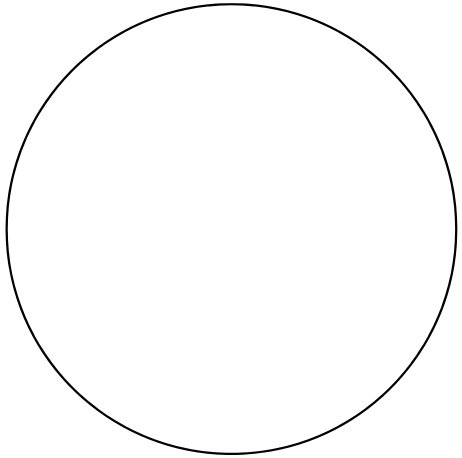
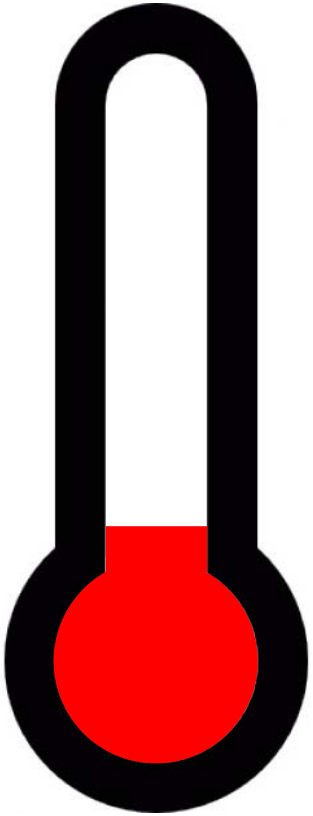


CF

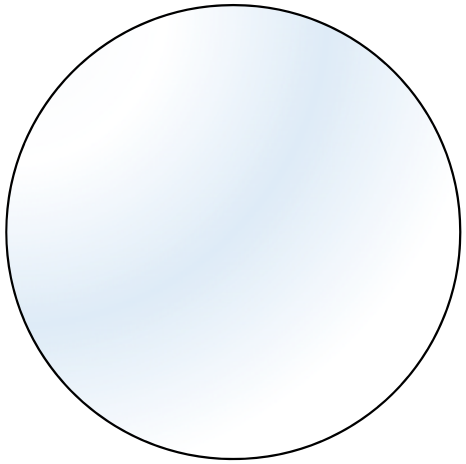
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



96 °C



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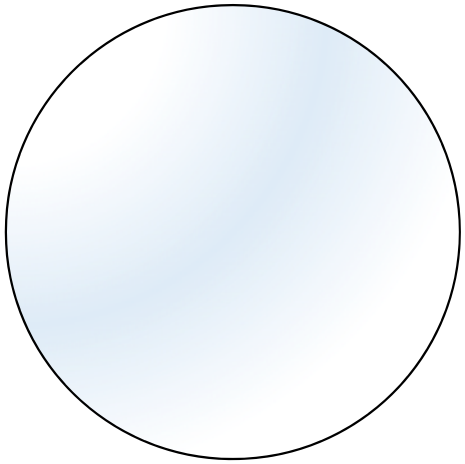

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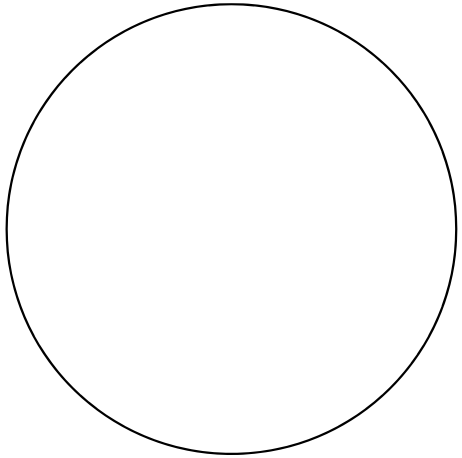
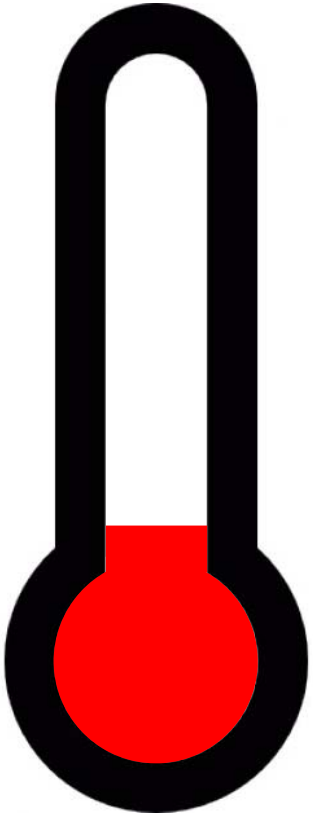


CF

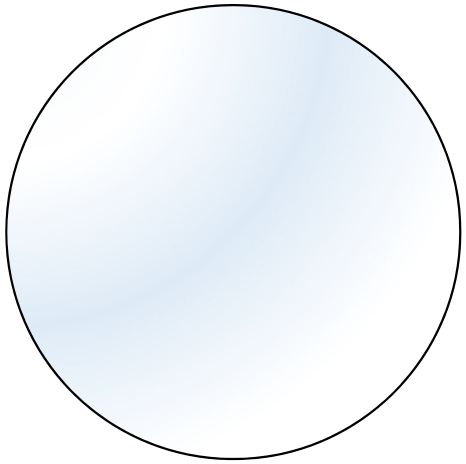
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



97 °C



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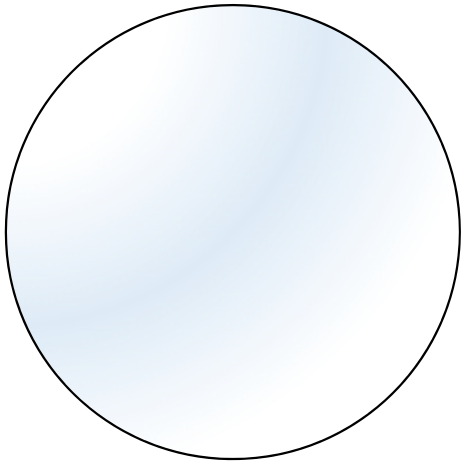

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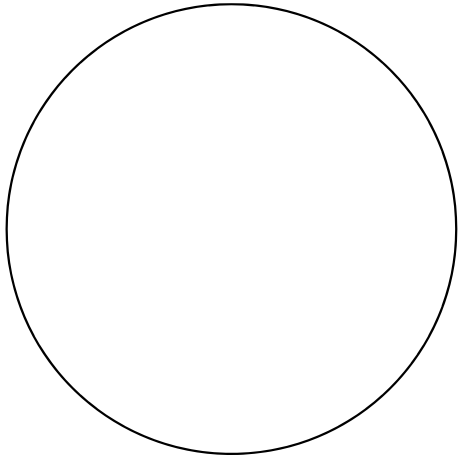
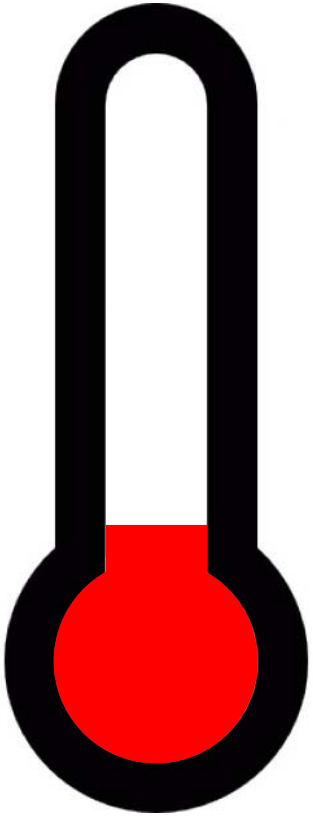


CF

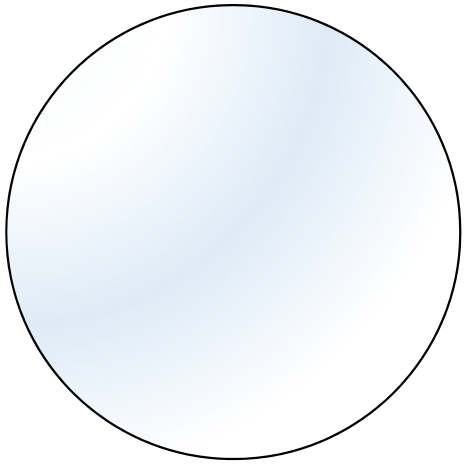
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



98 °C



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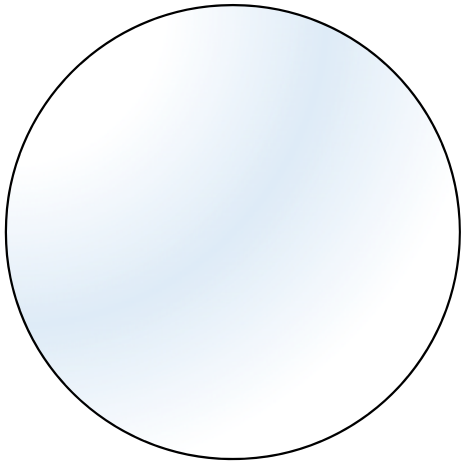

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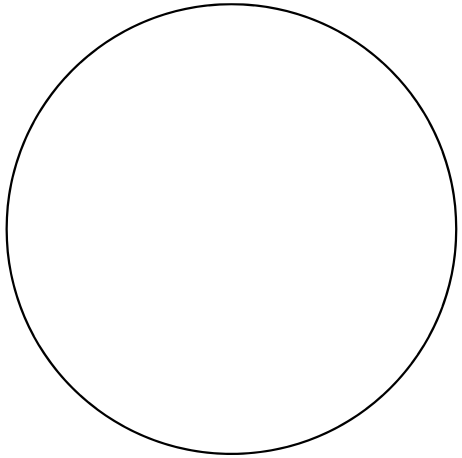
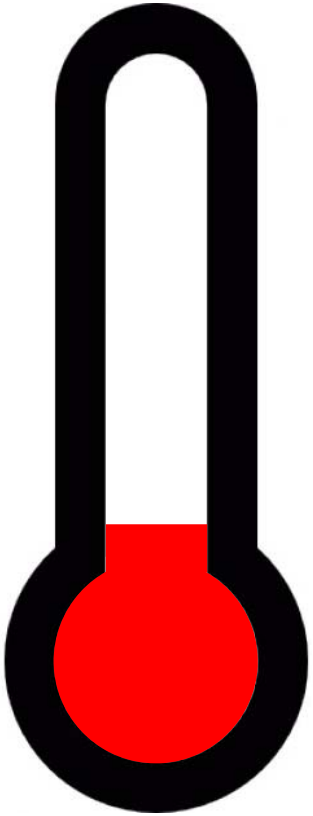


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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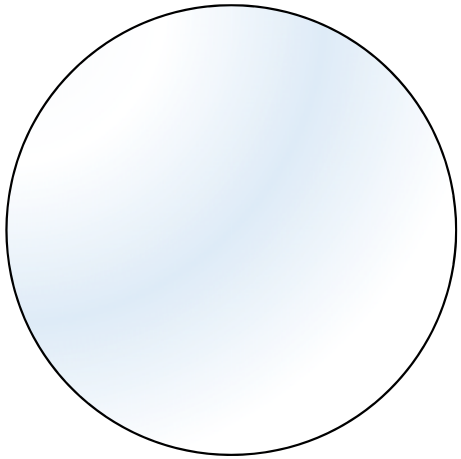

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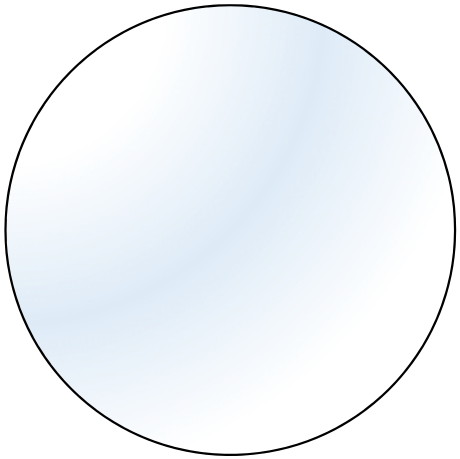

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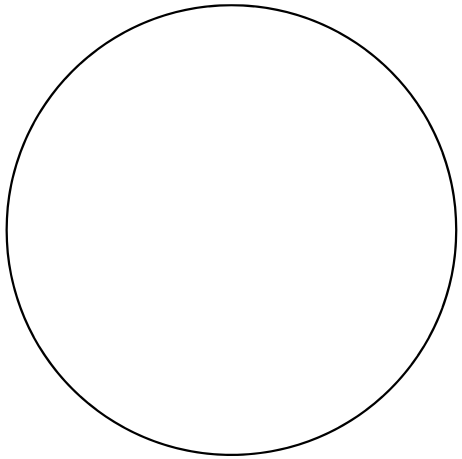

CF

1 cm

Results

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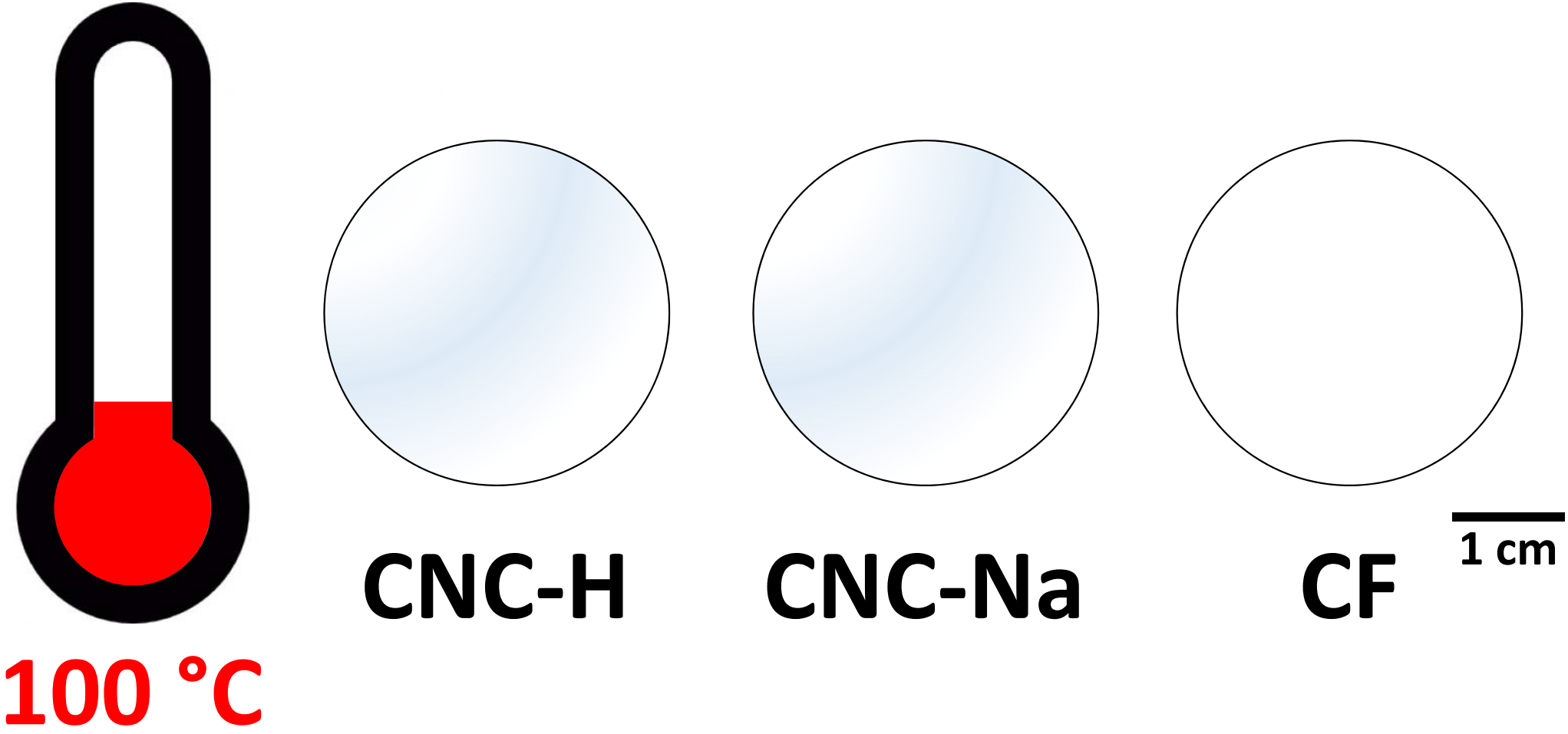

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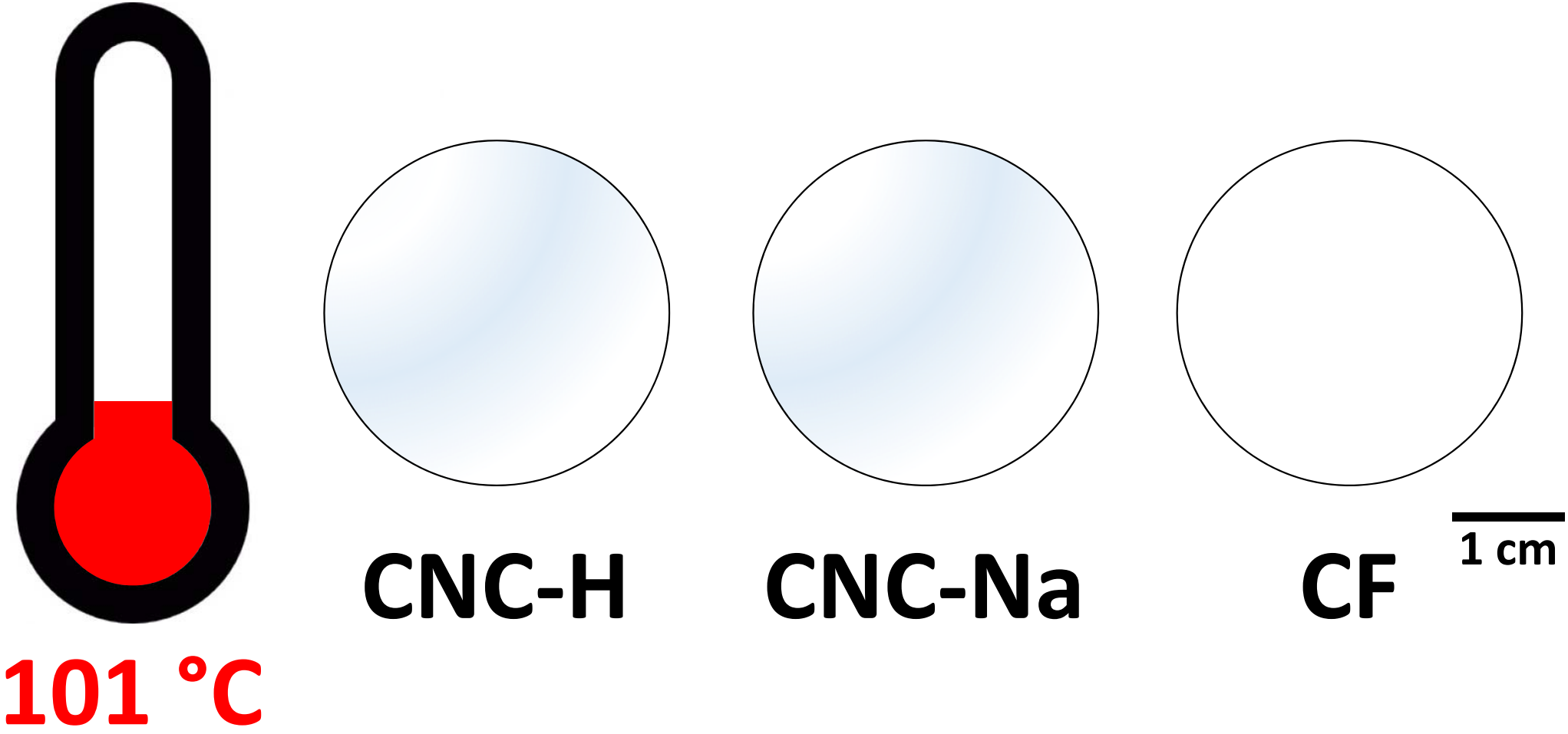

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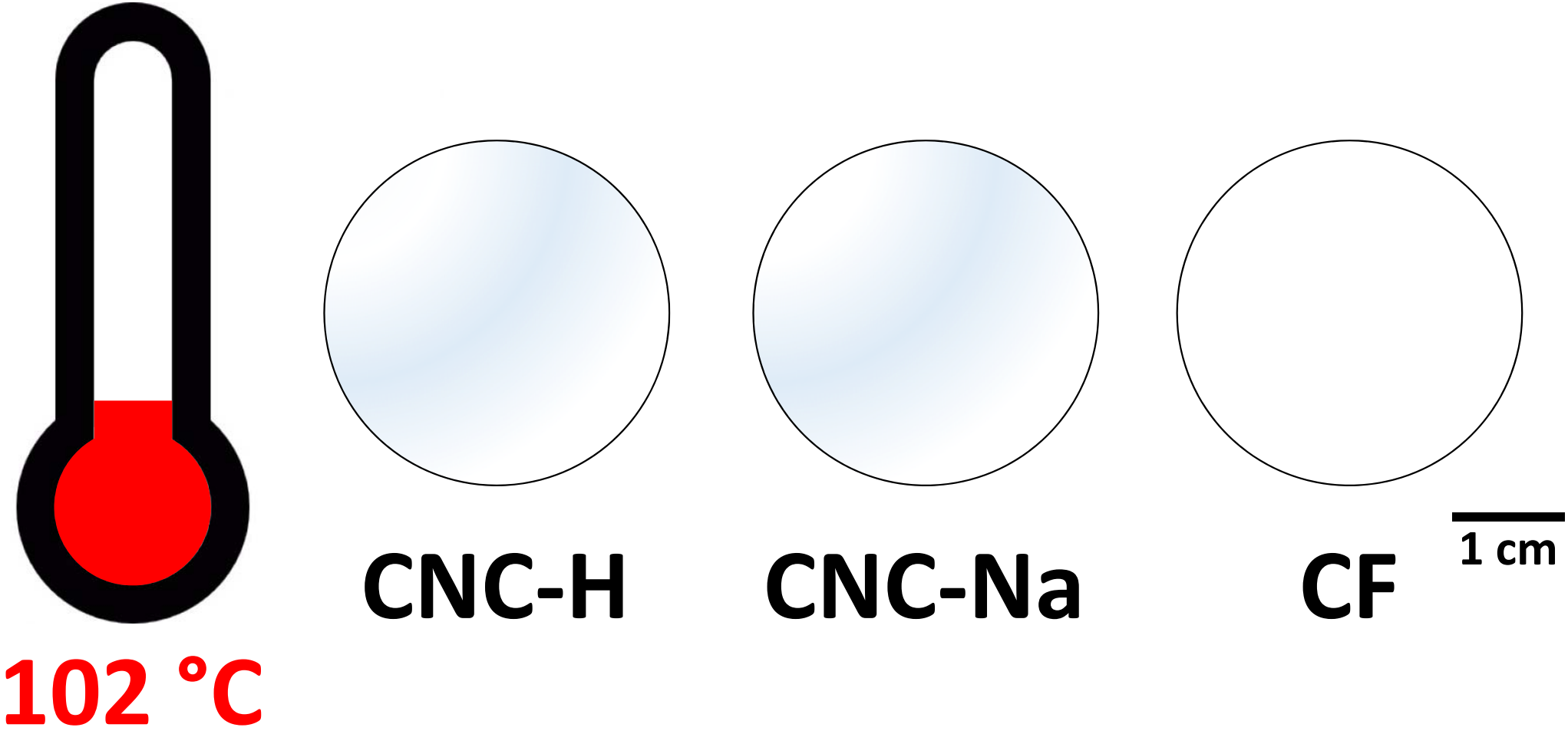

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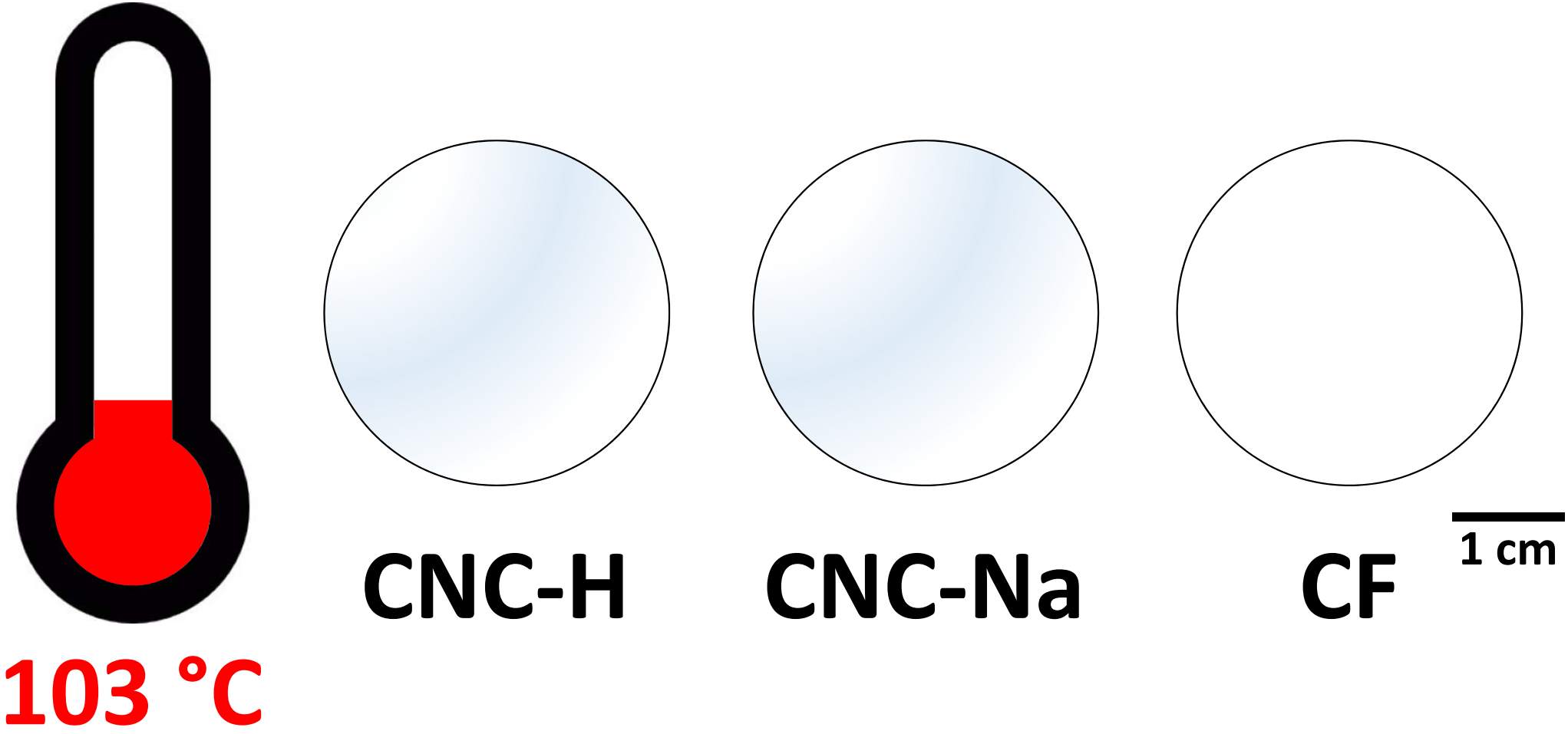

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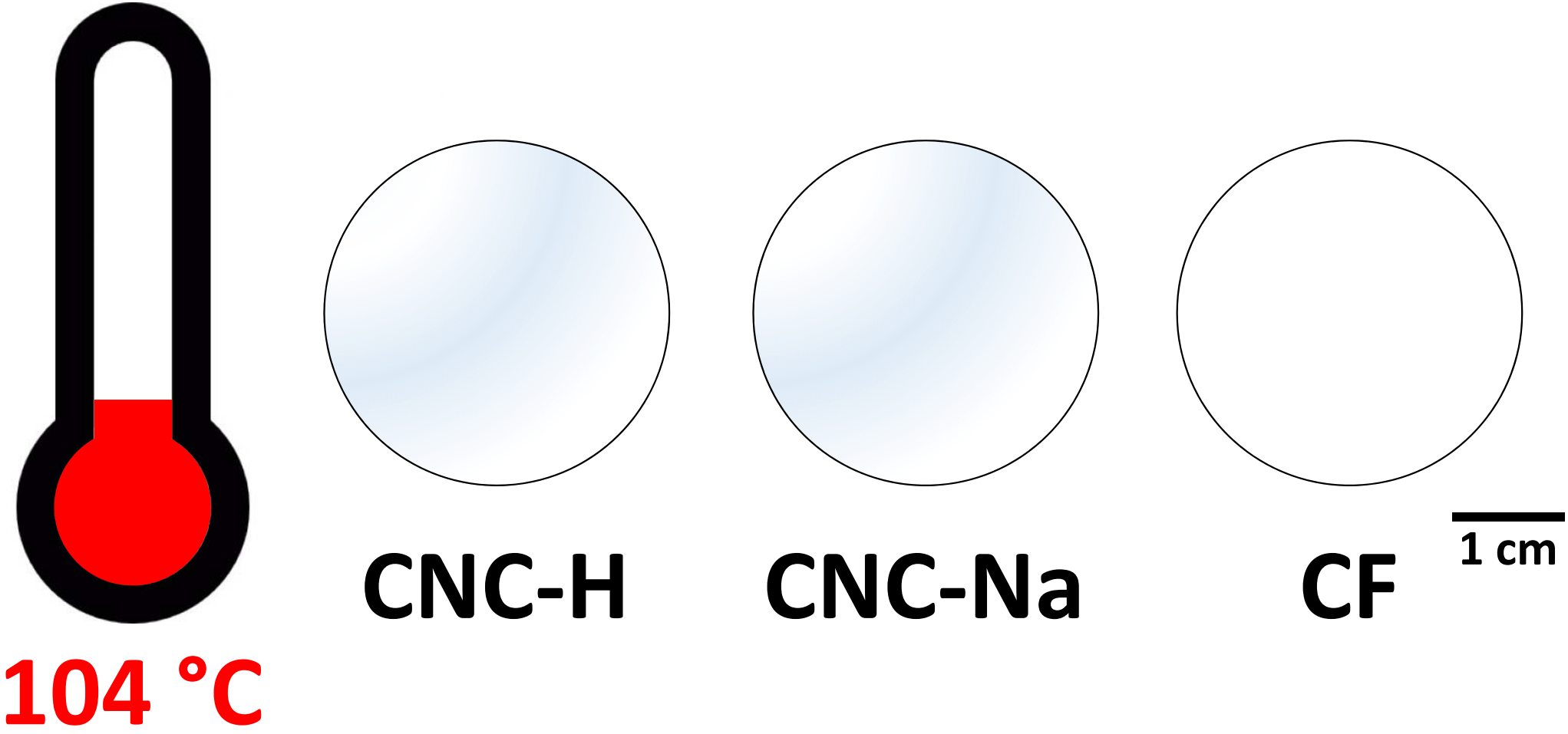

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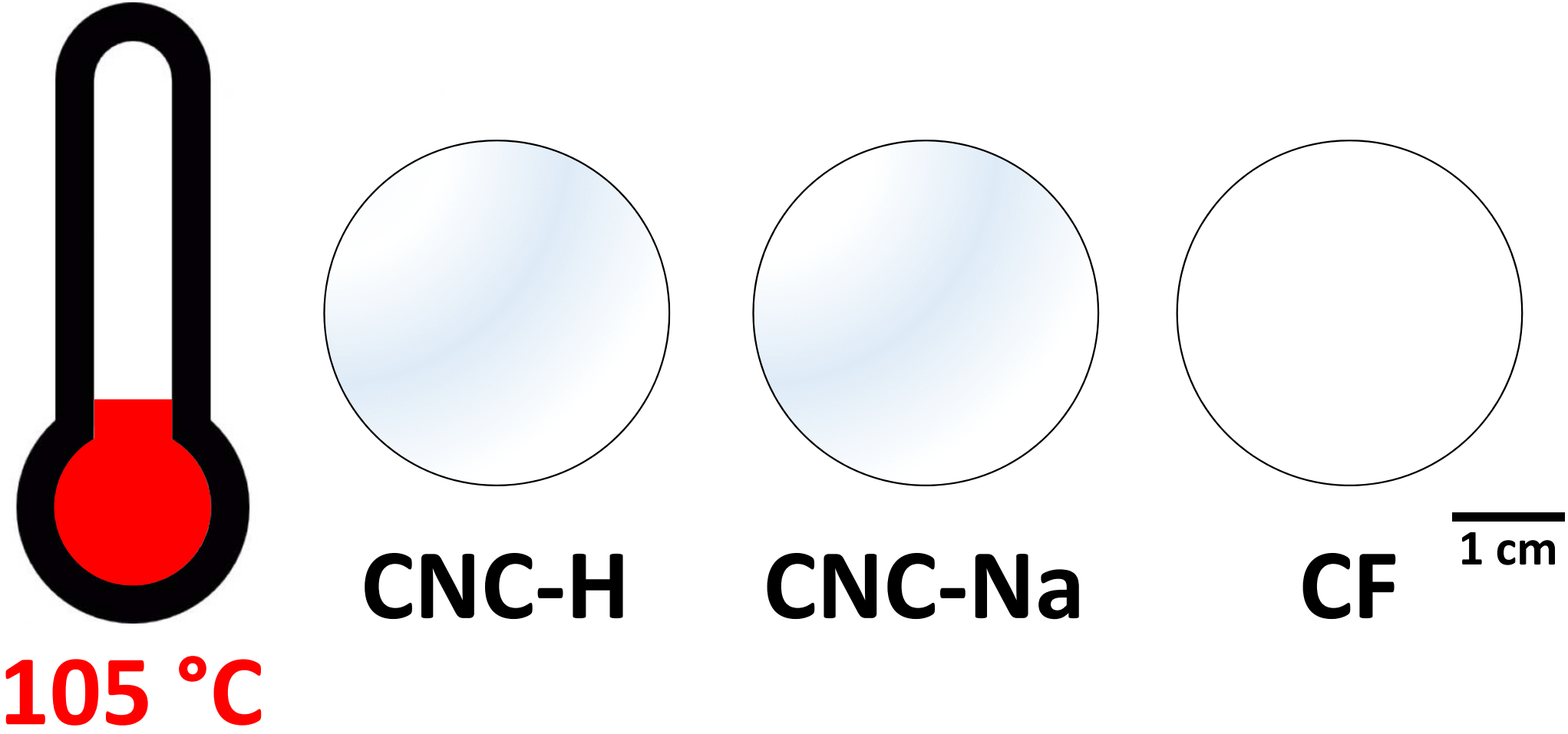

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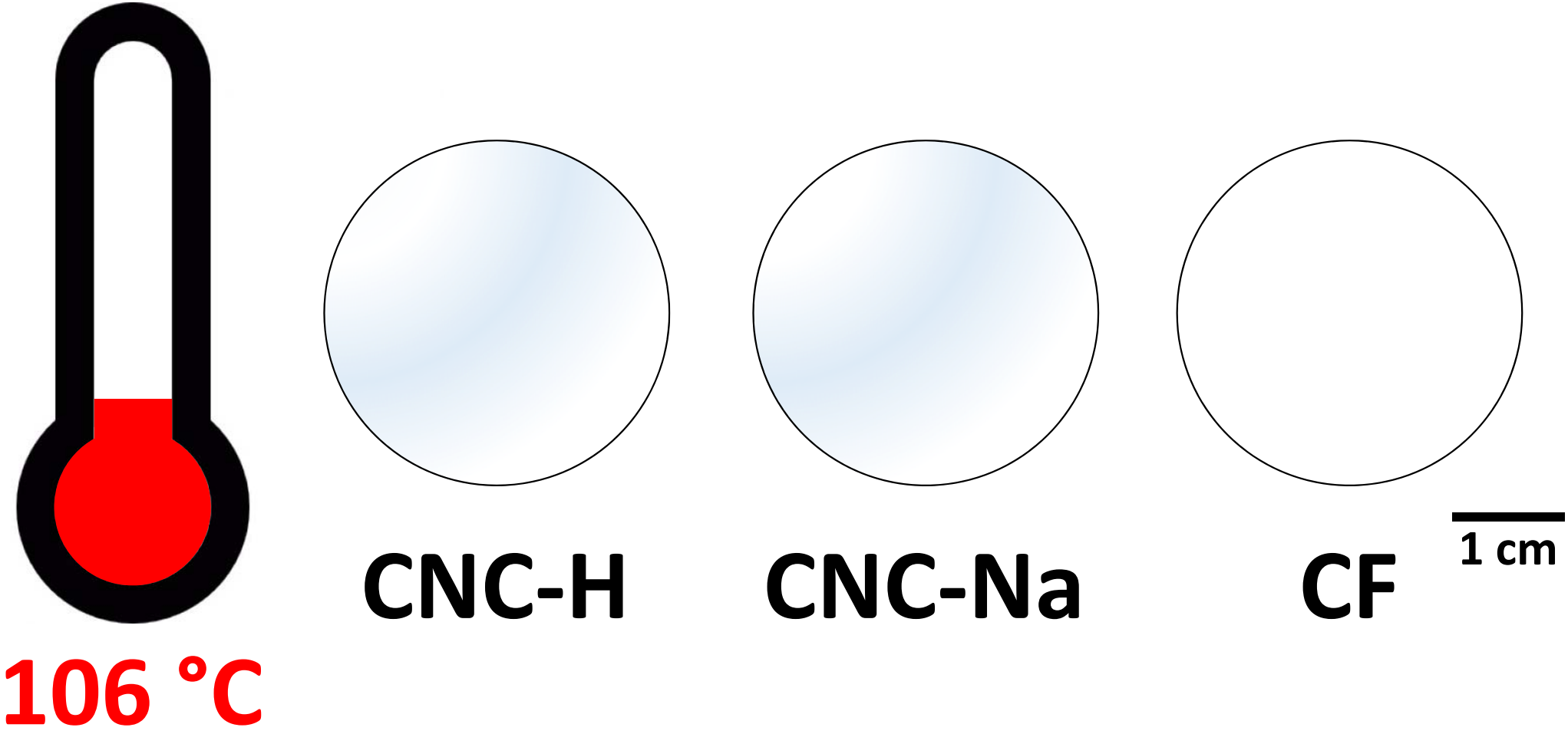

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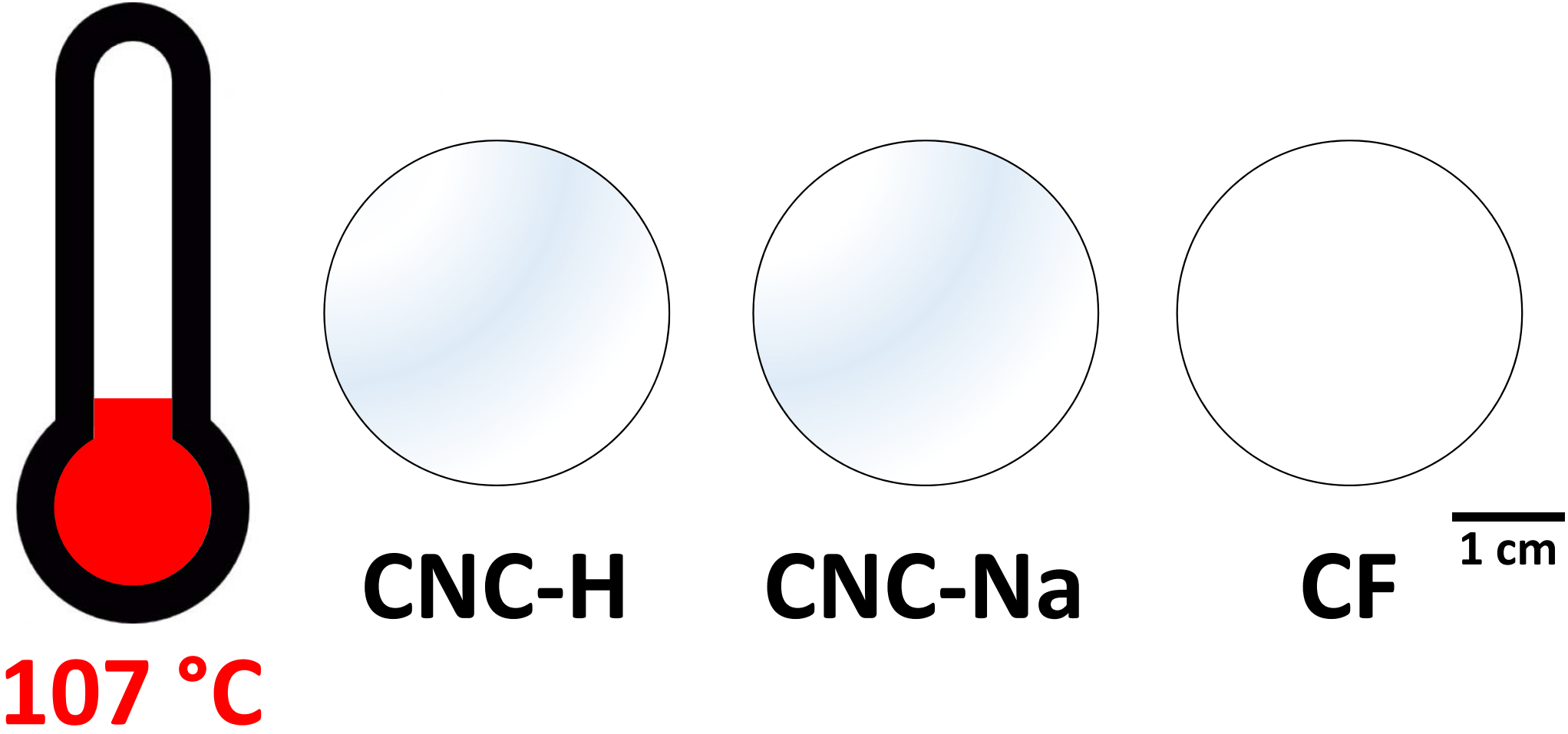

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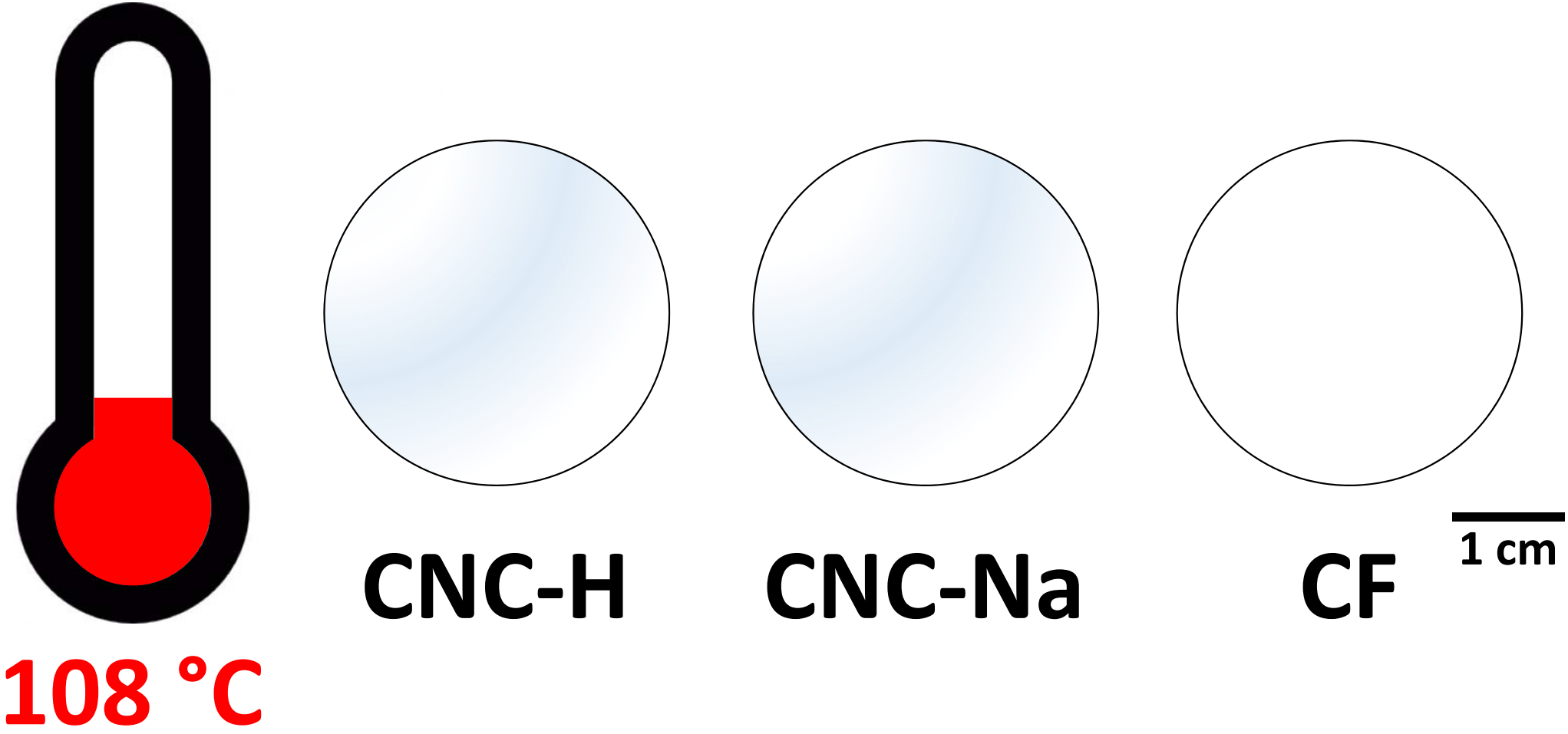

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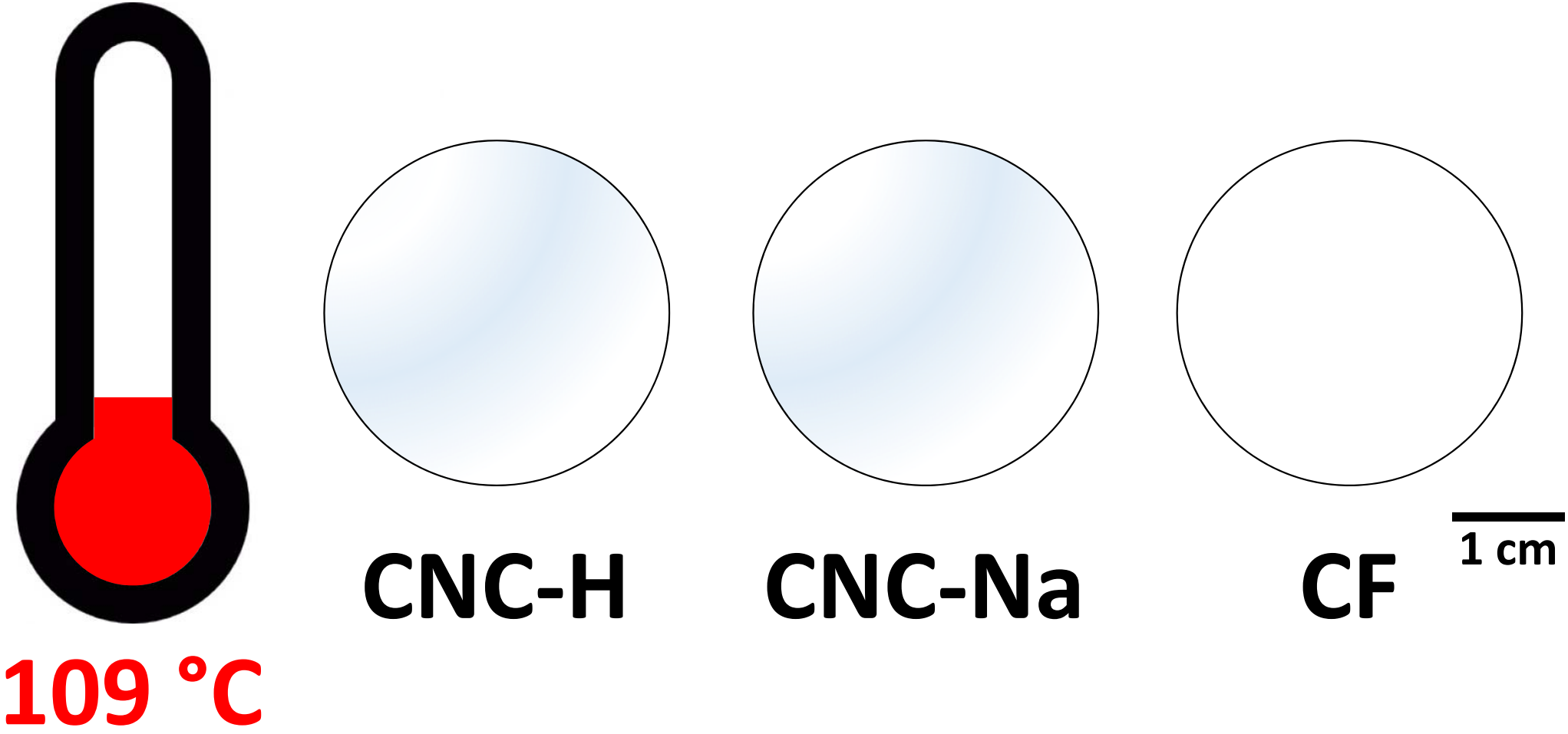

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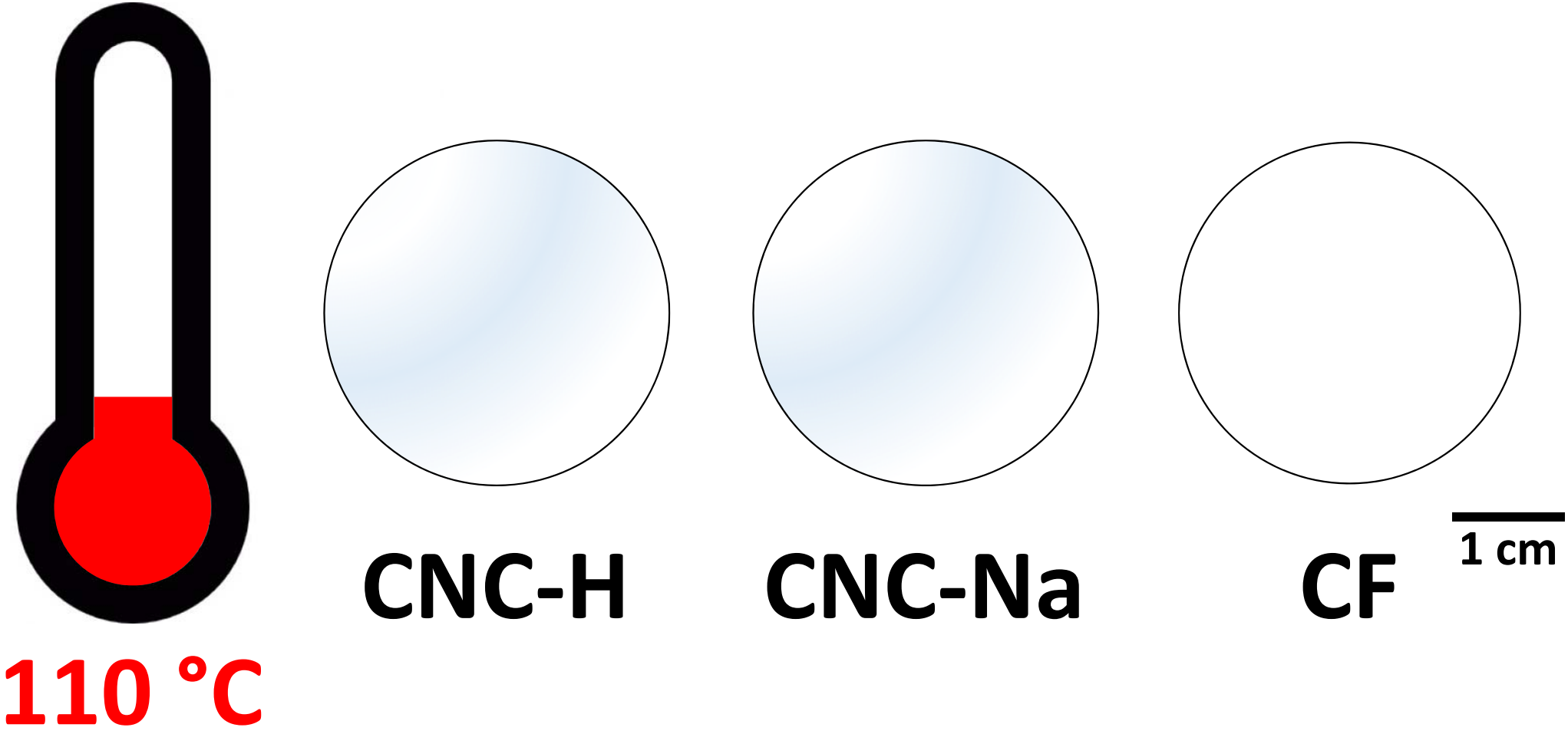

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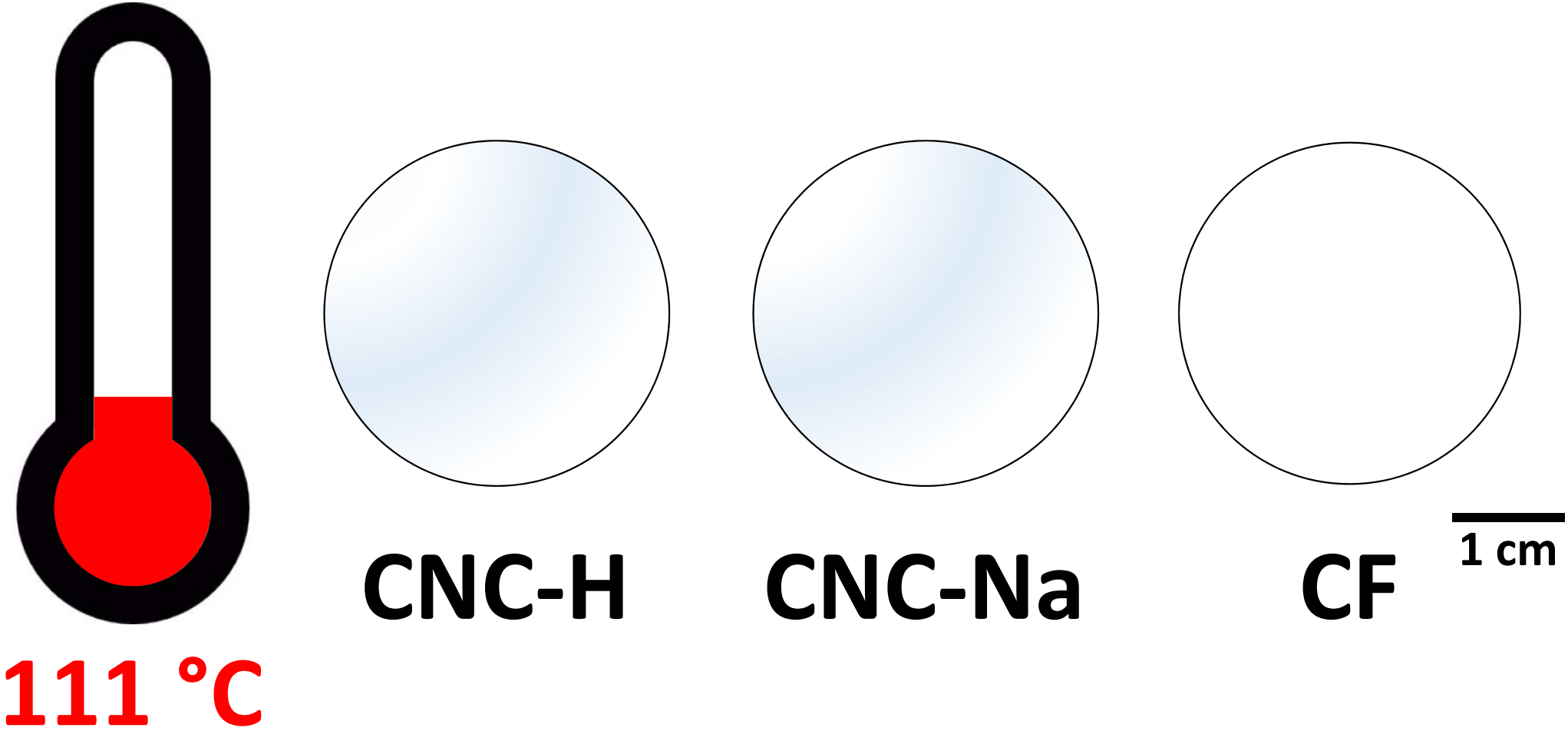

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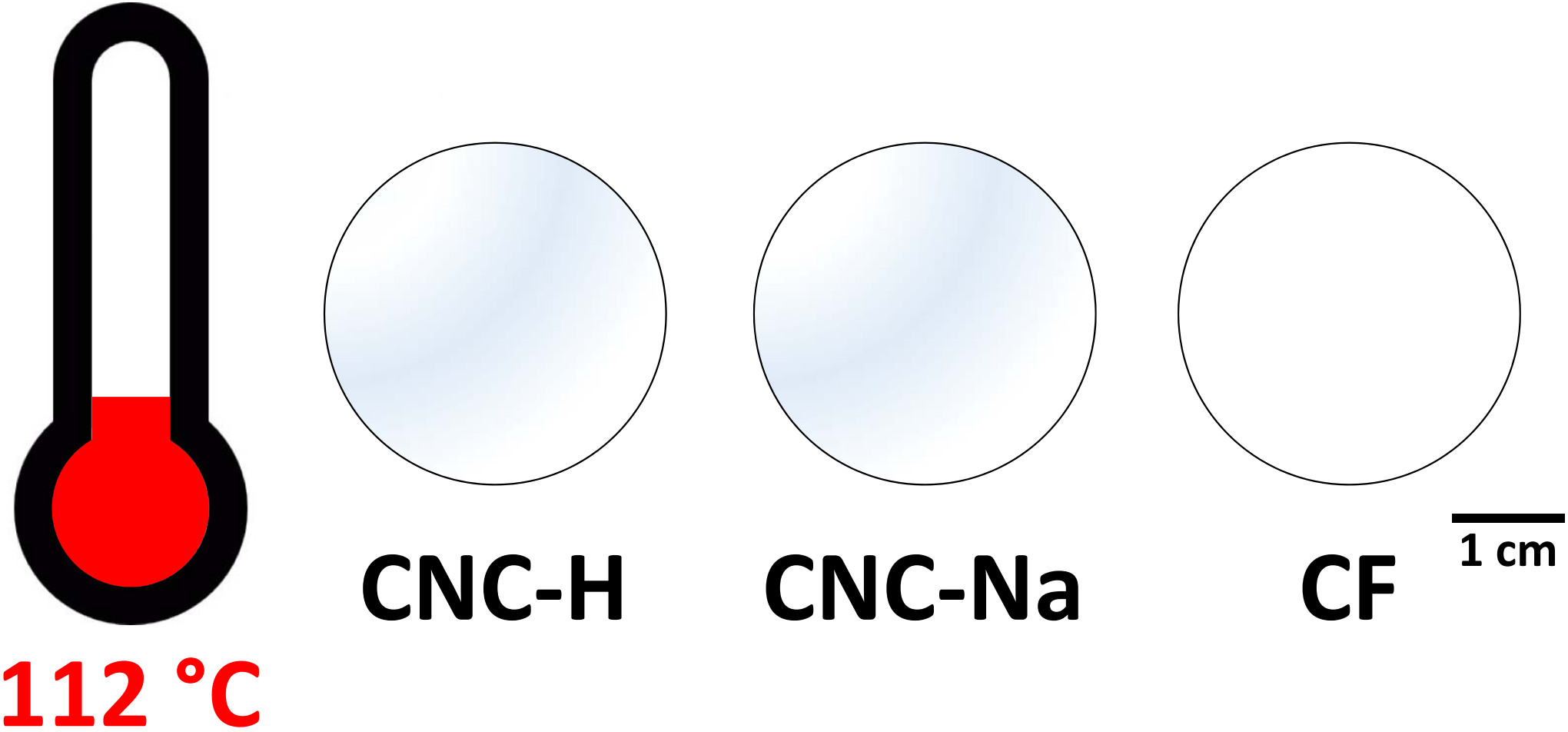

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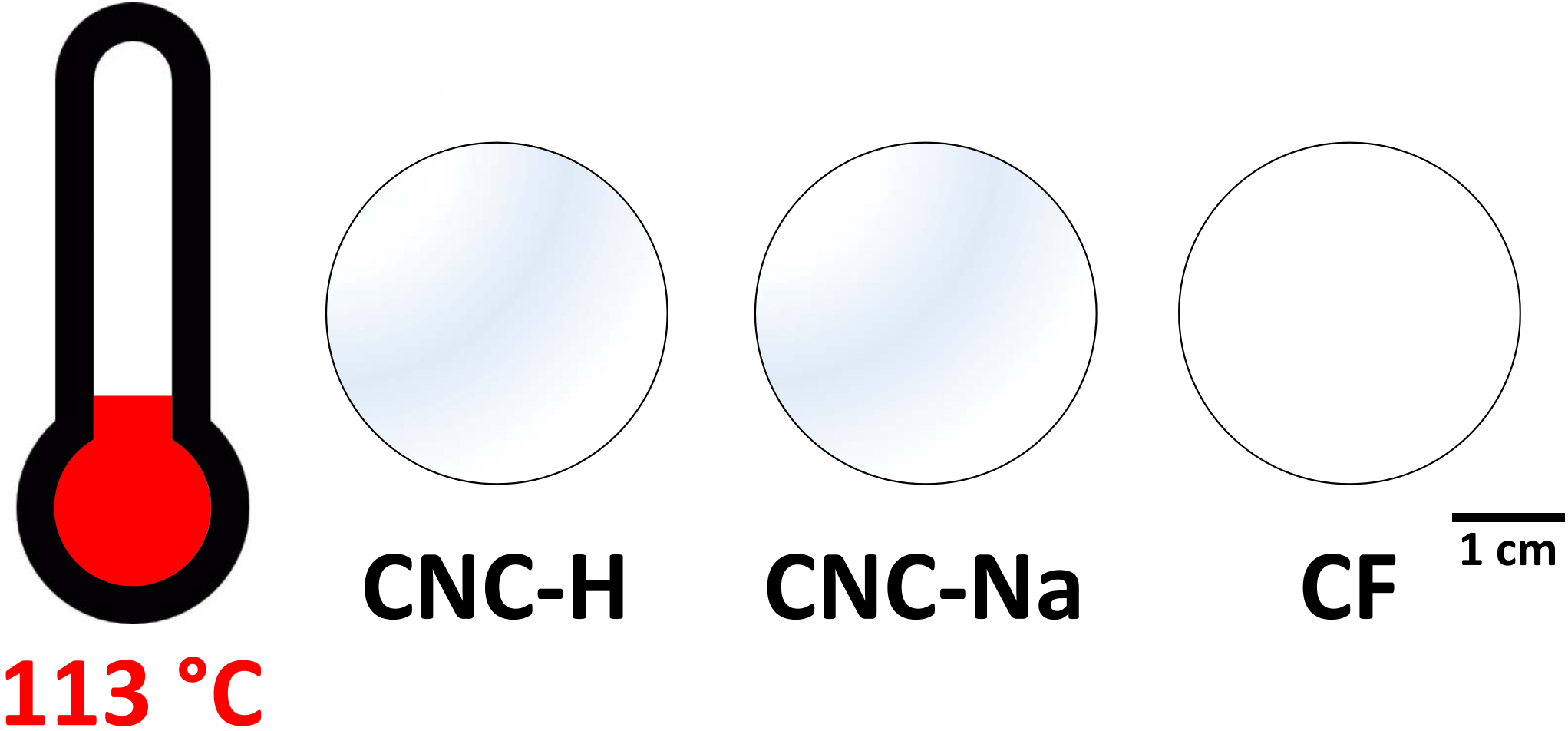

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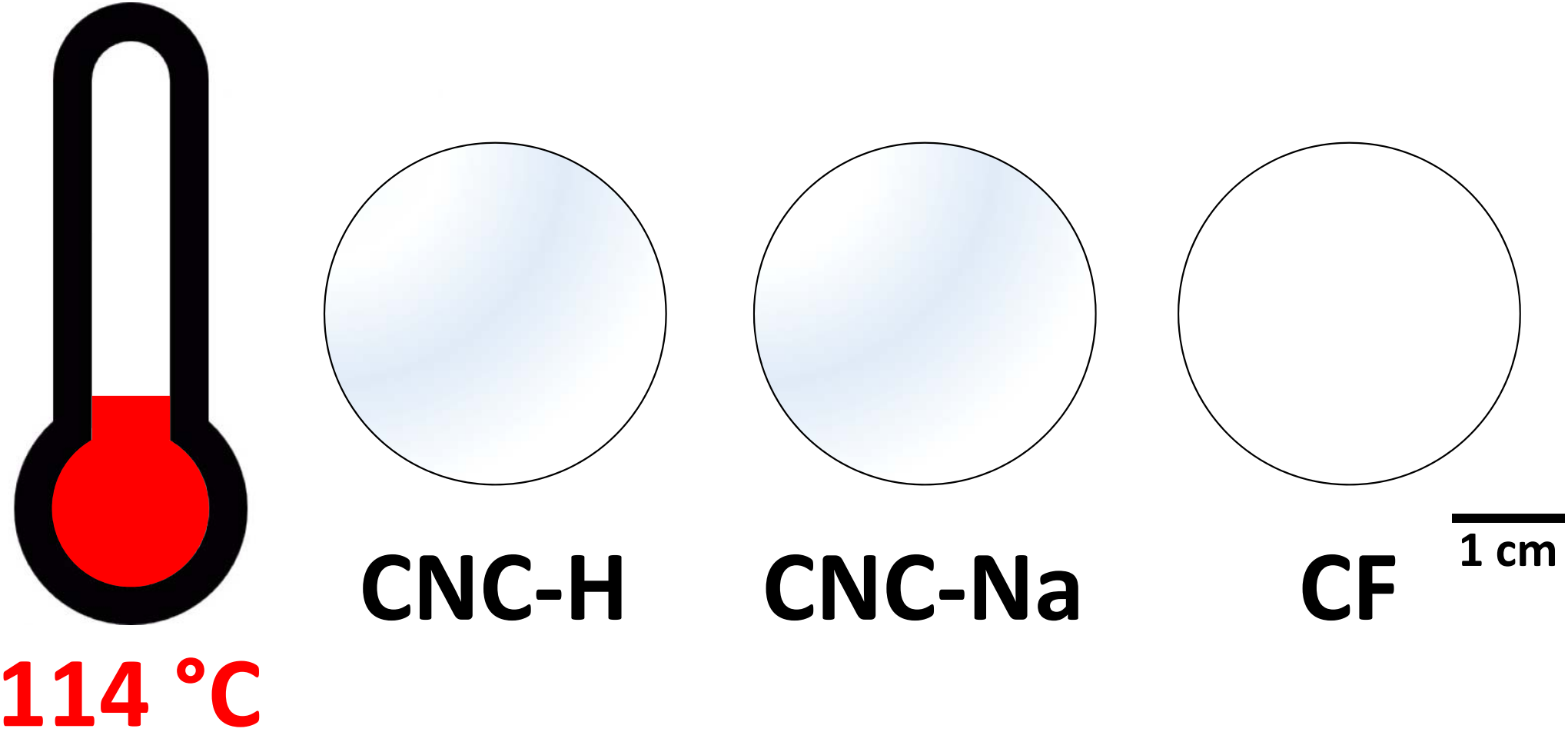

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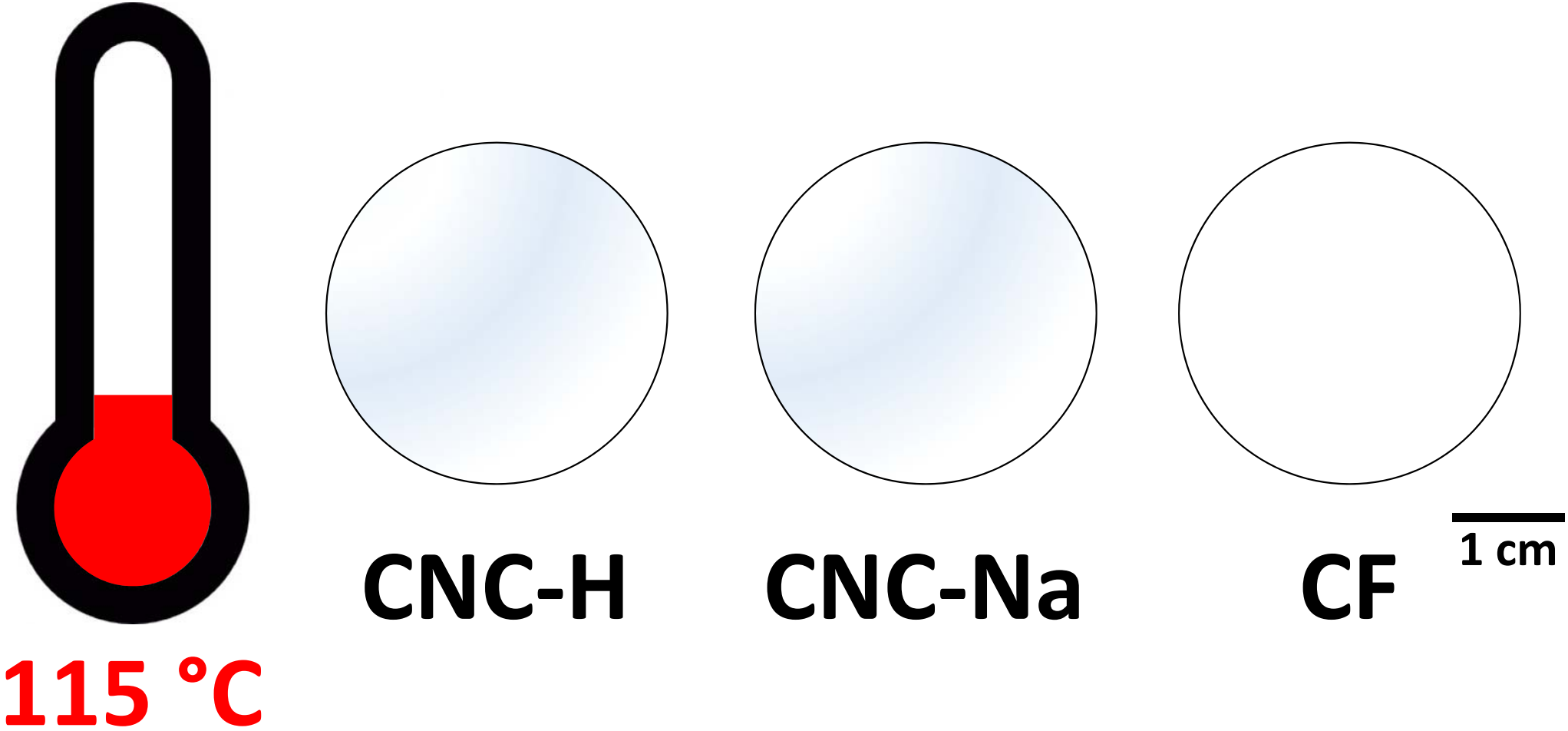

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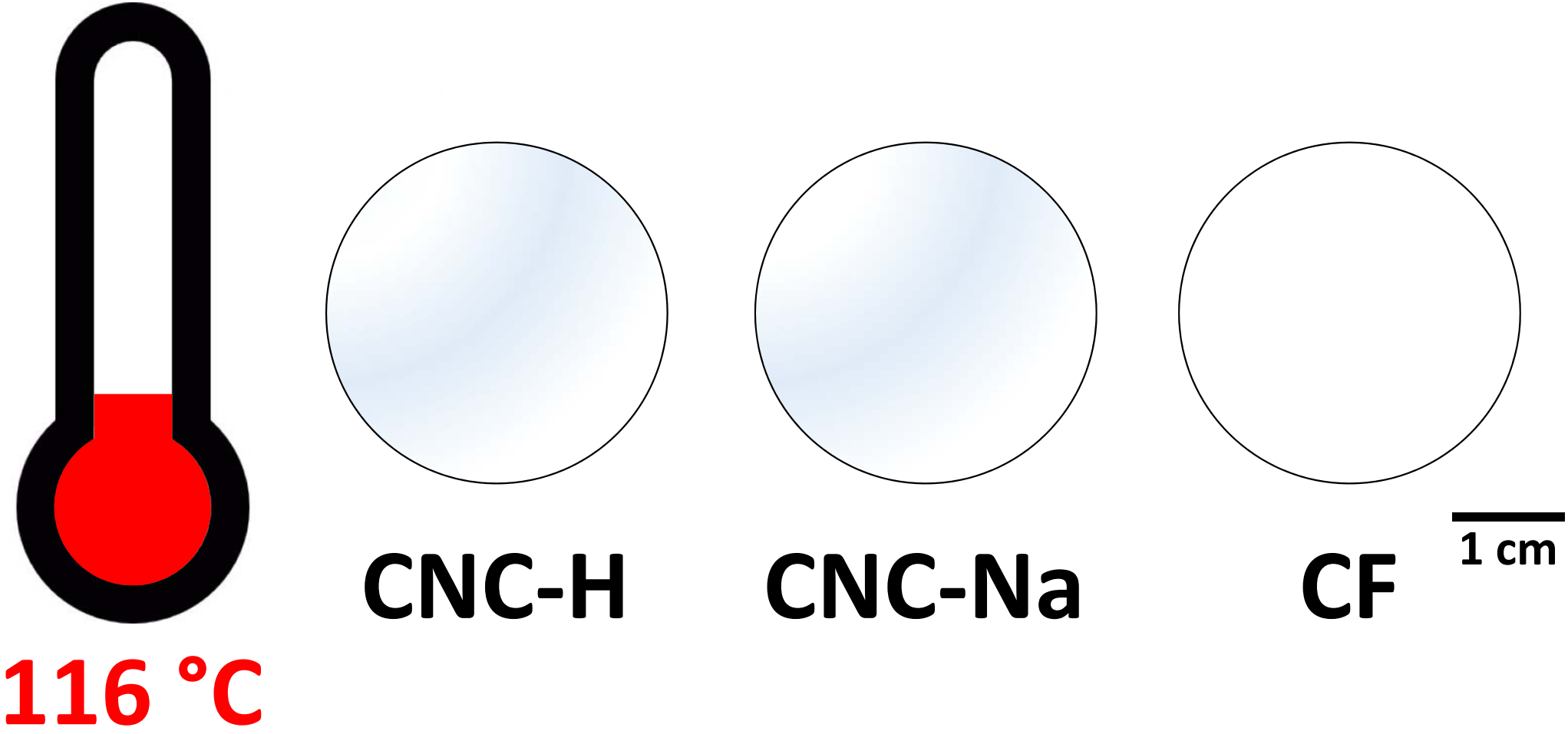

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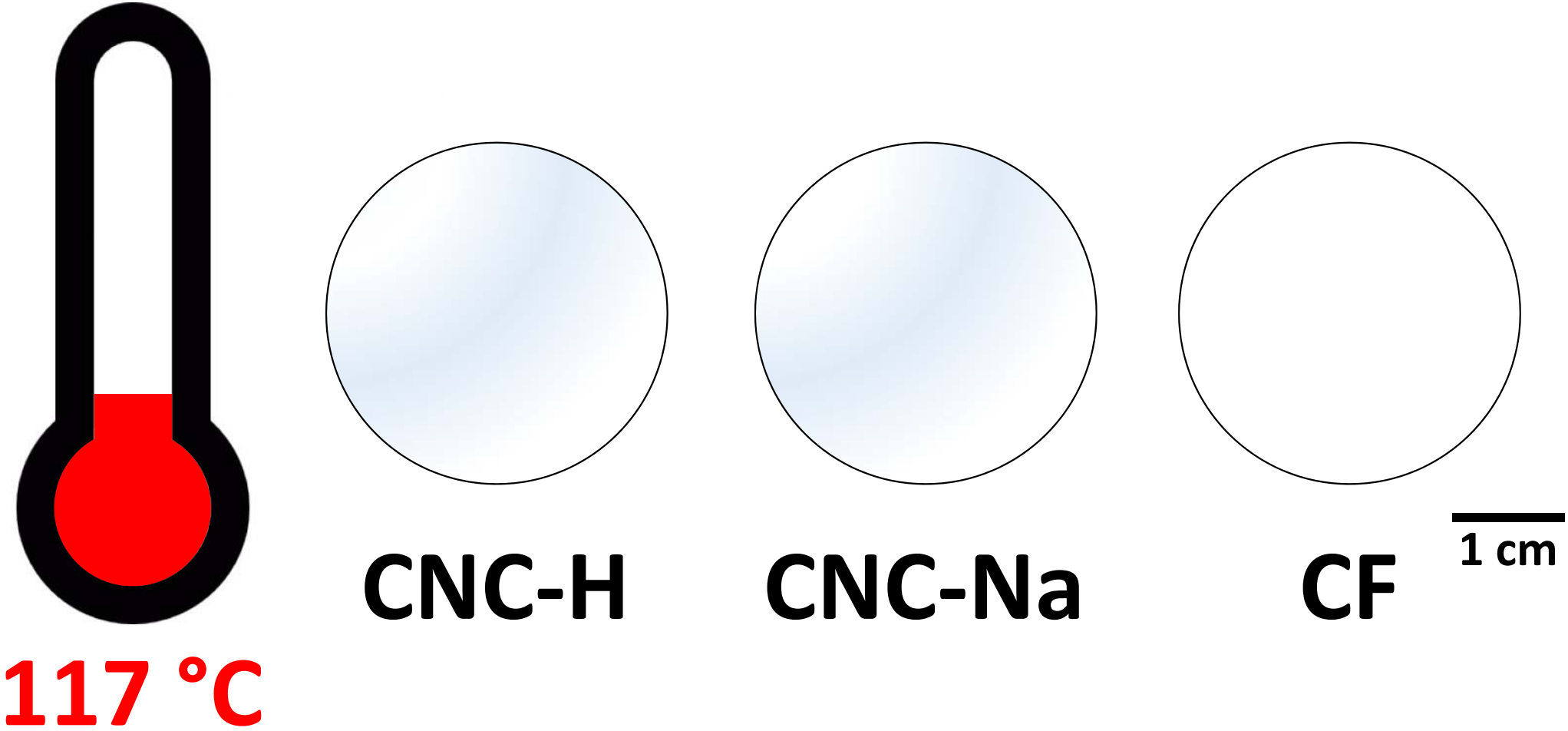

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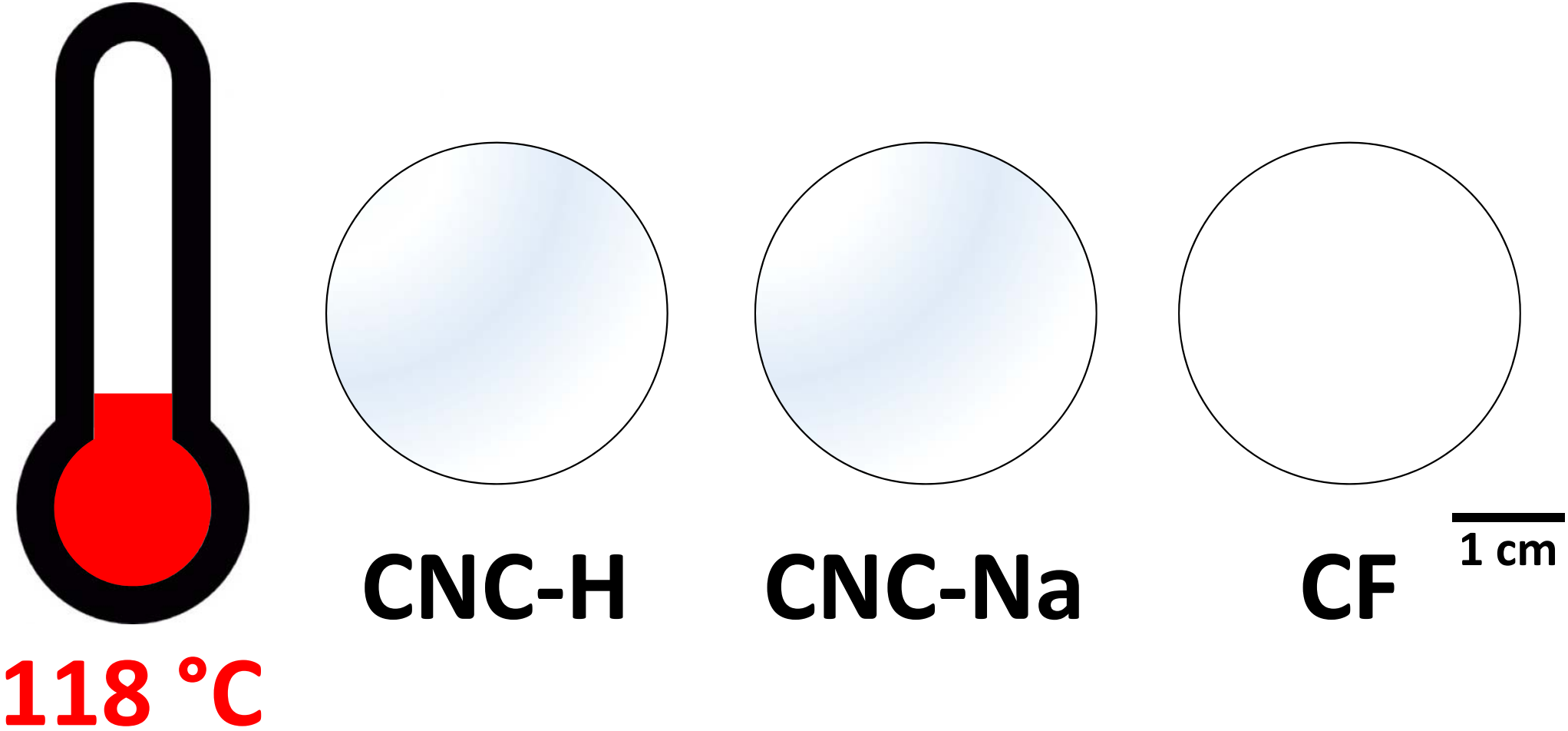

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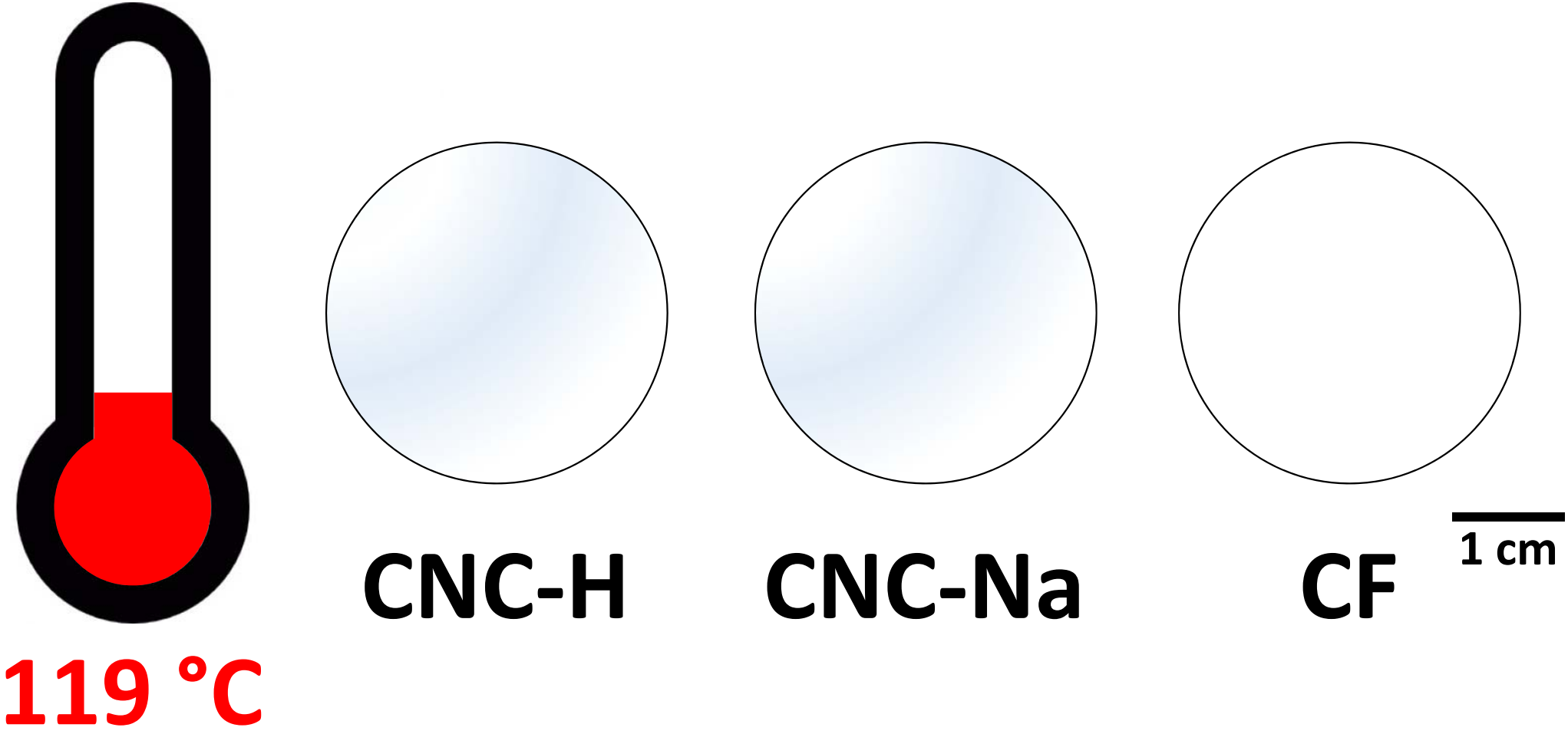

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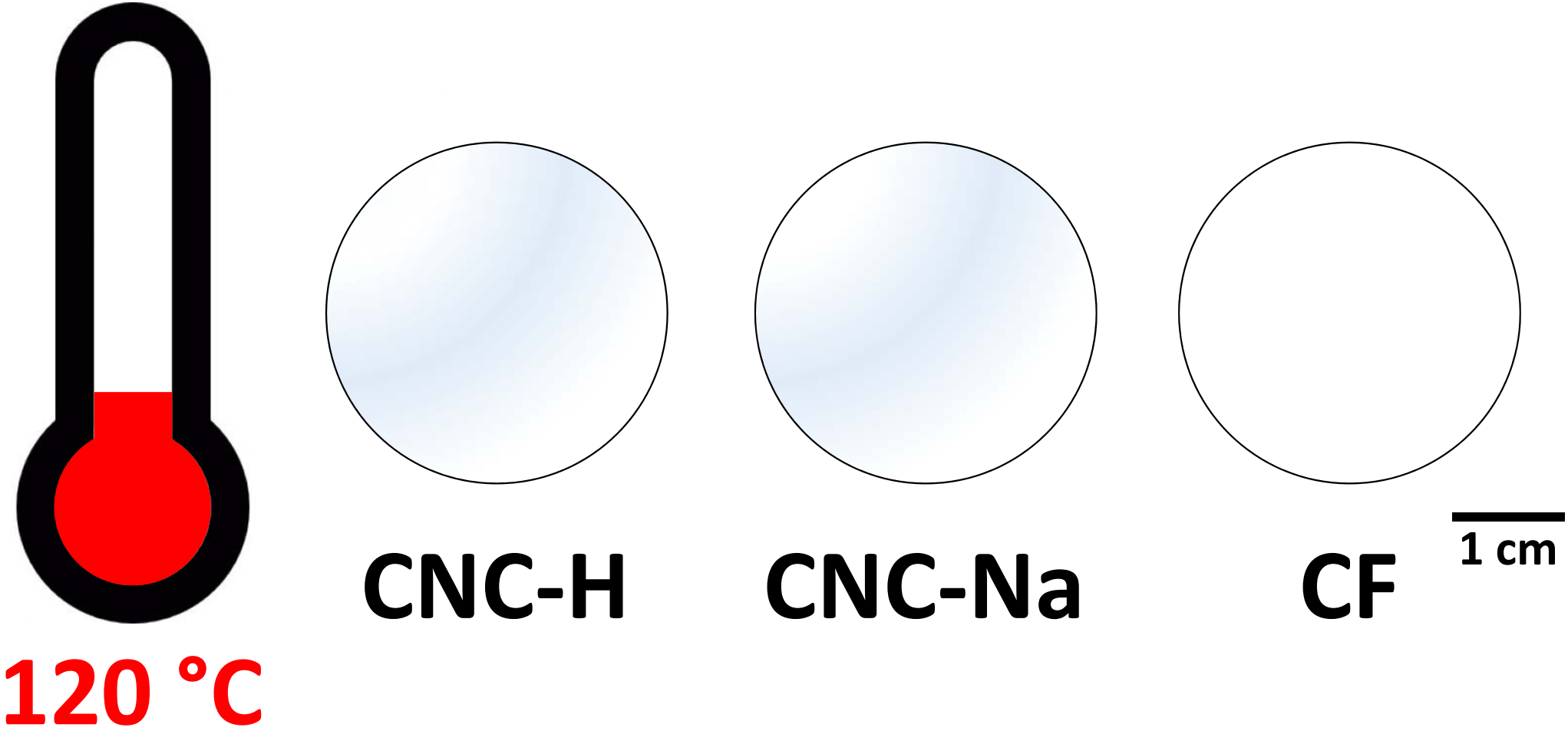

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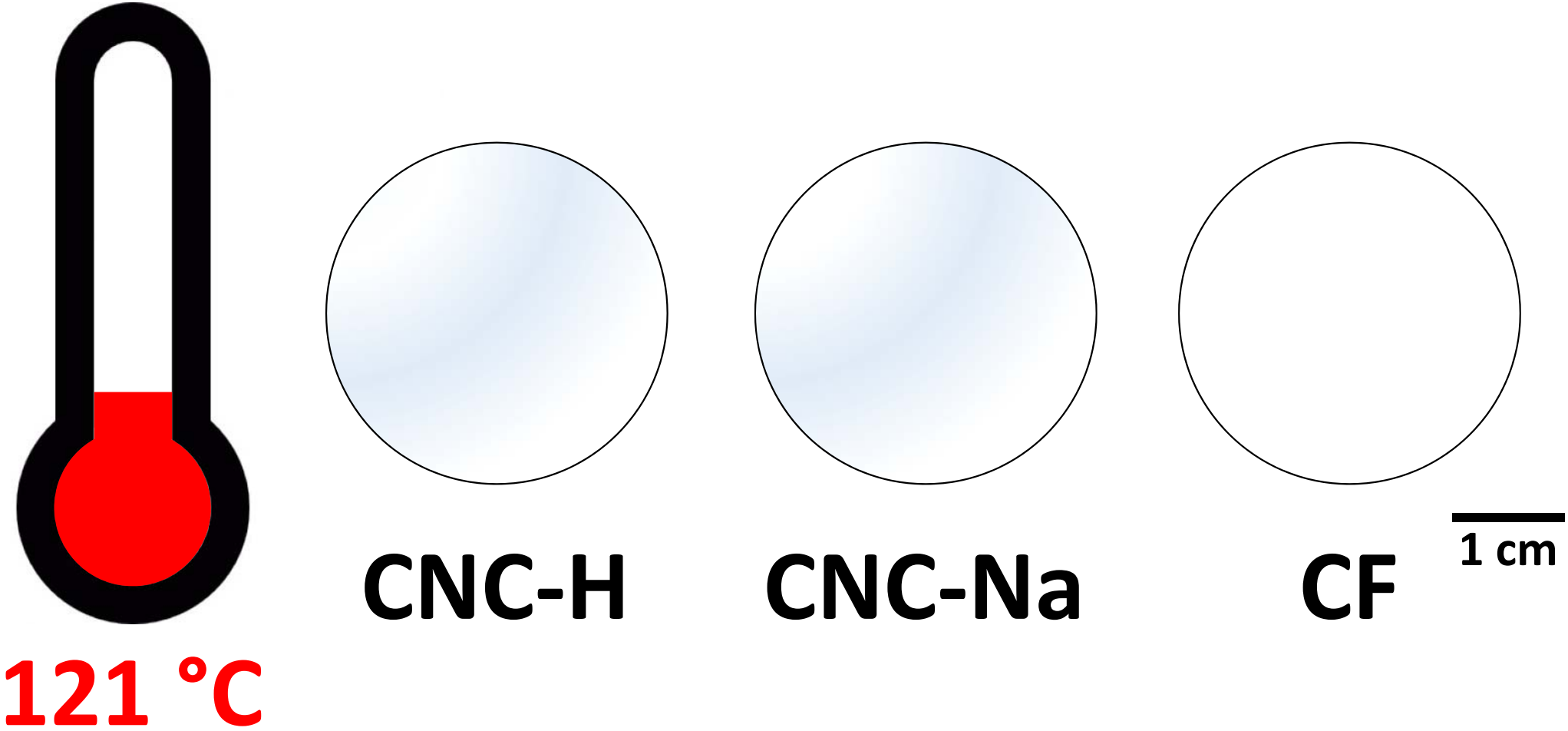

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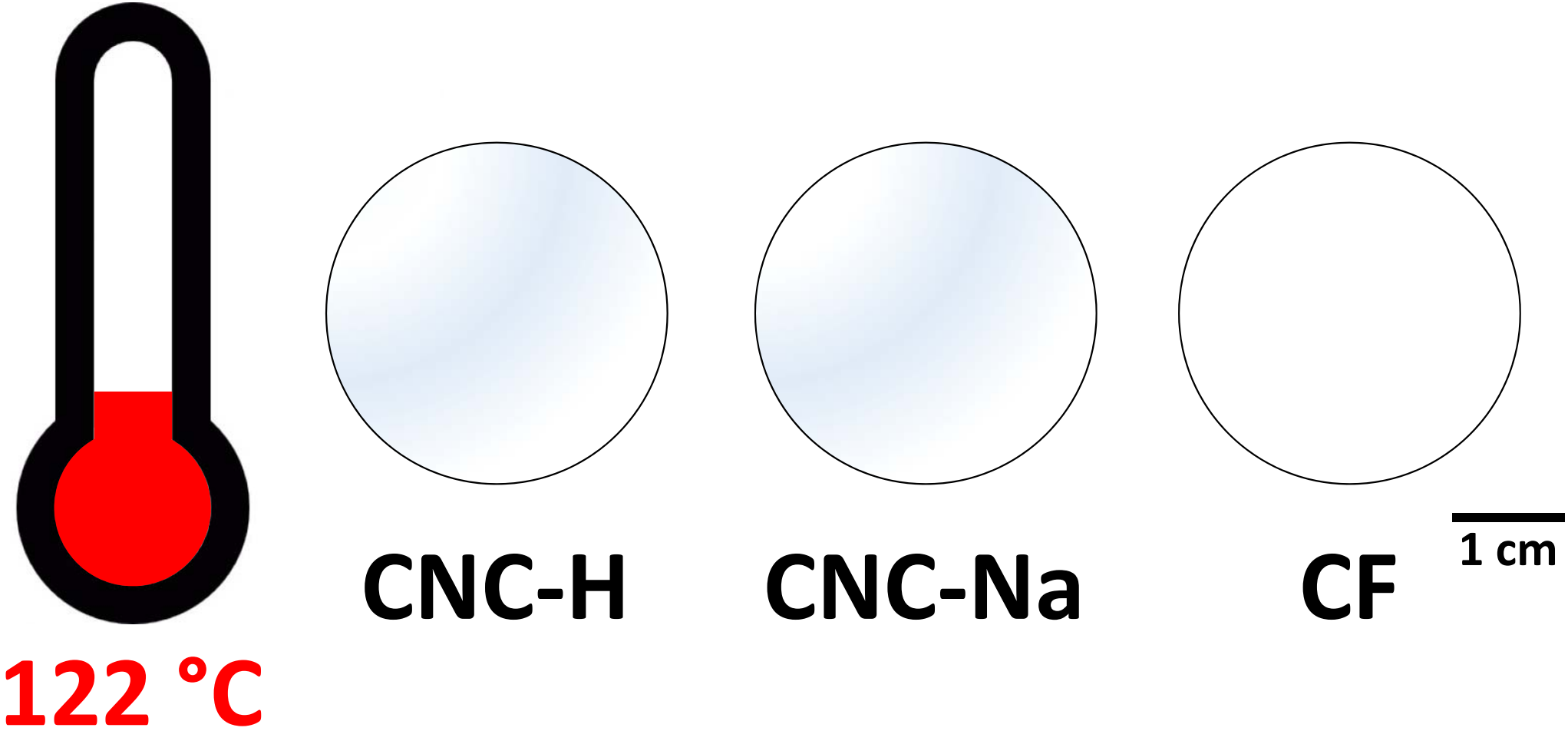

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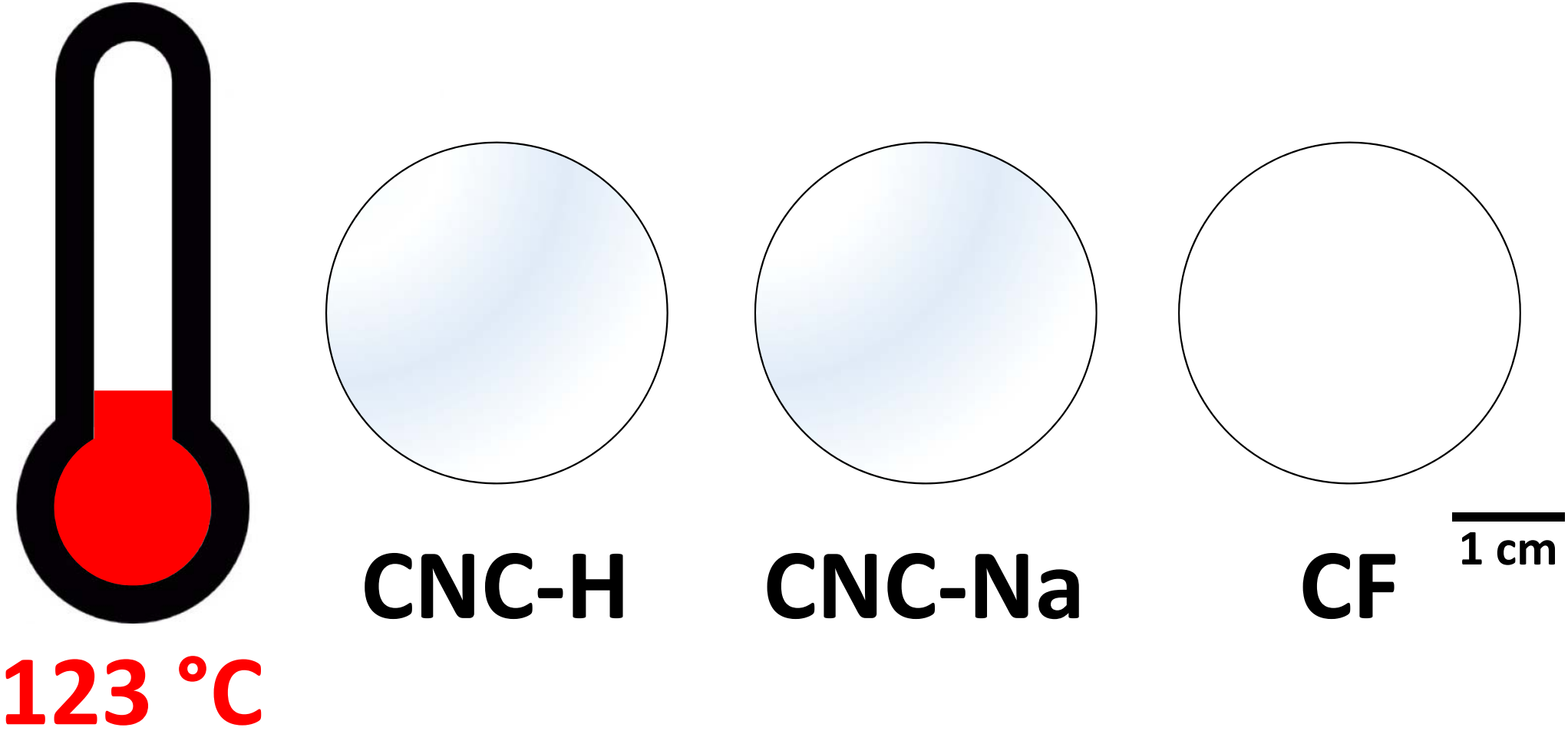

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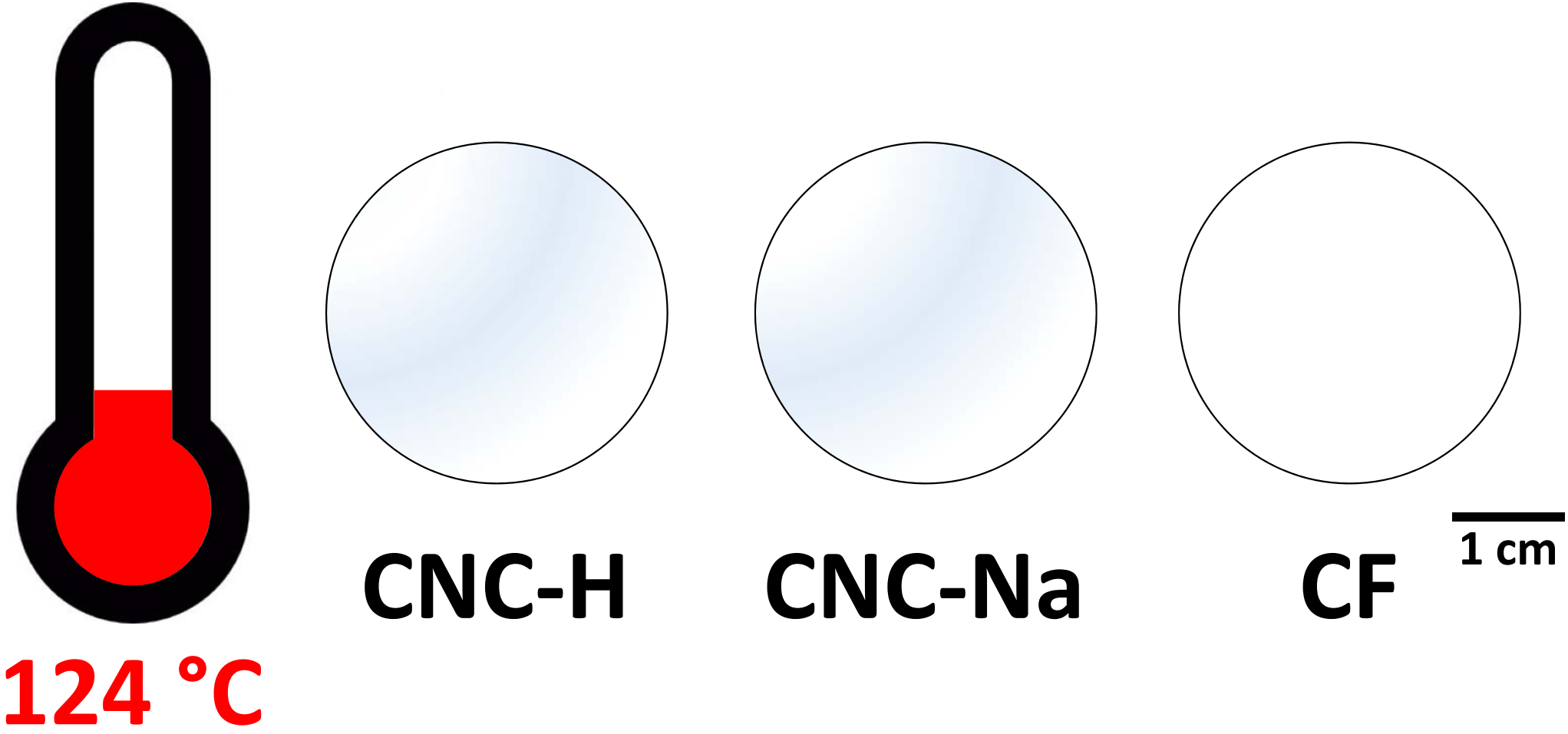

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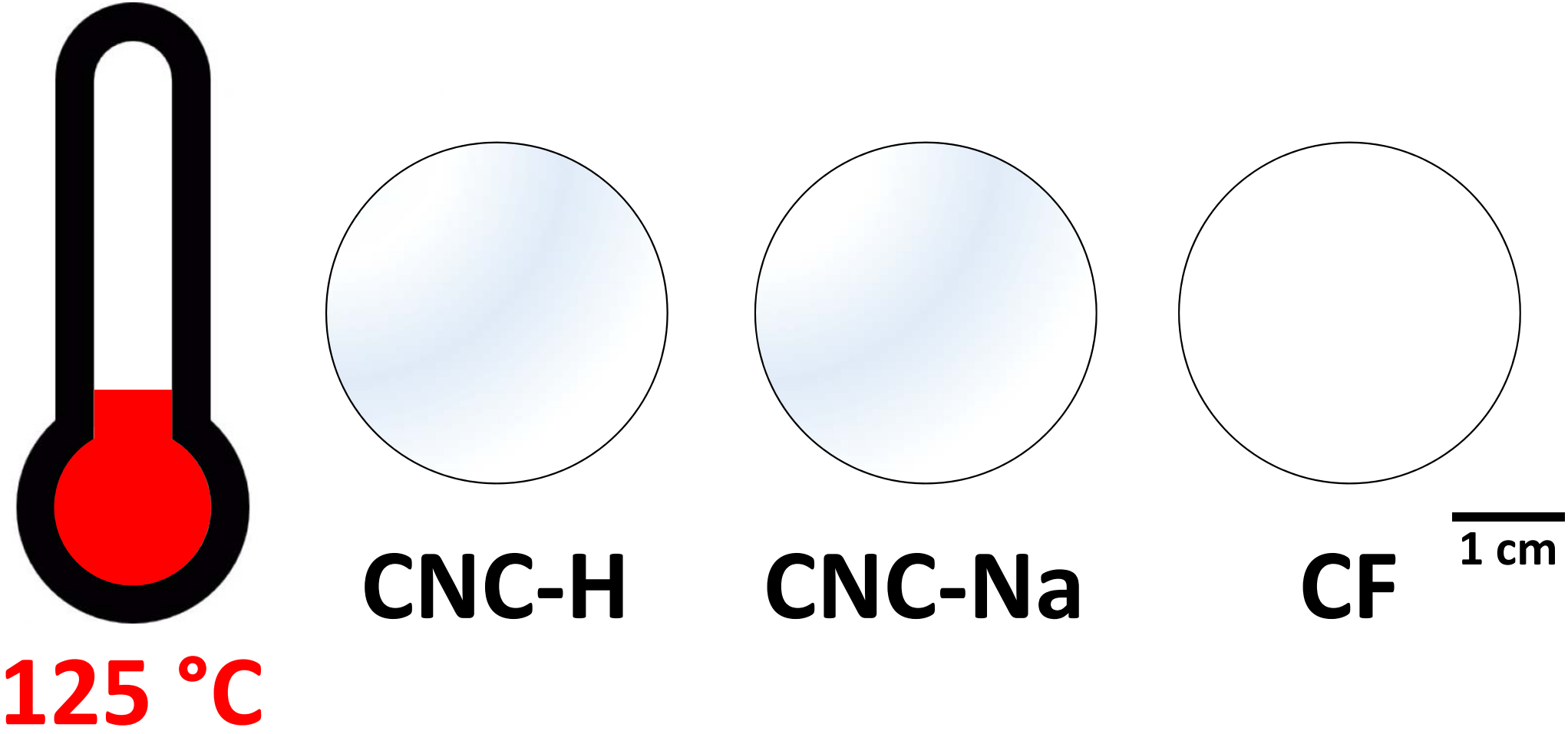

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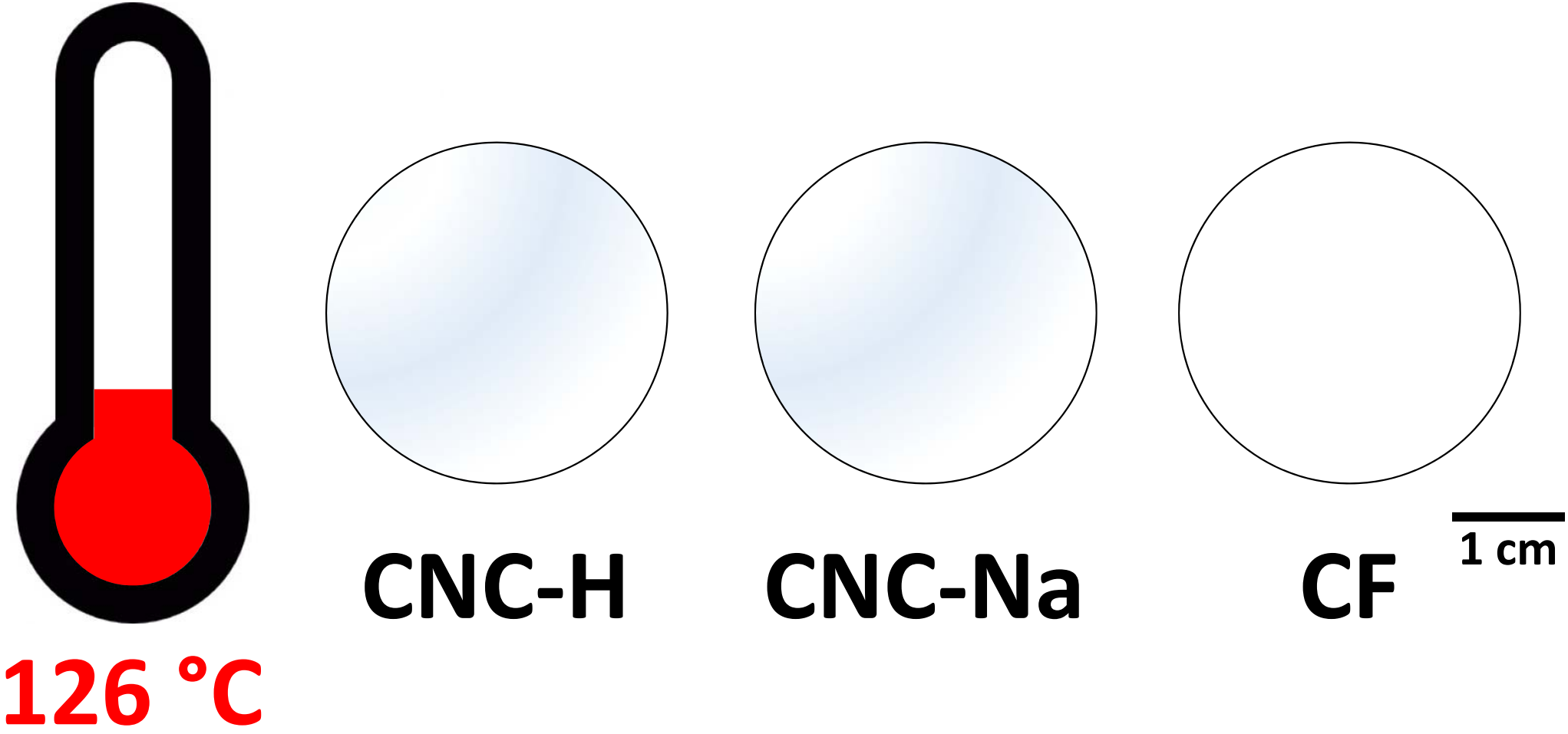

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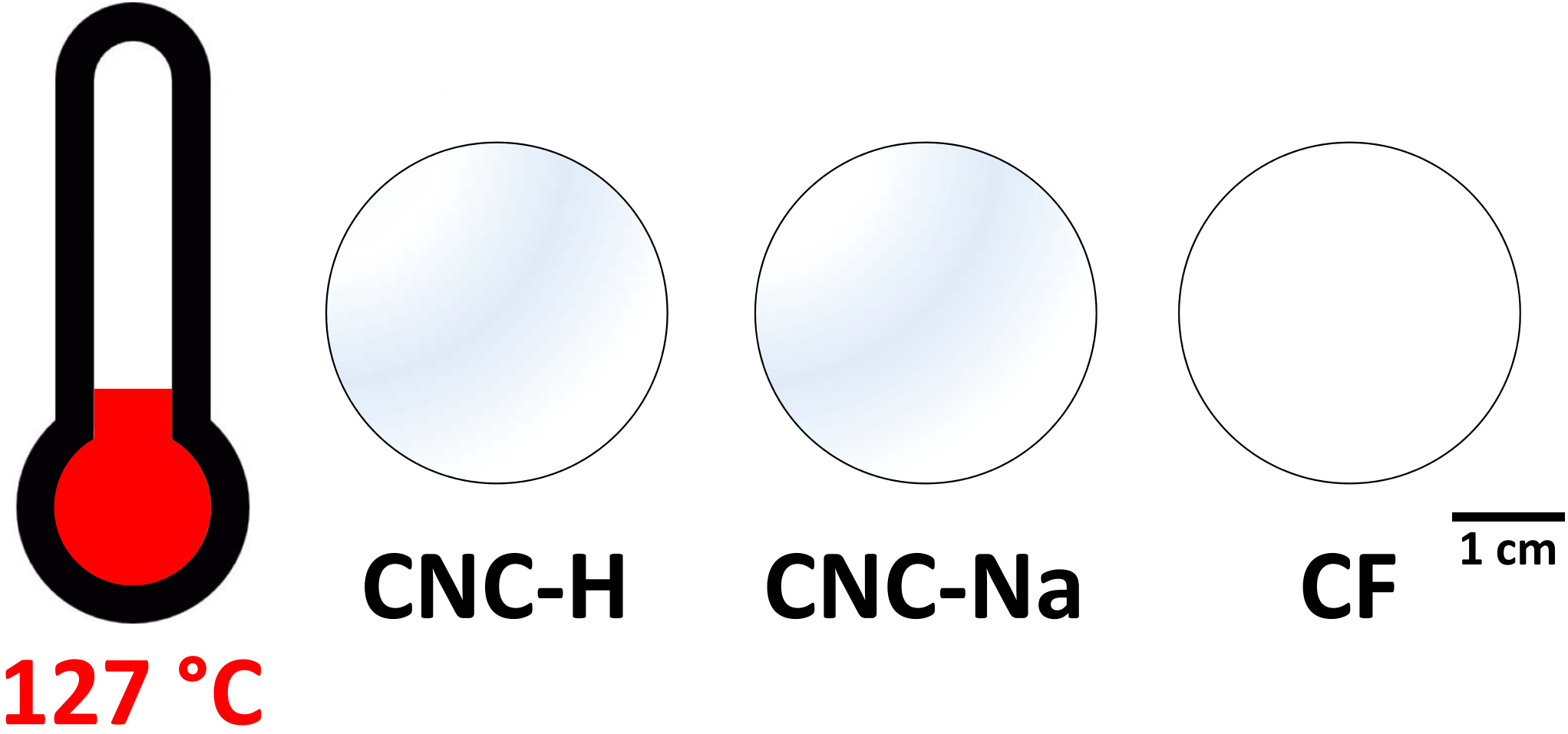

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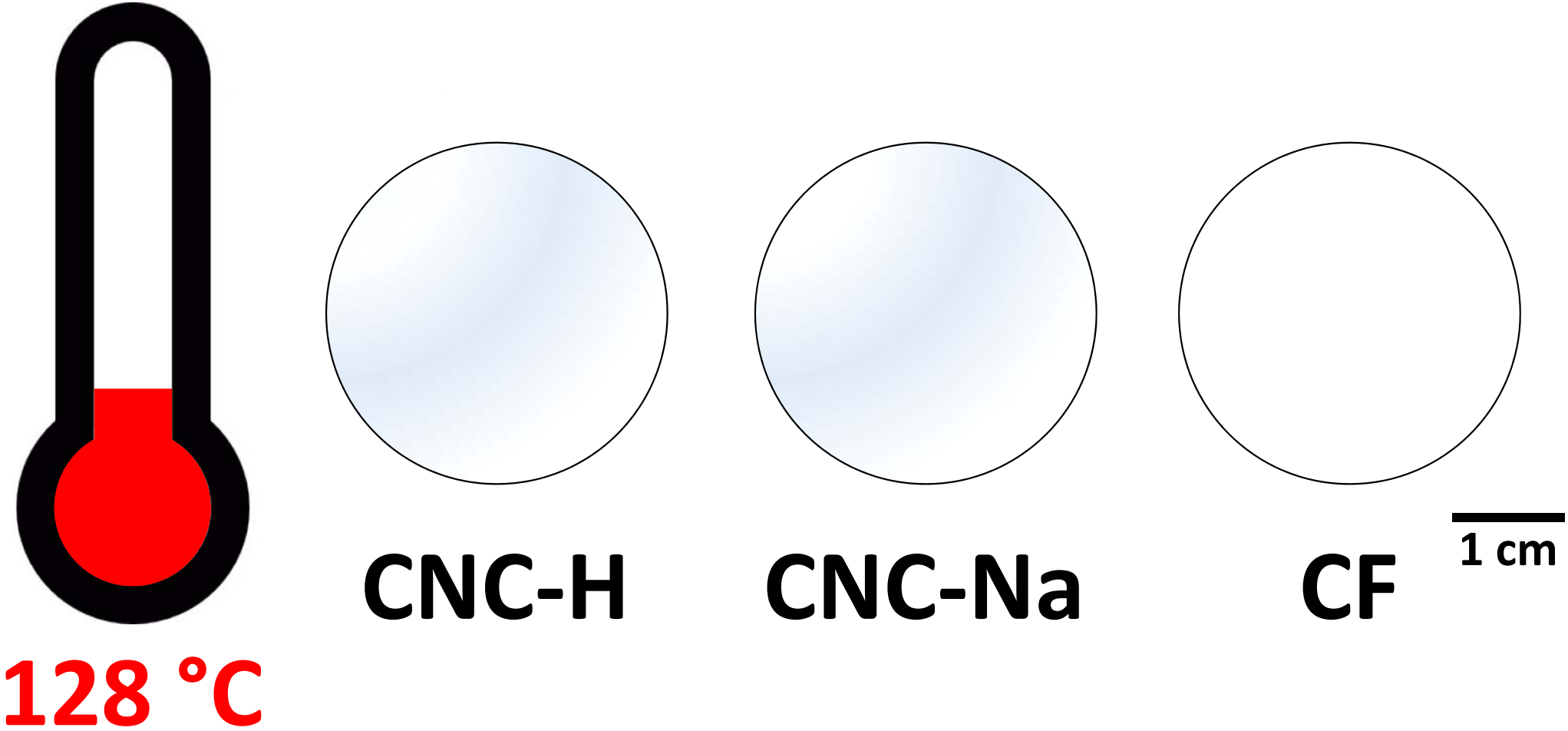

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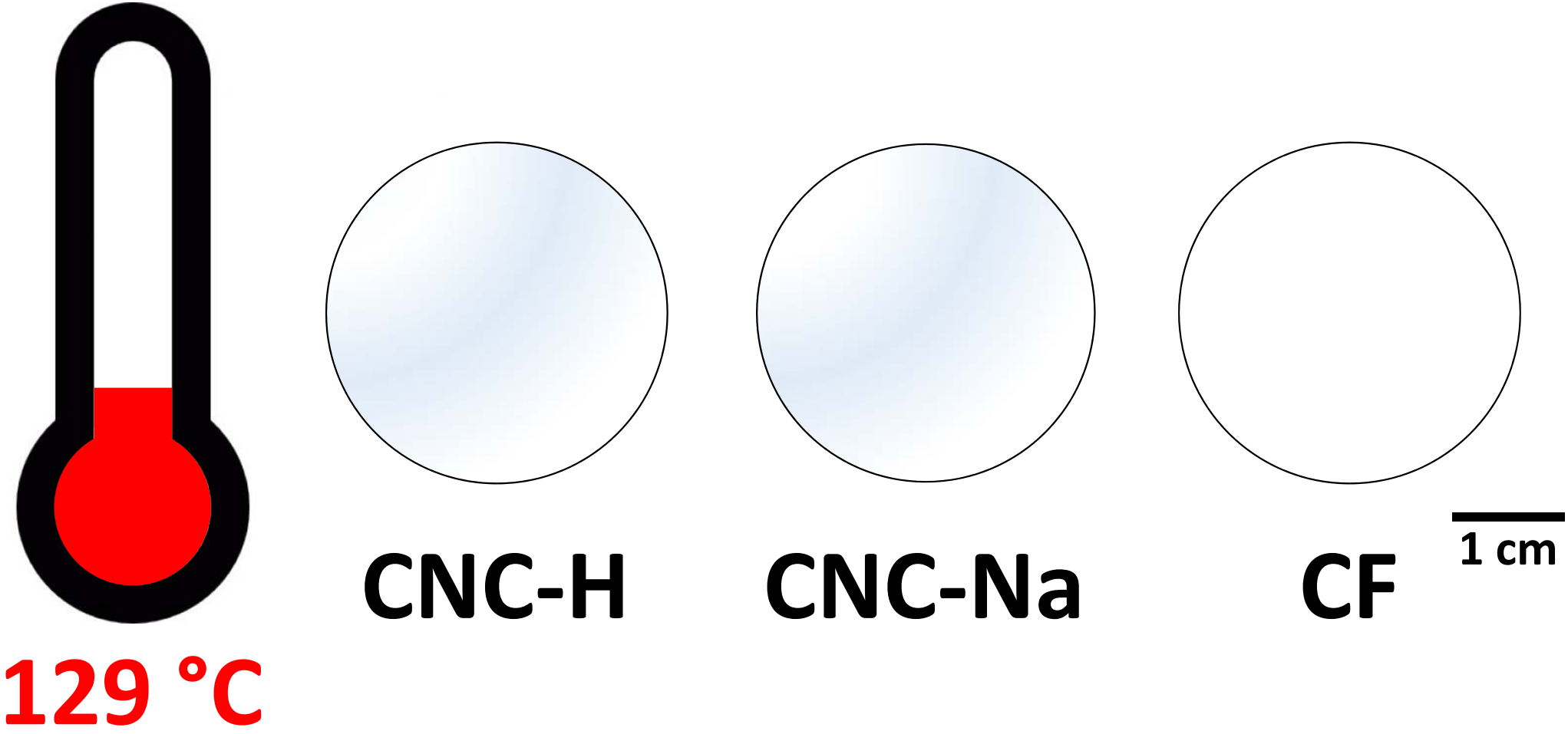

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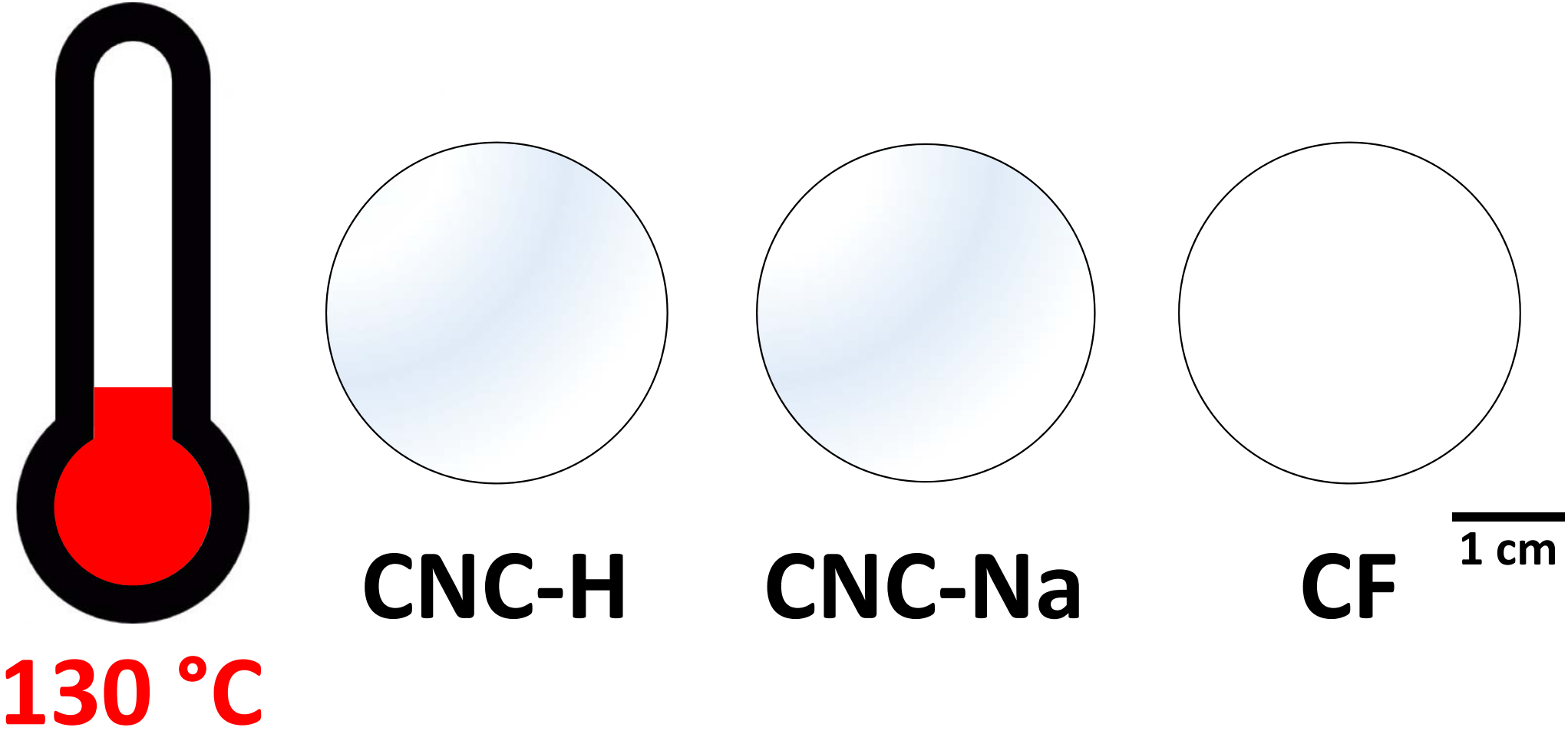

Results

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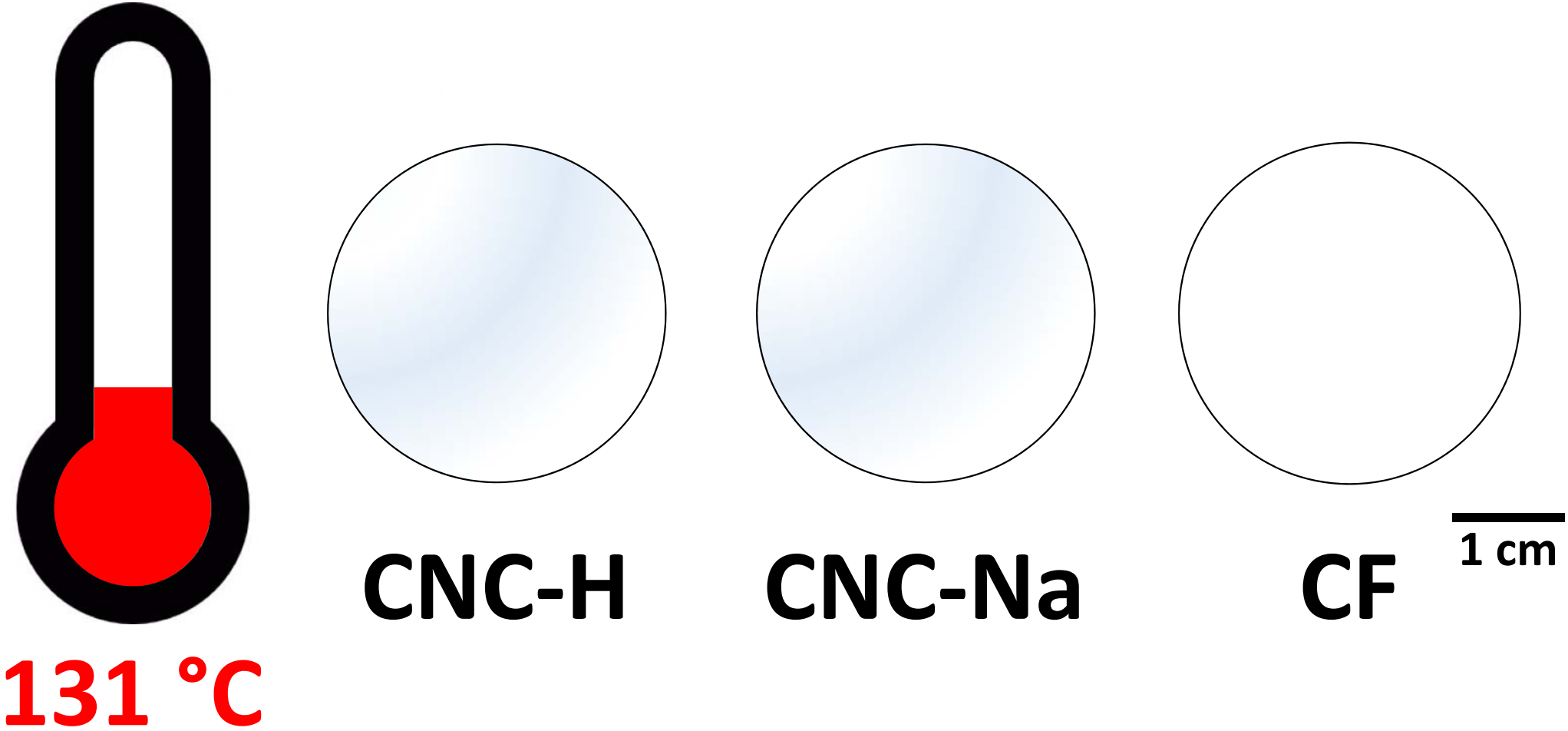
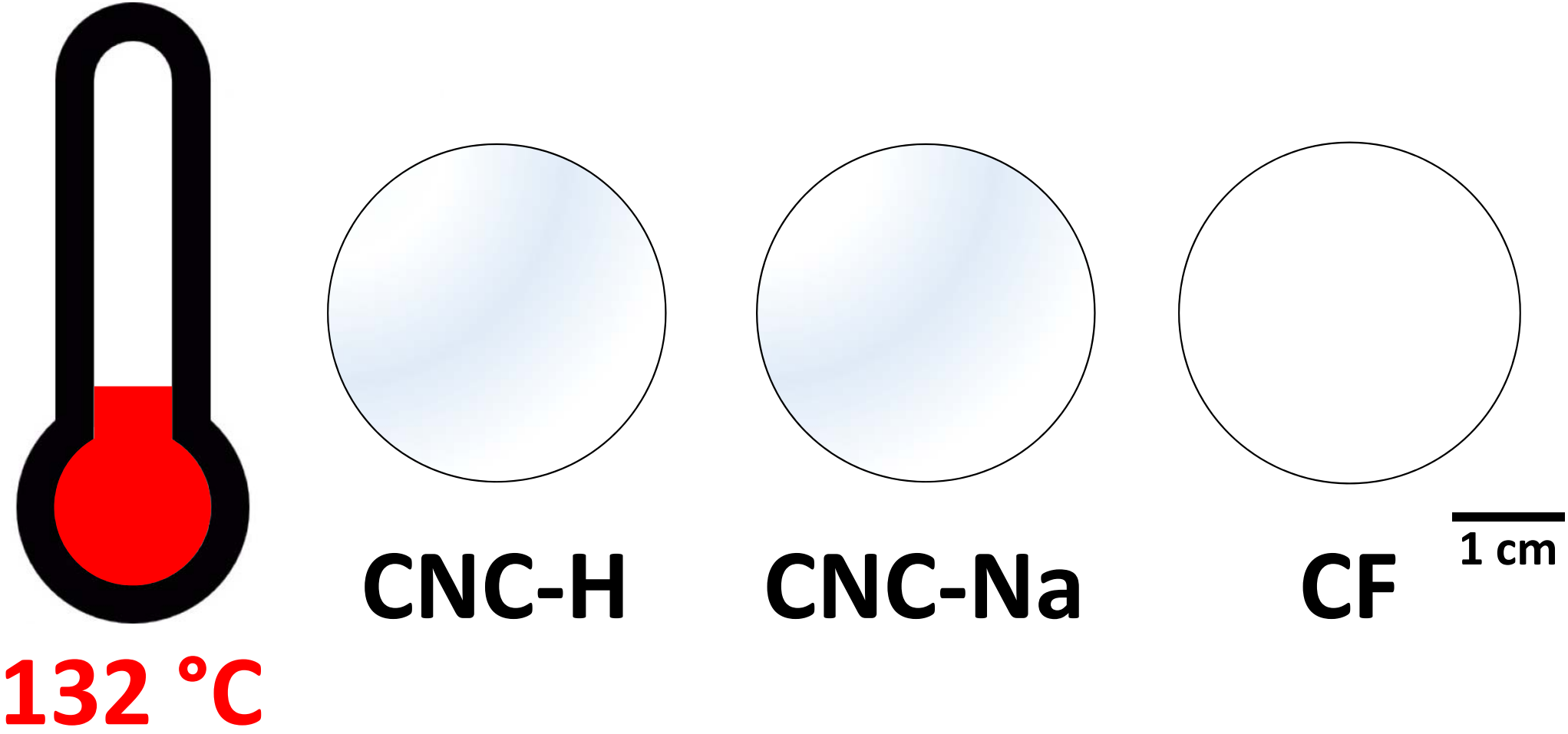


Results

THE UNIVERSITY OF BRITISH COLUMBIA



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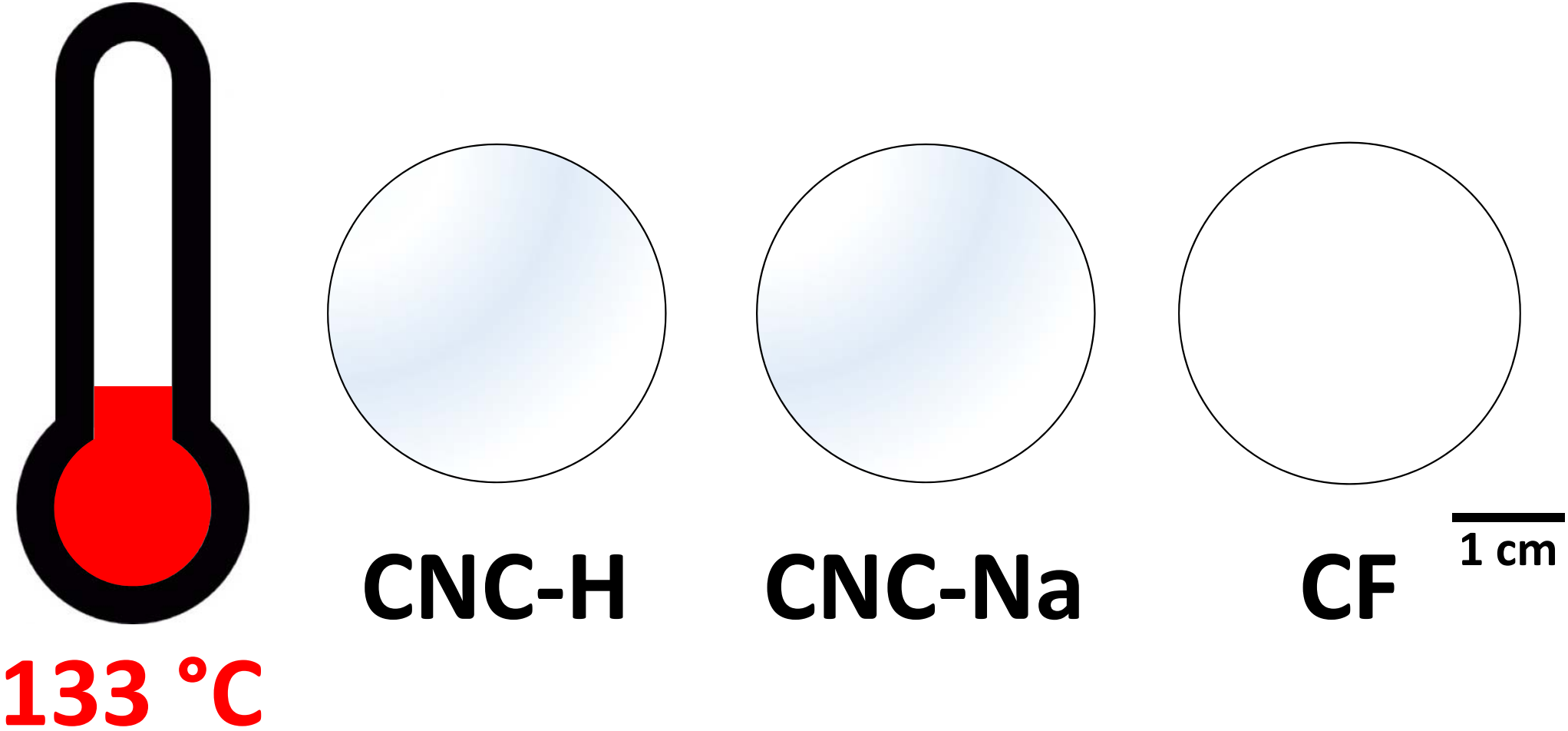

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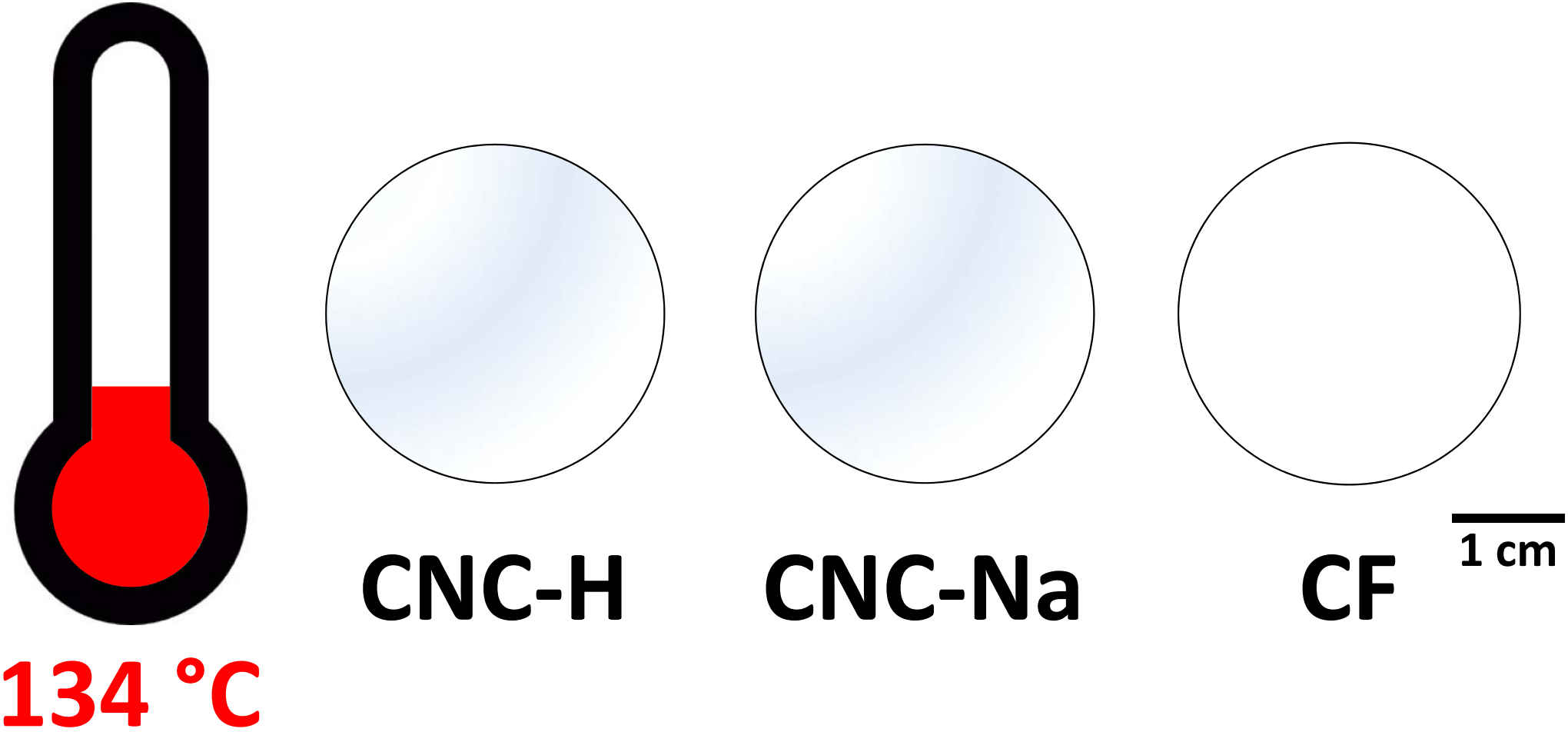

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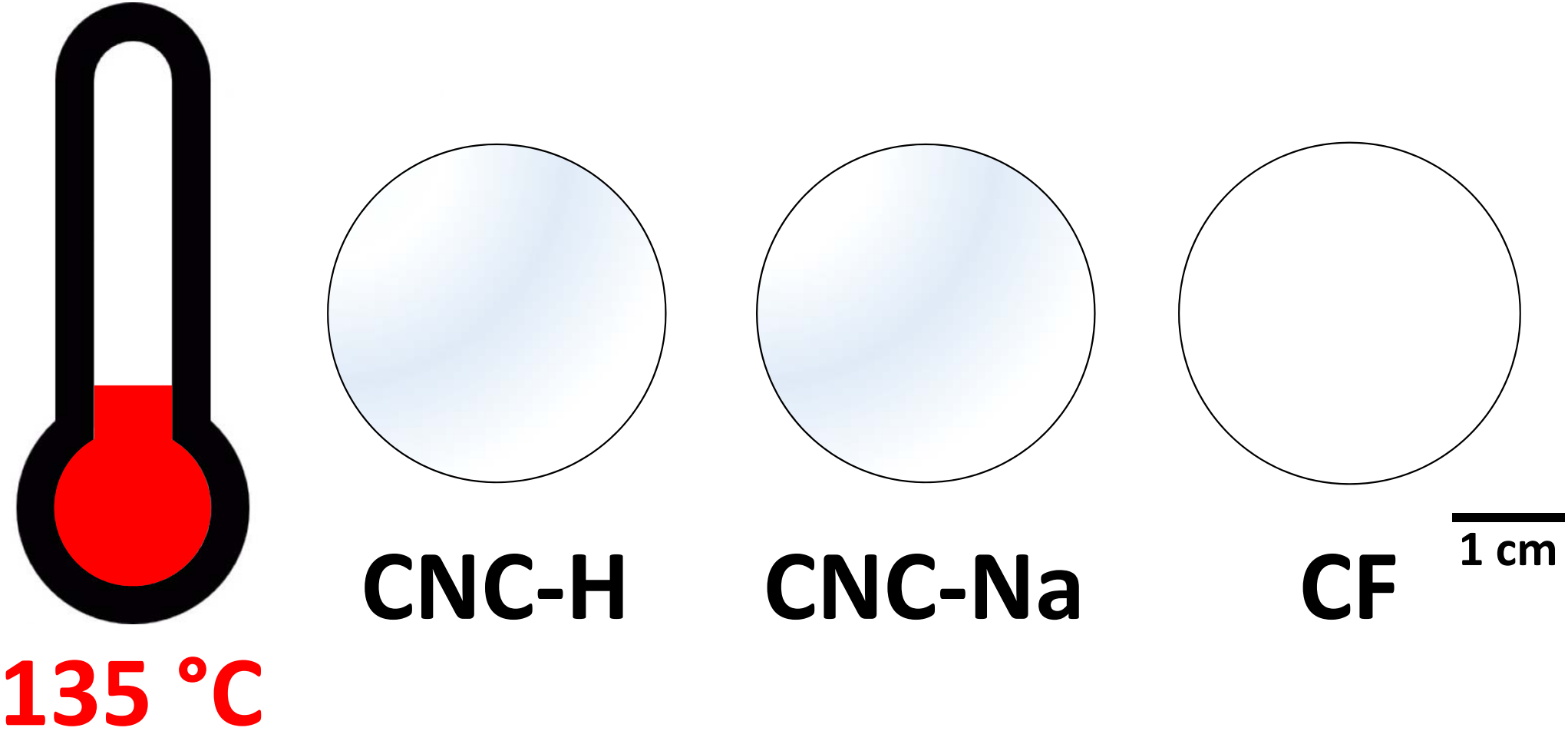

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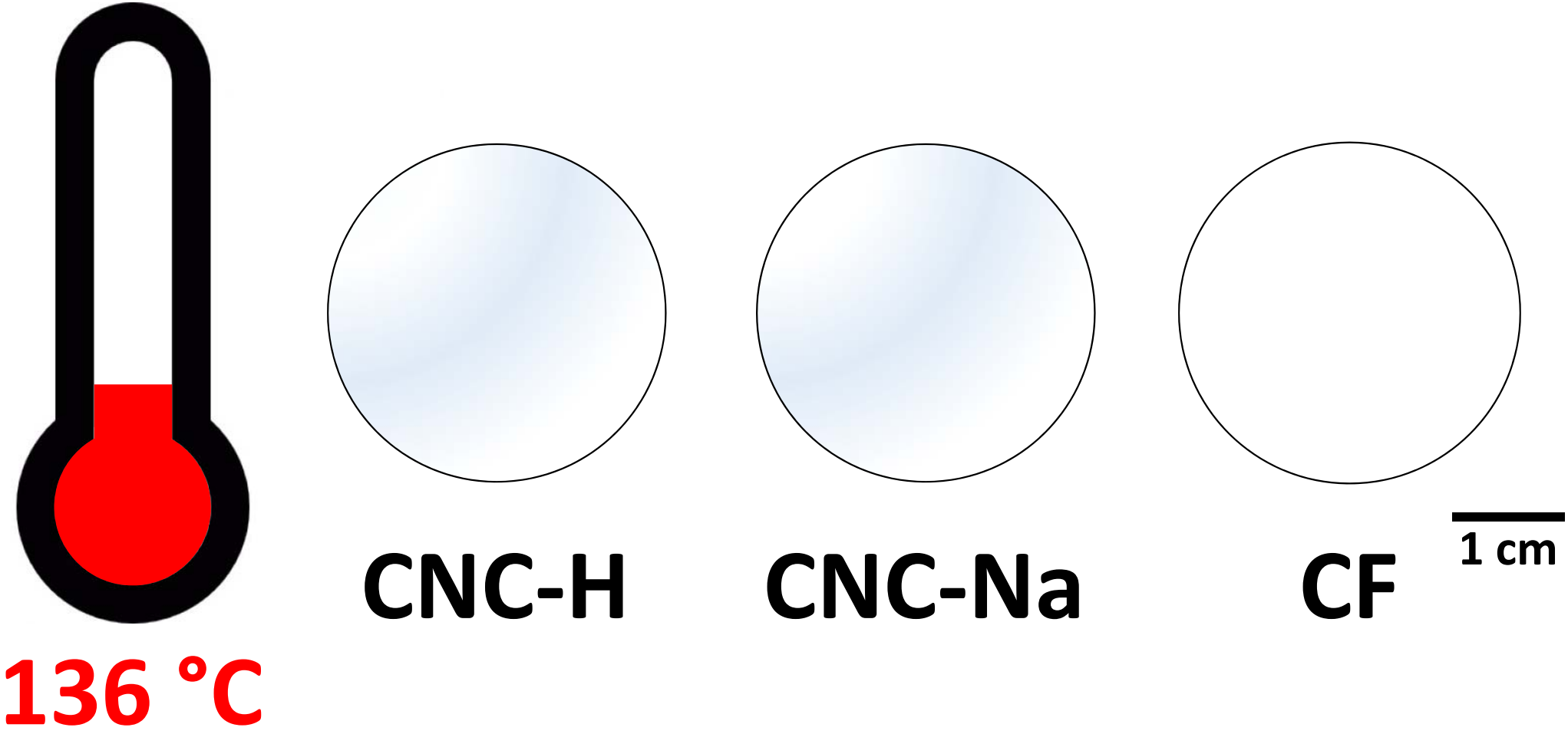

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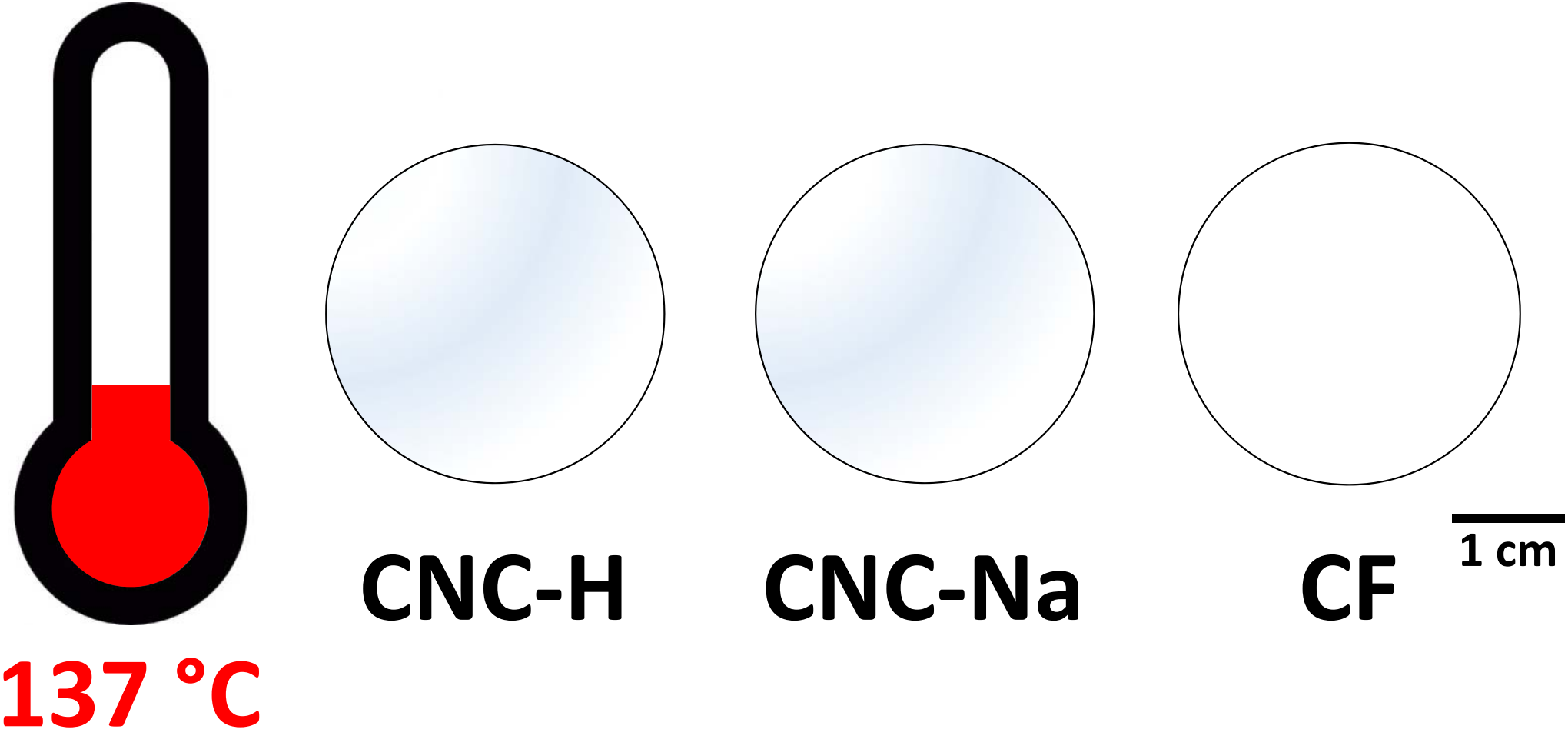

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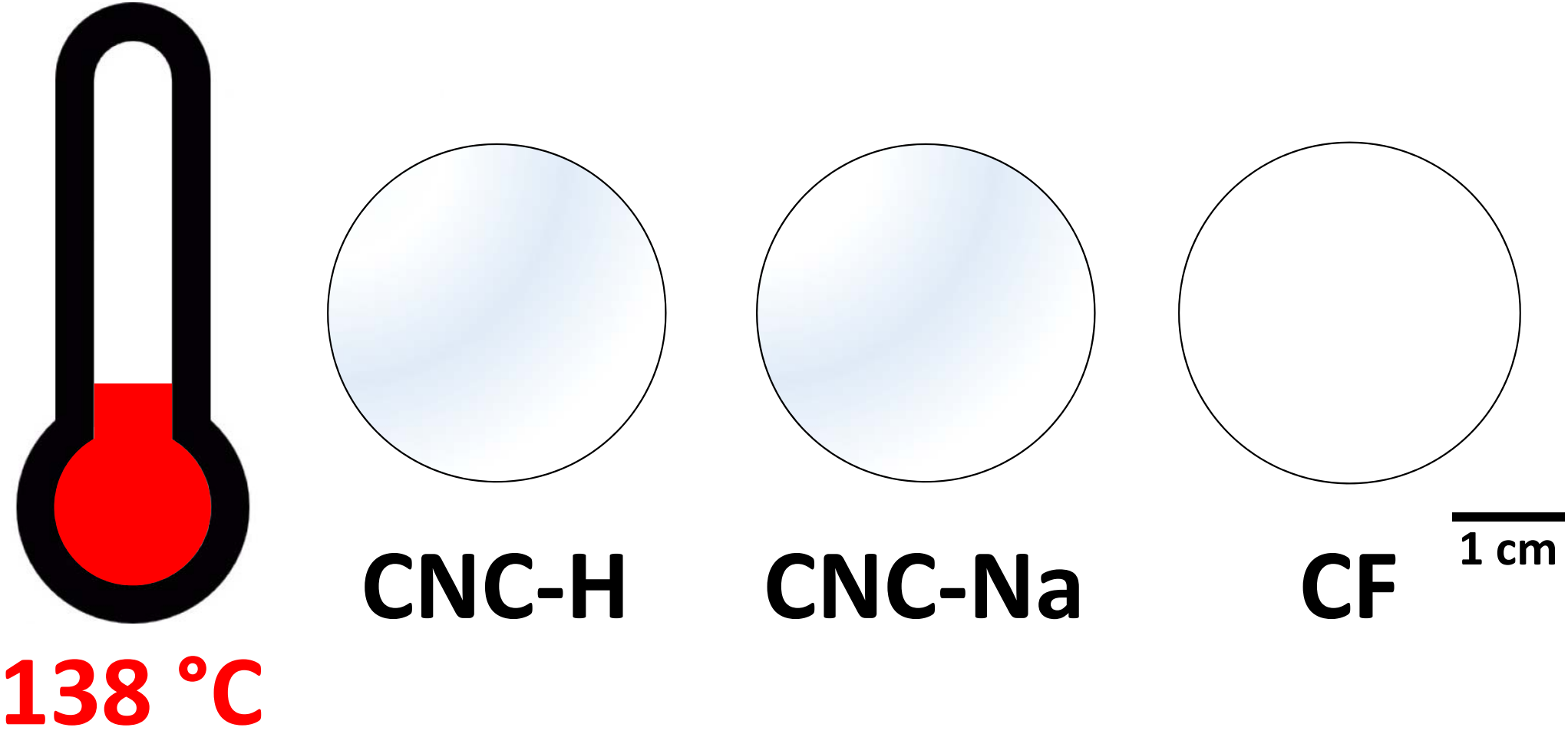

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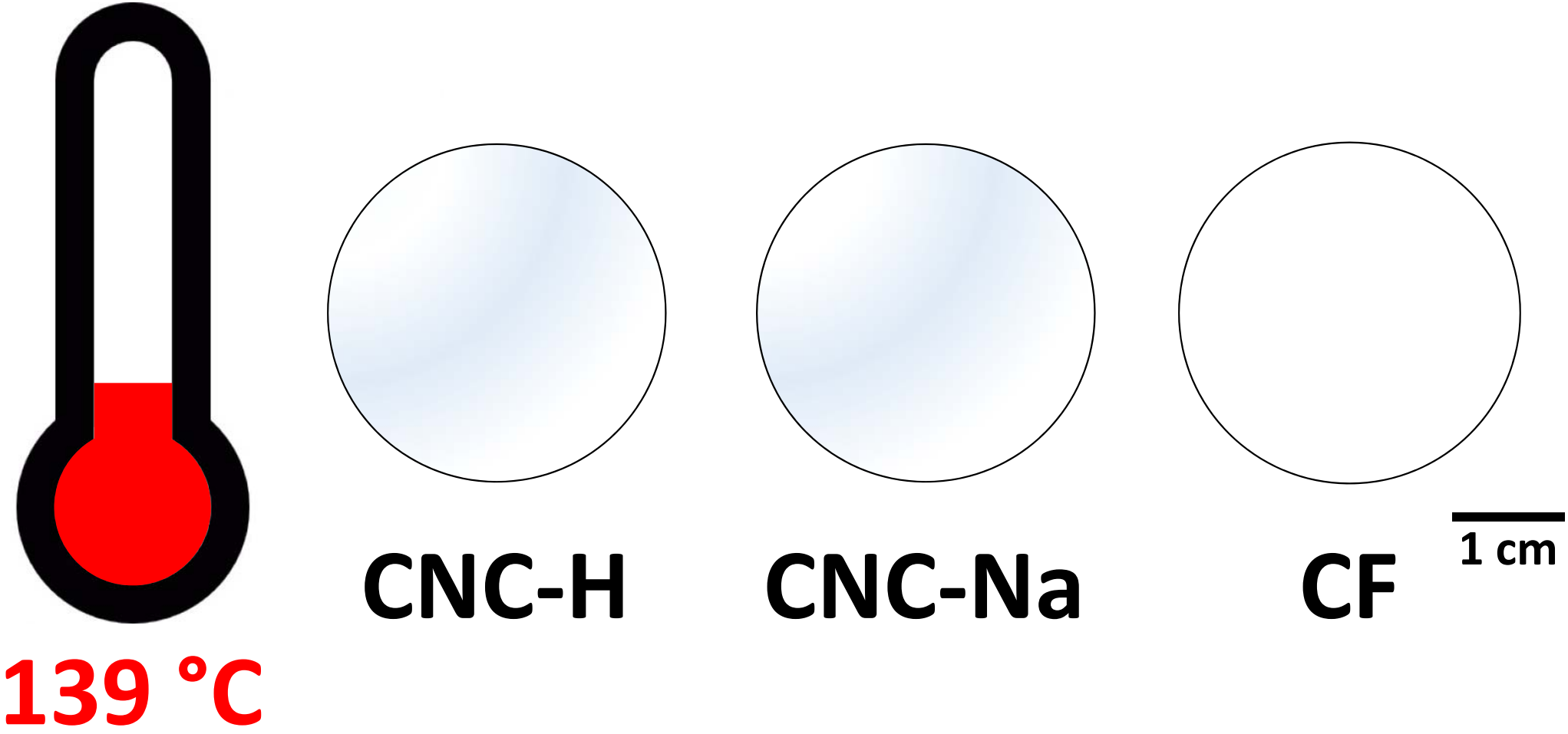

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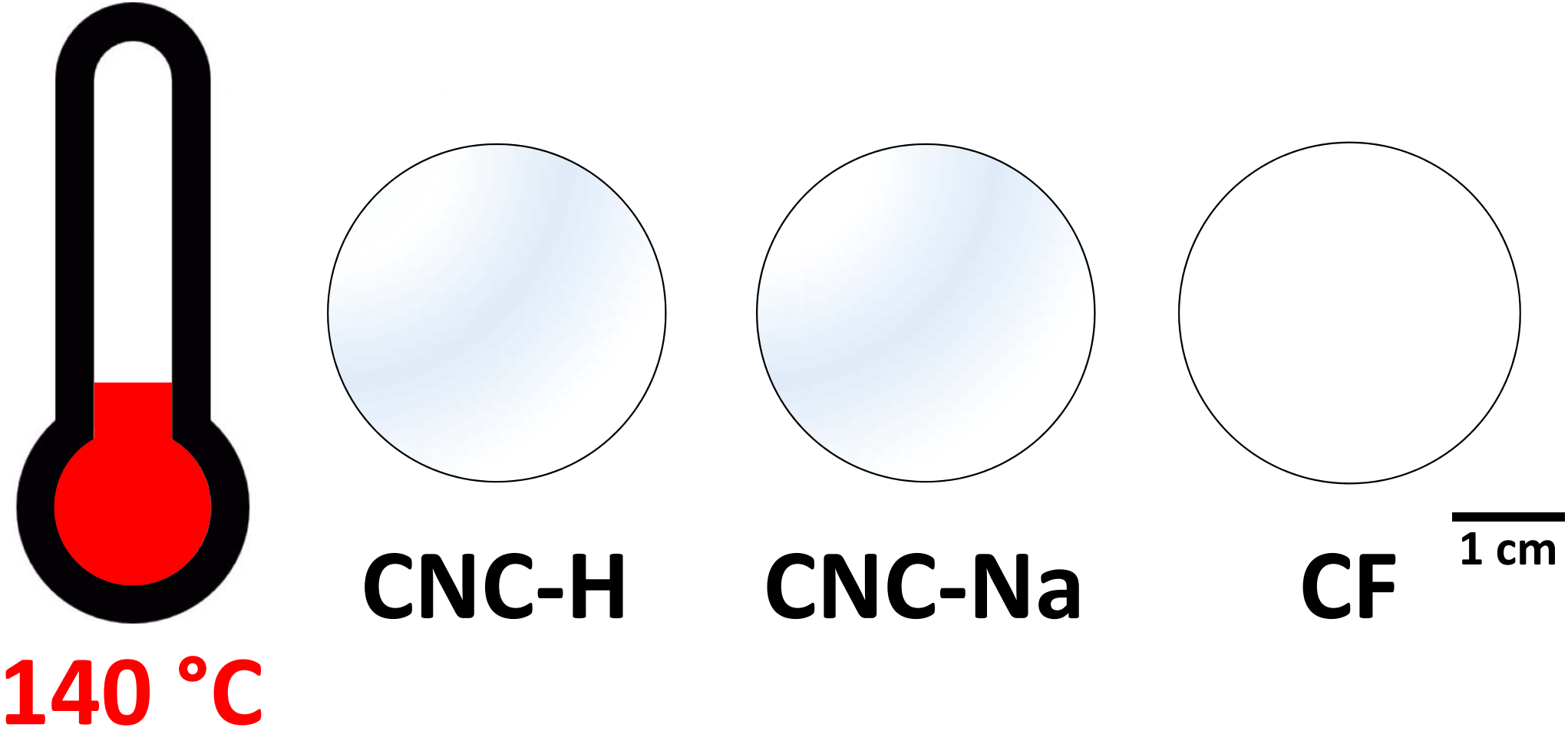

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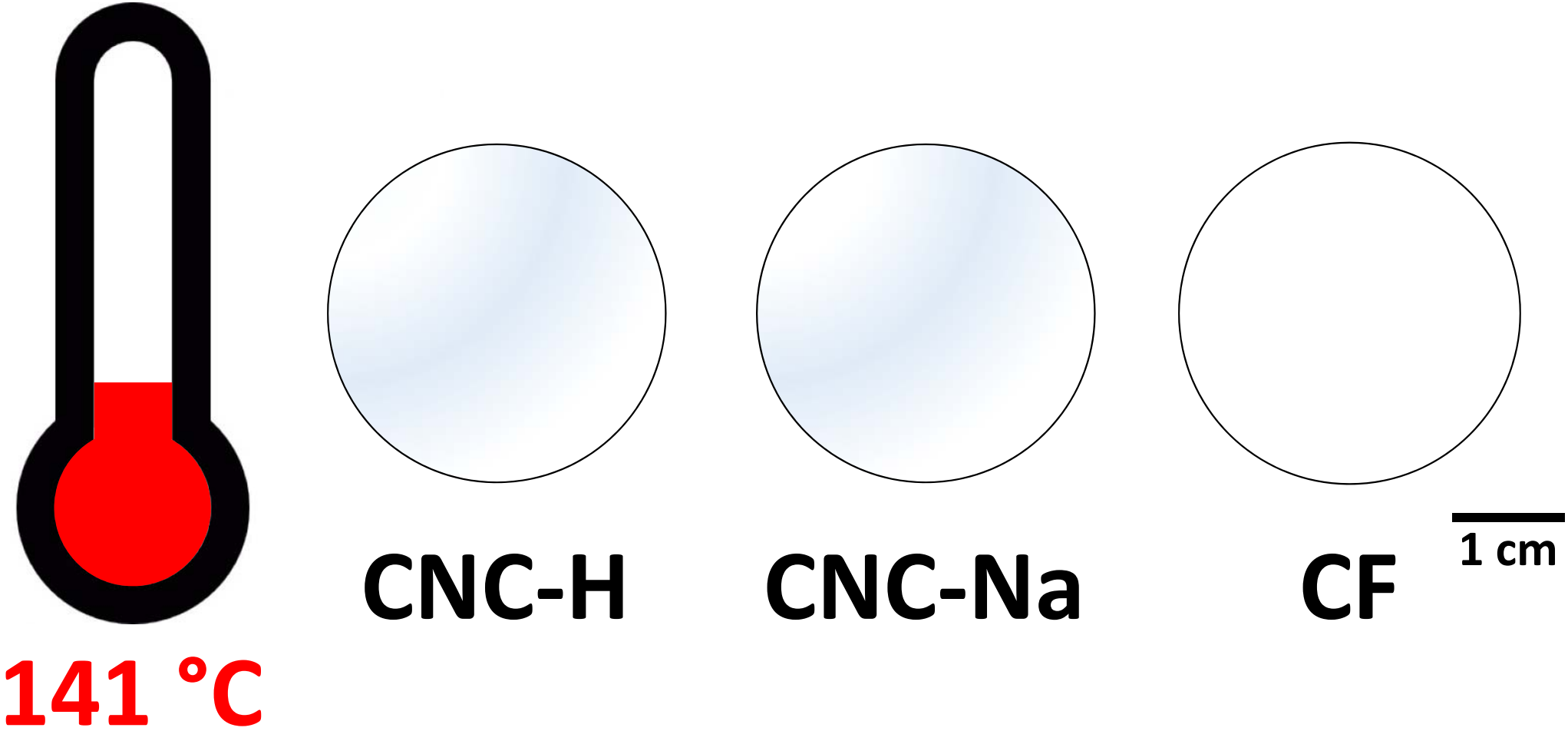

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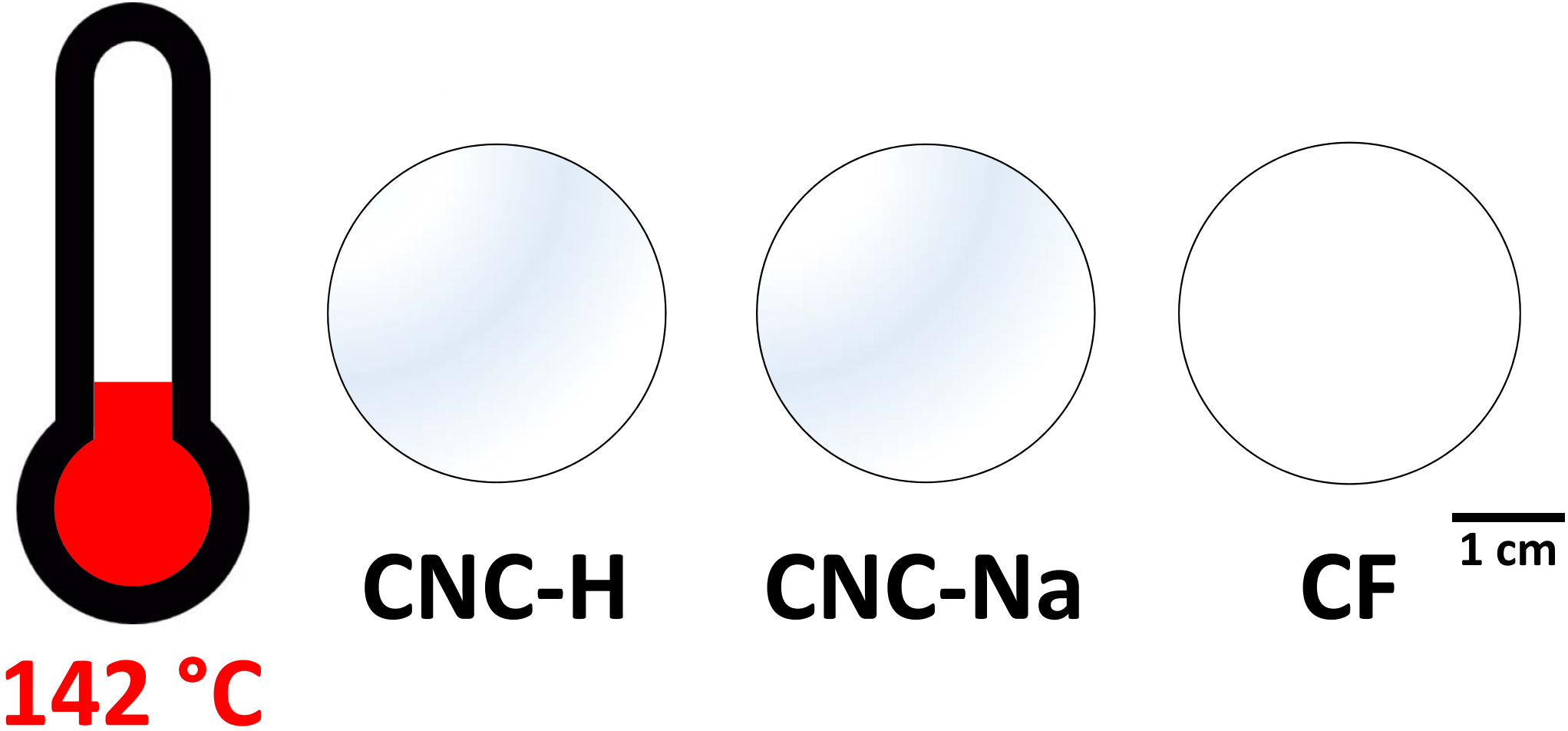

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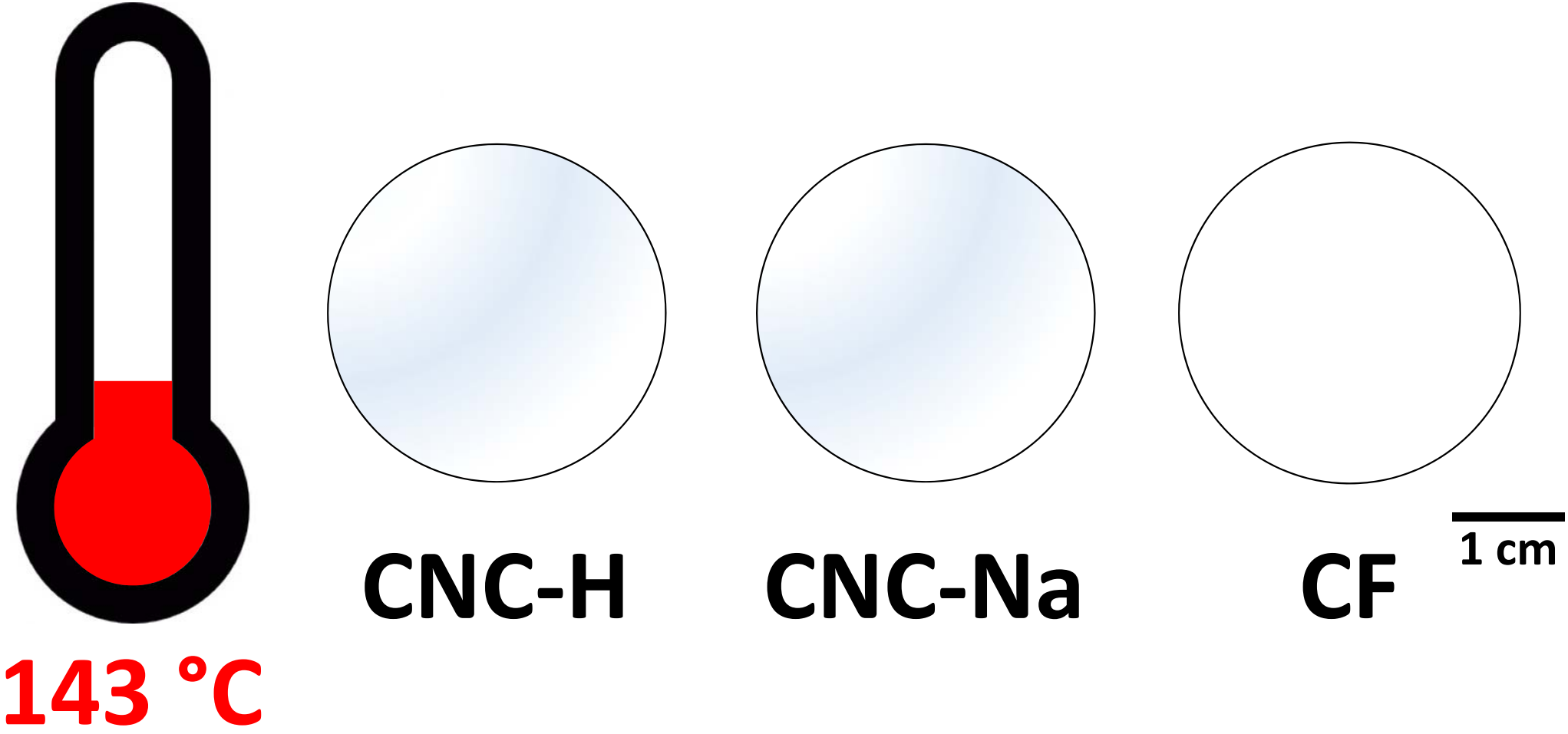

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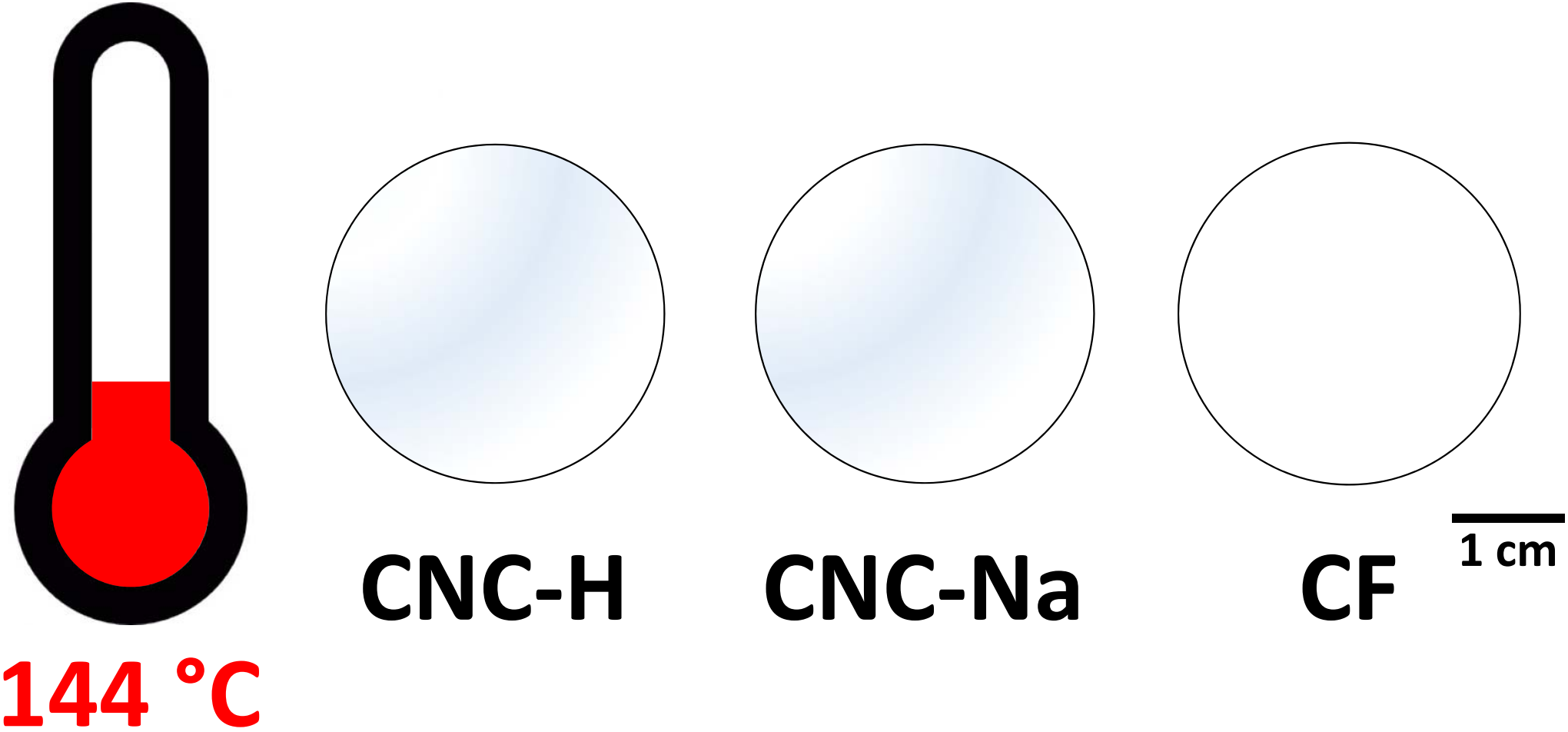

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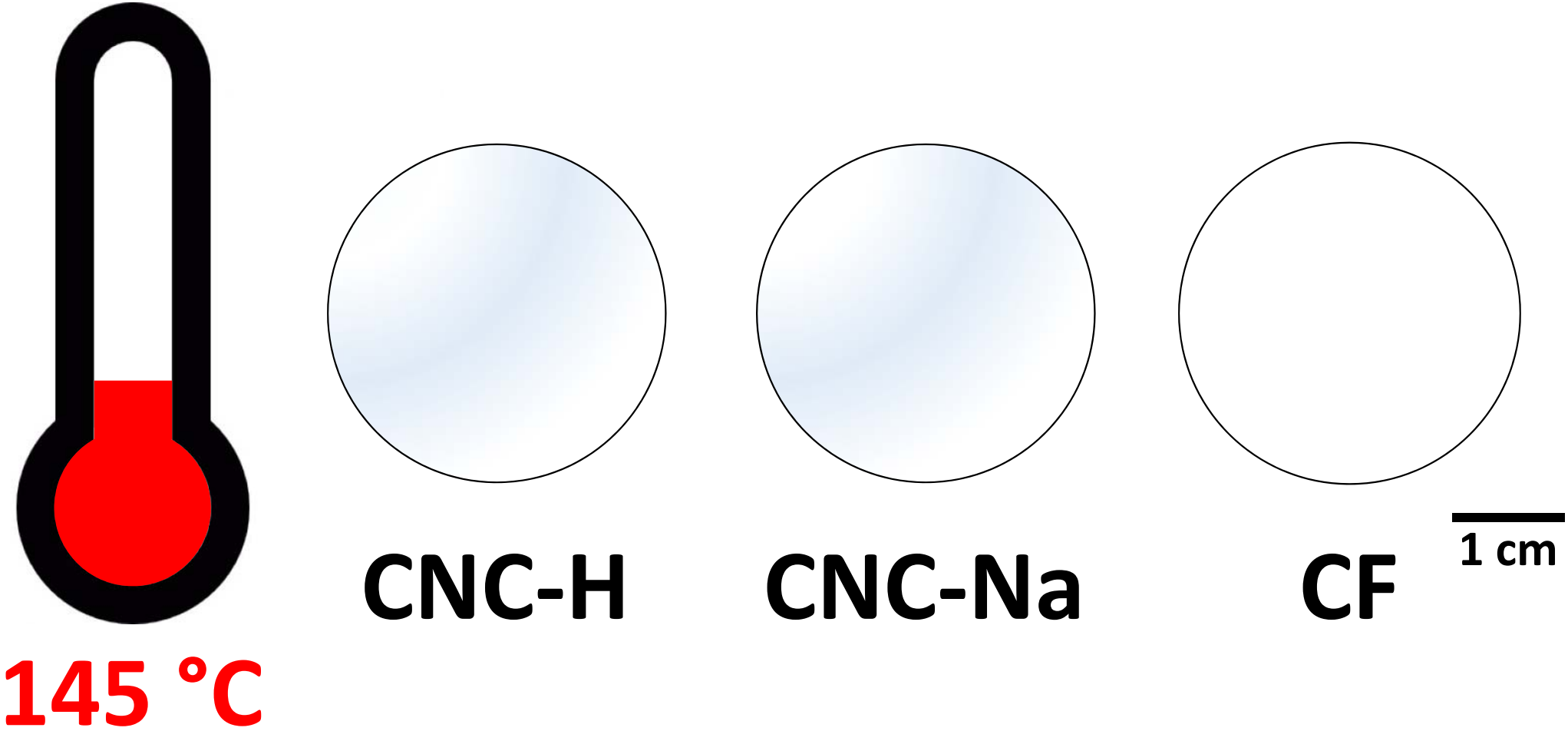

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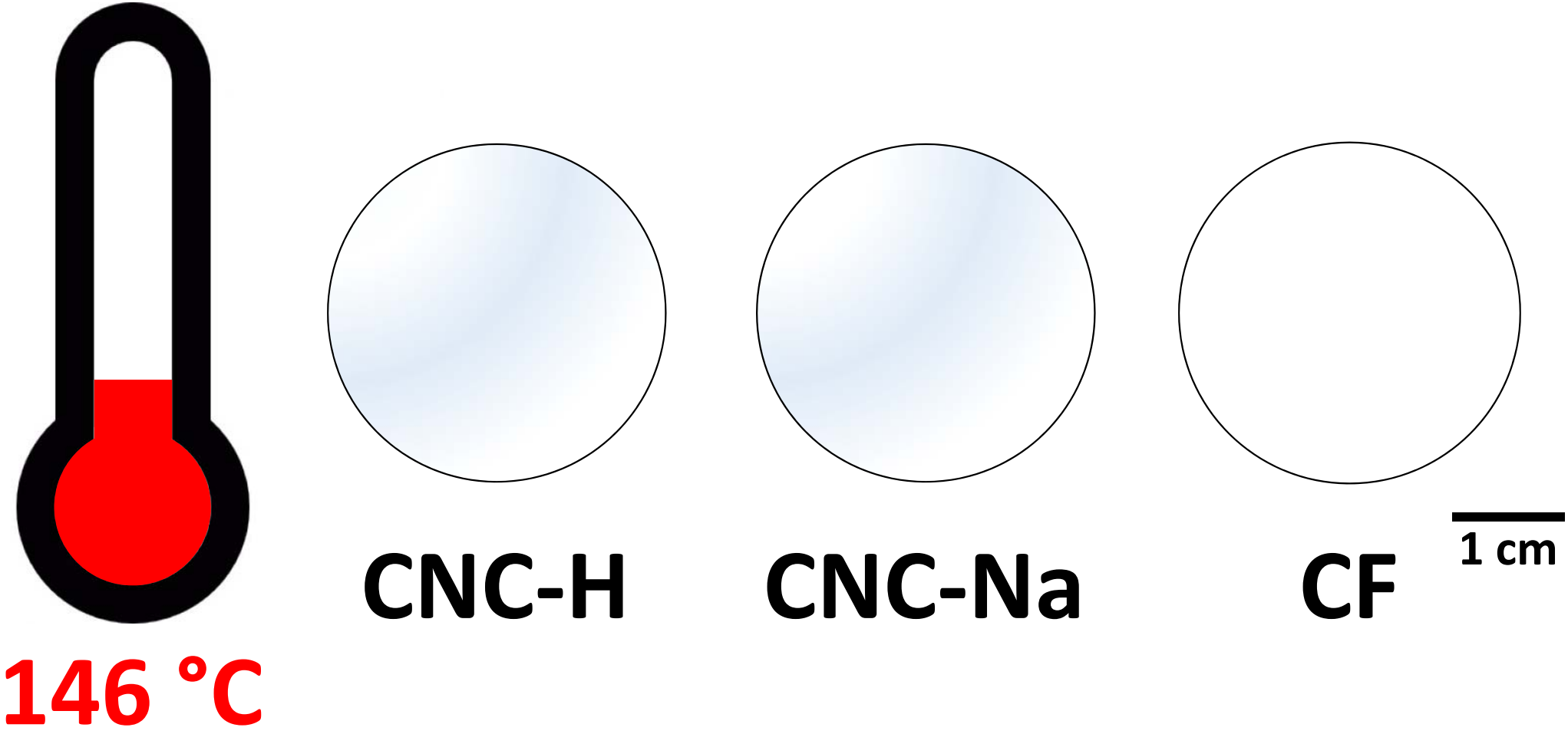

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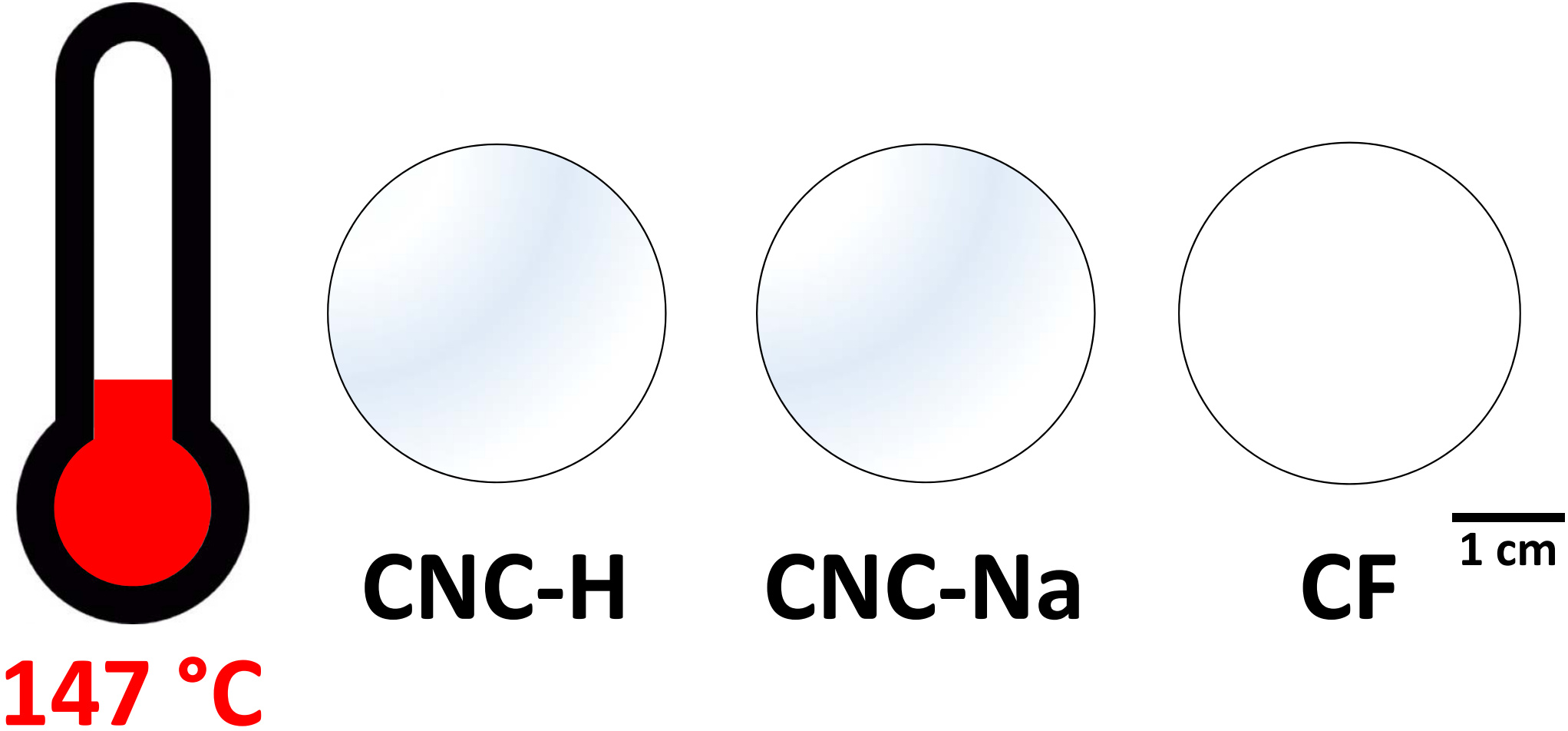

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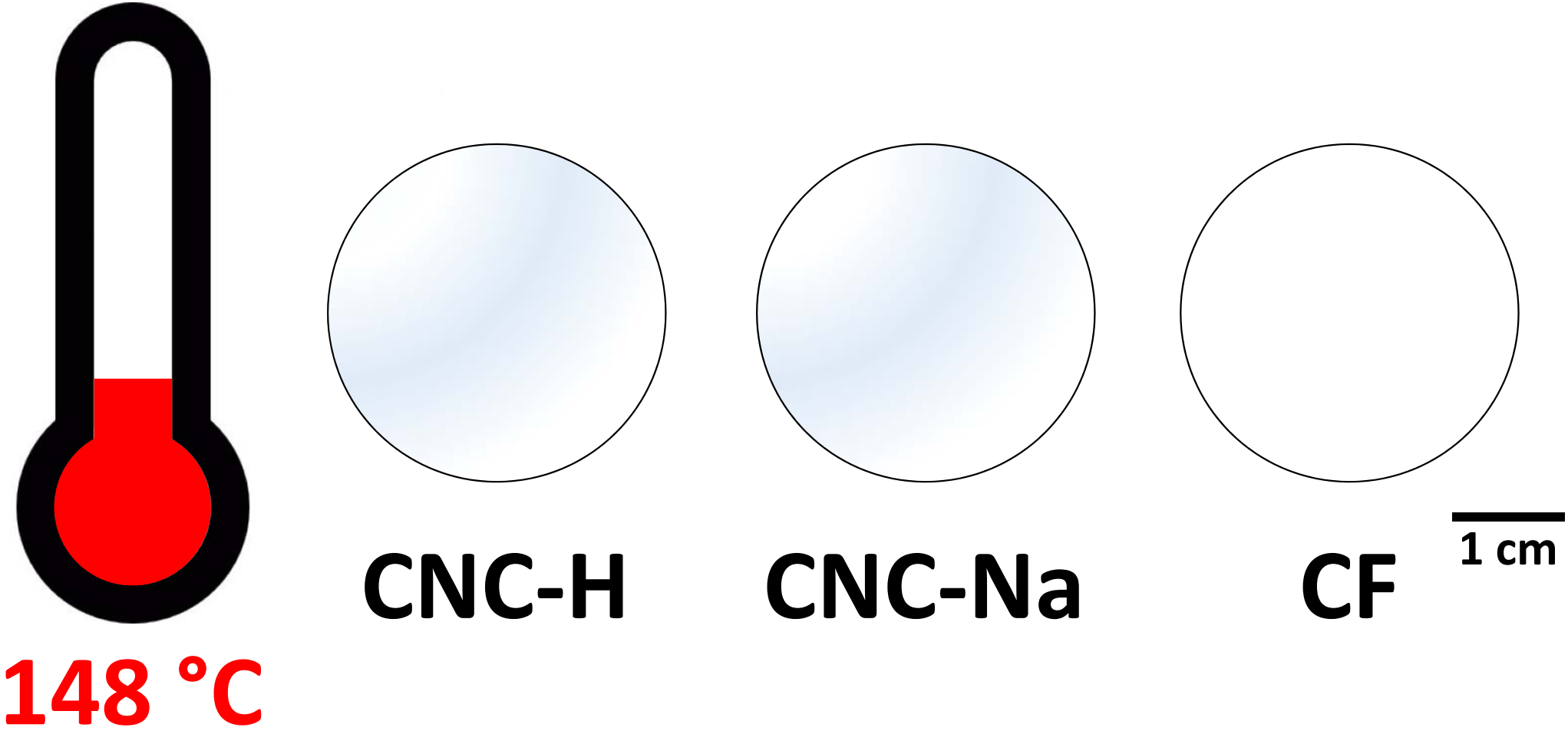

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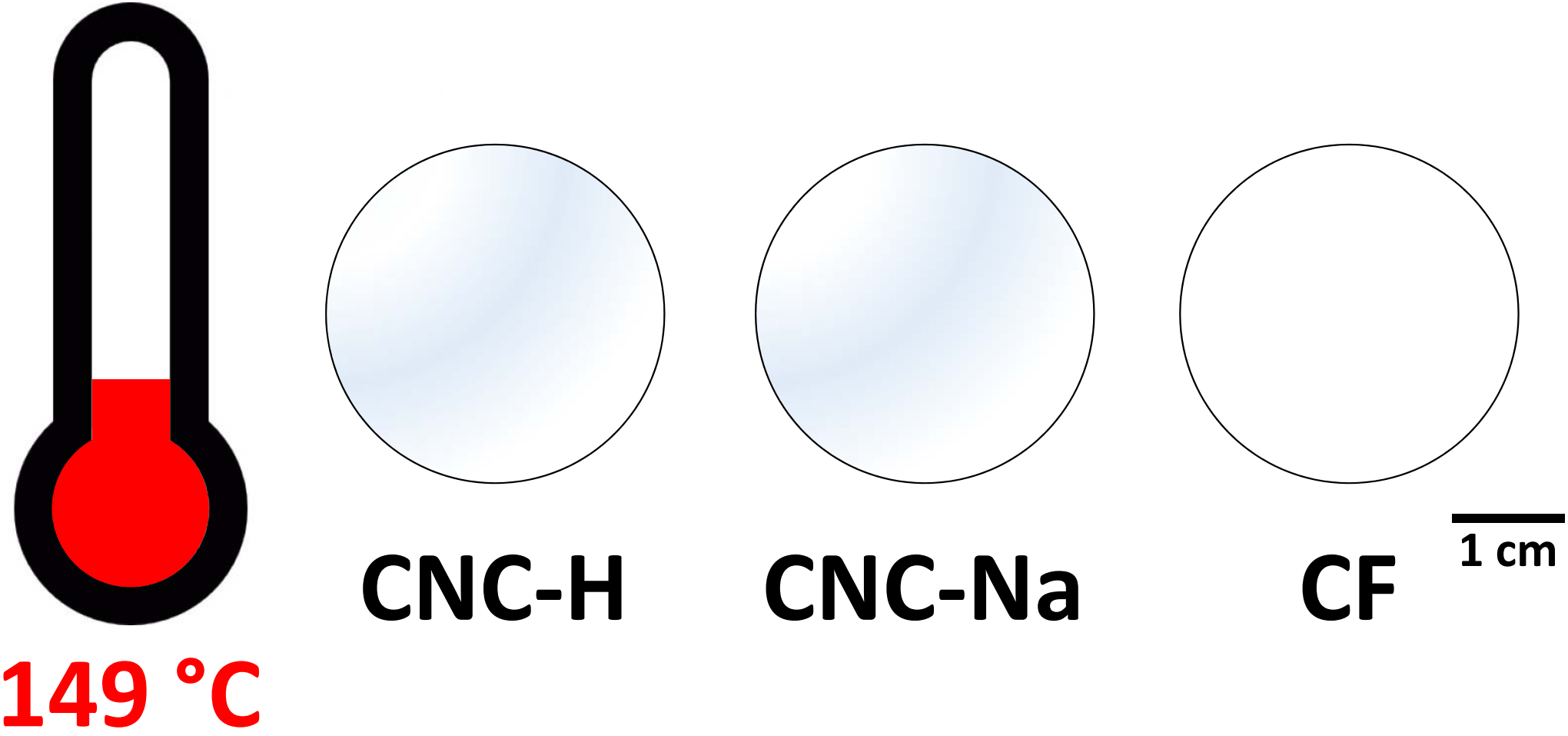

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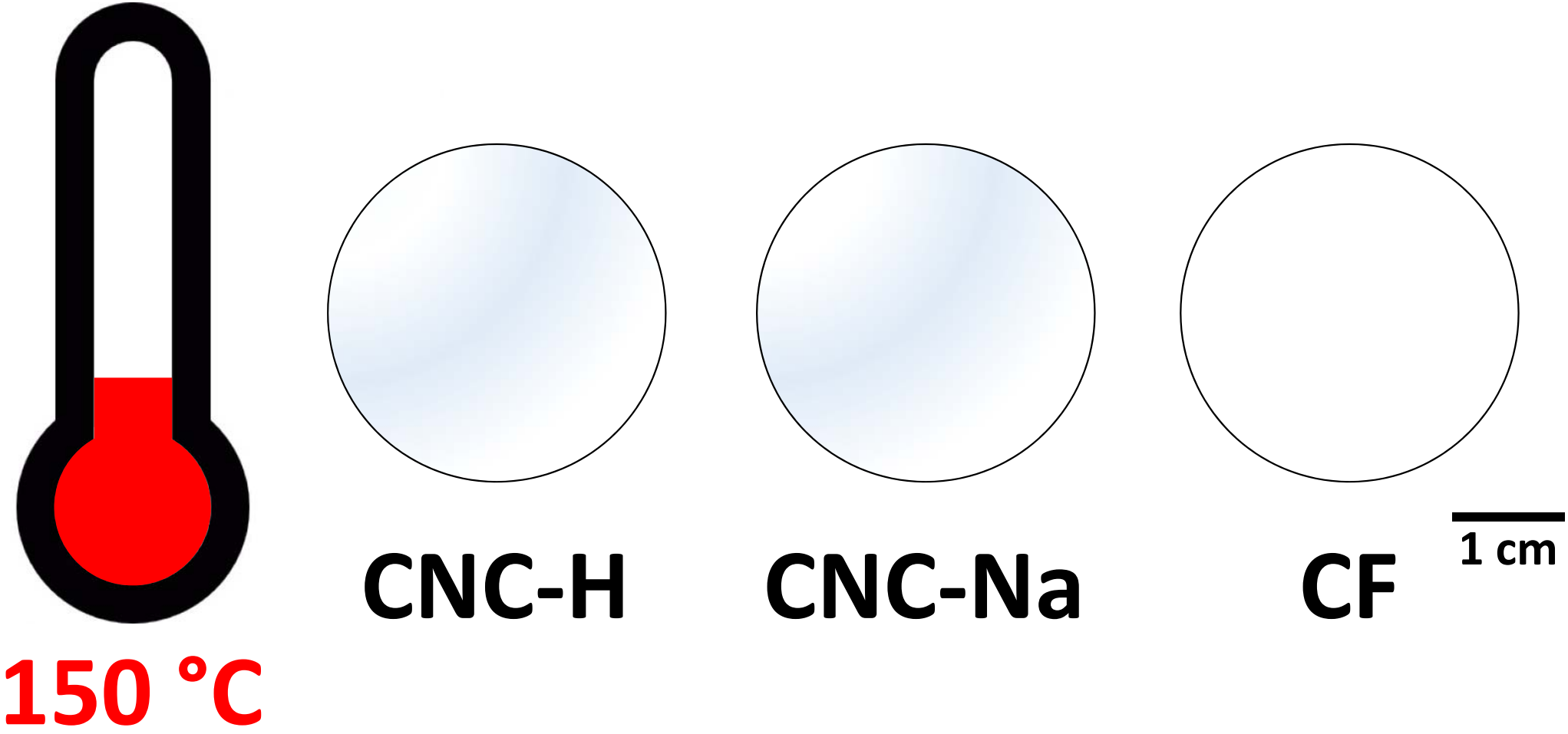

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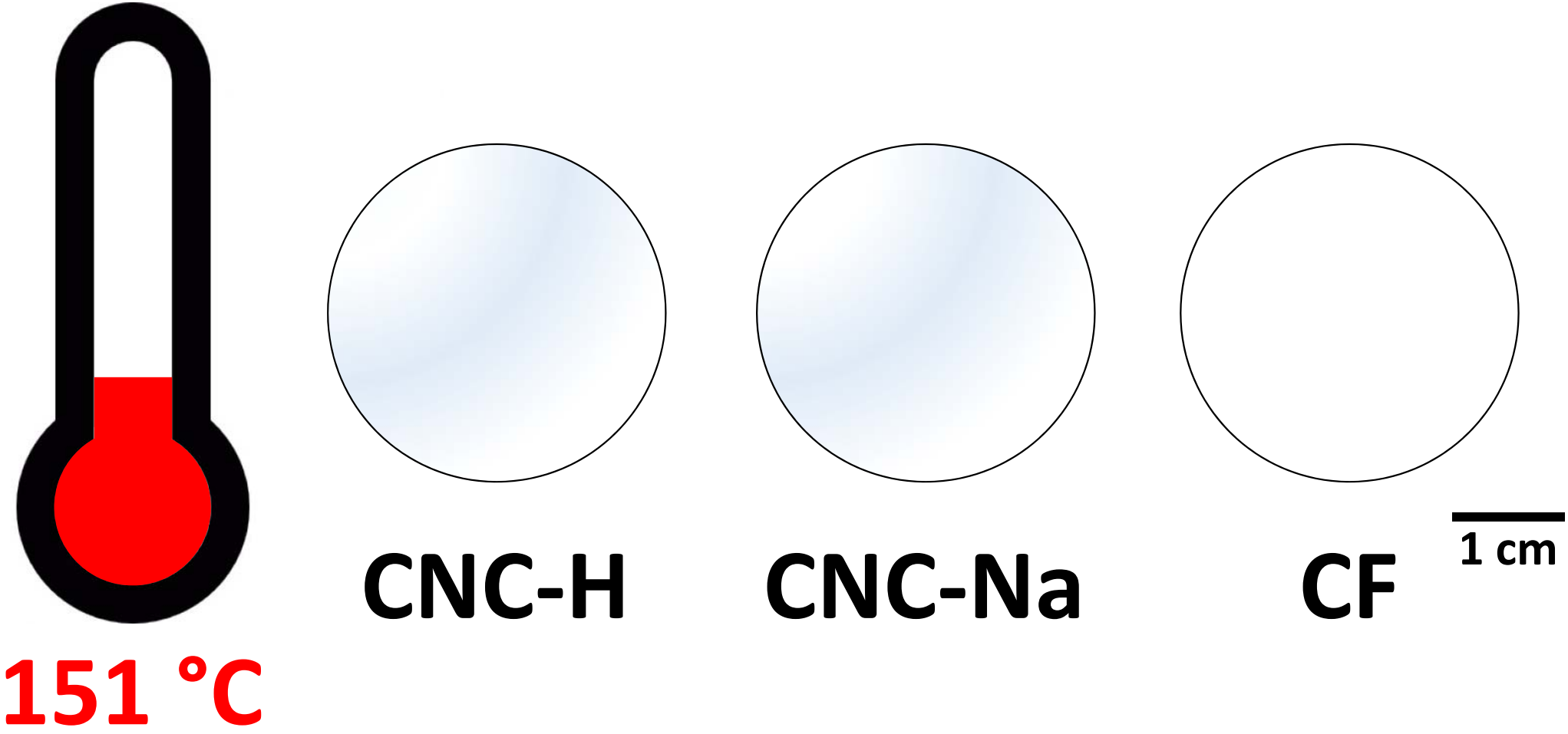

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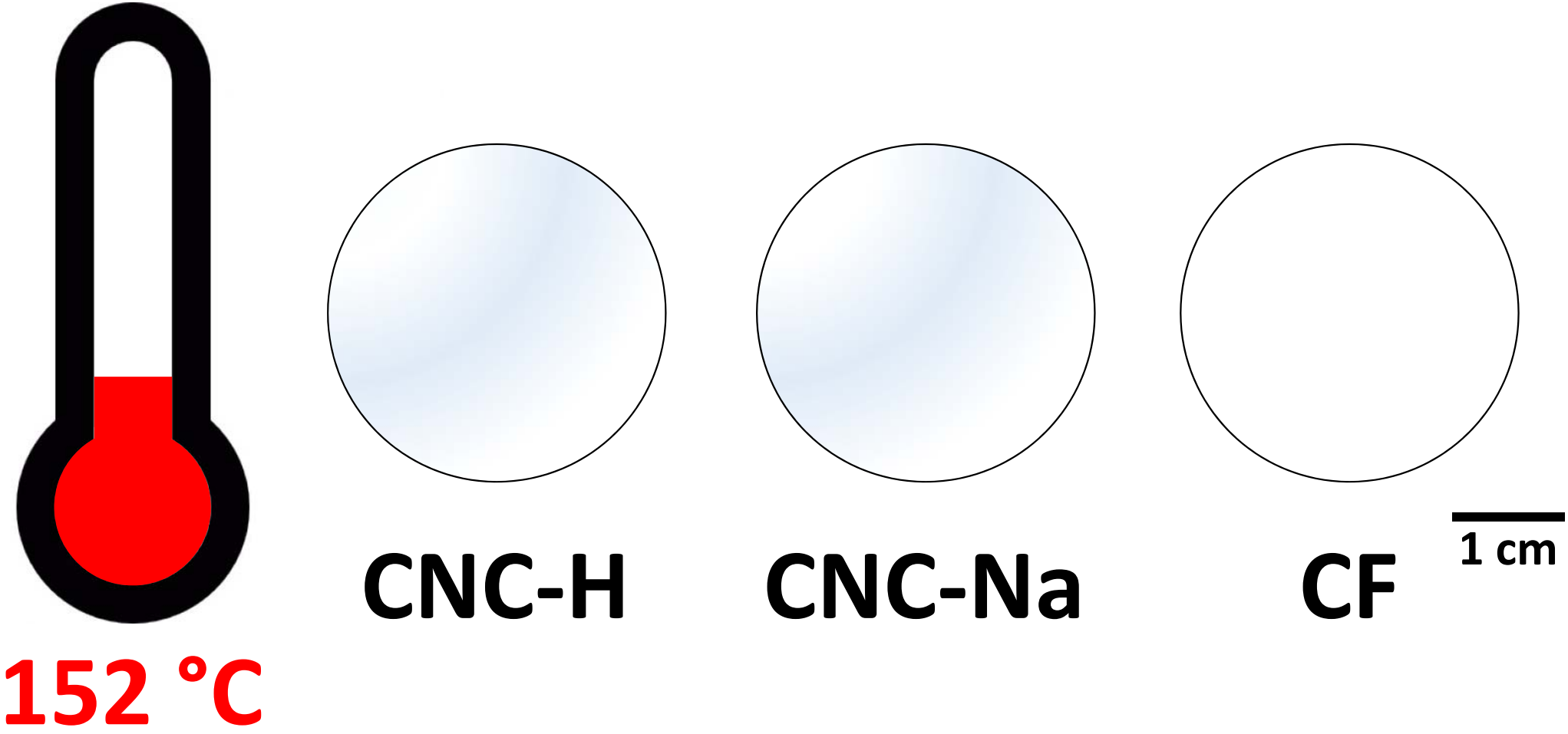

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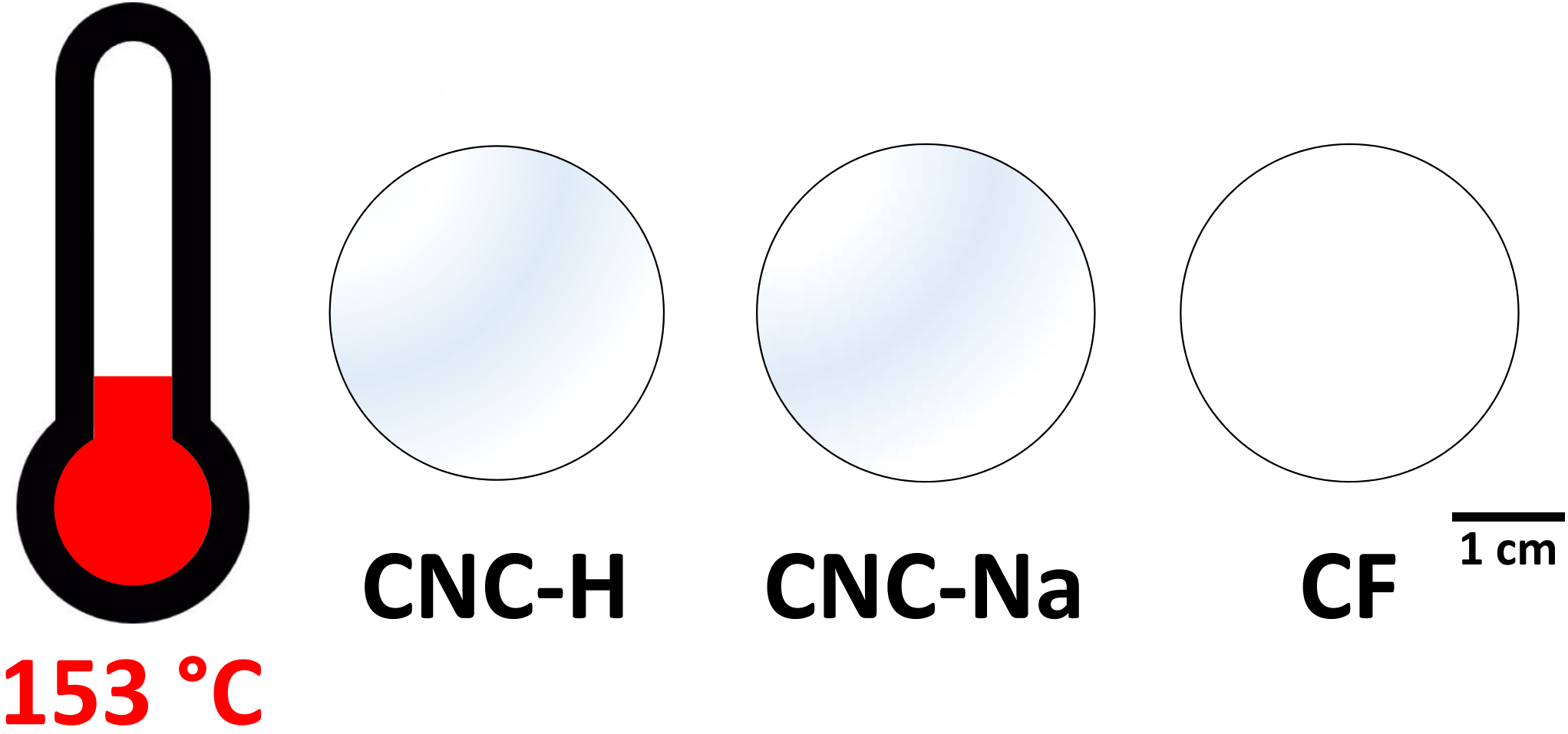

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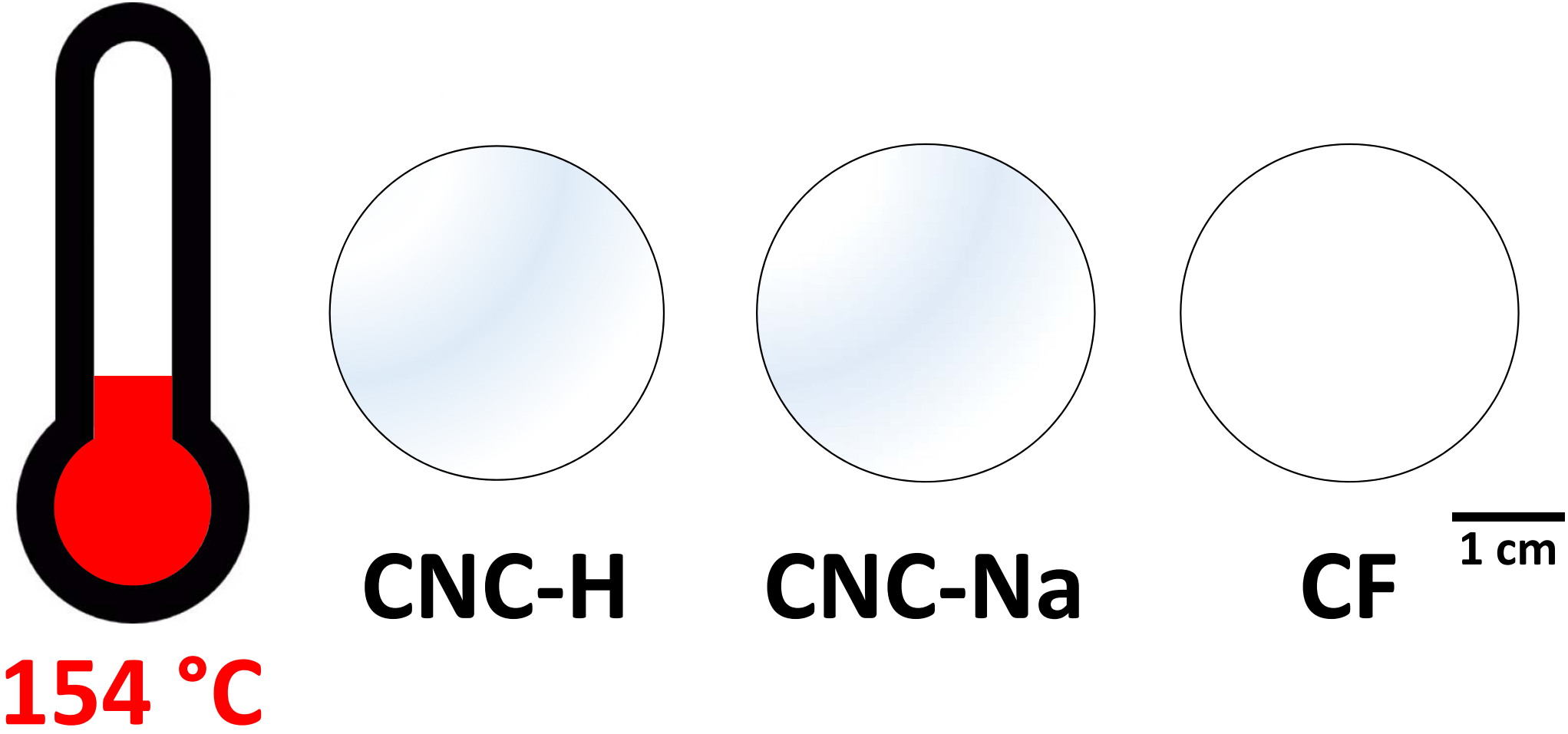

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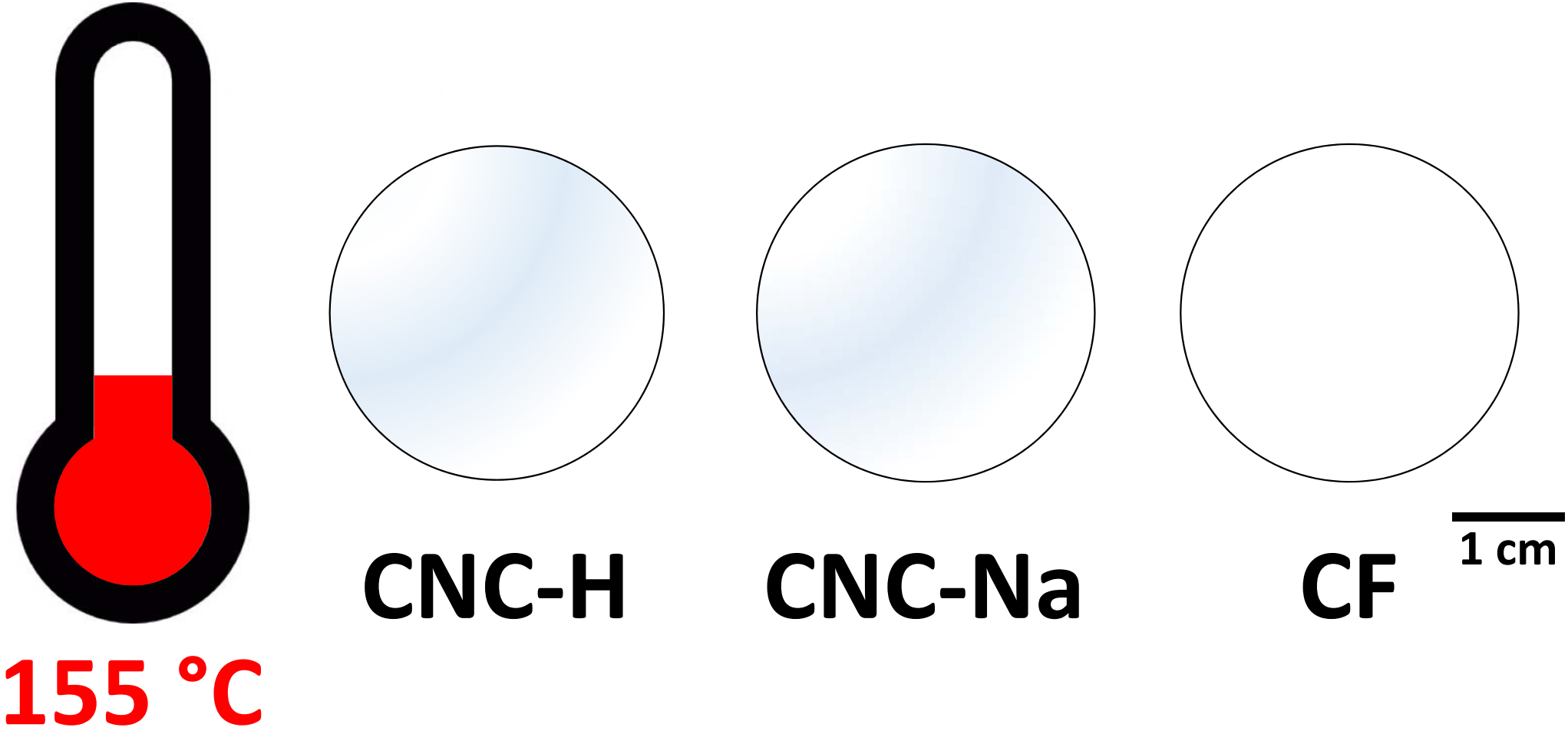

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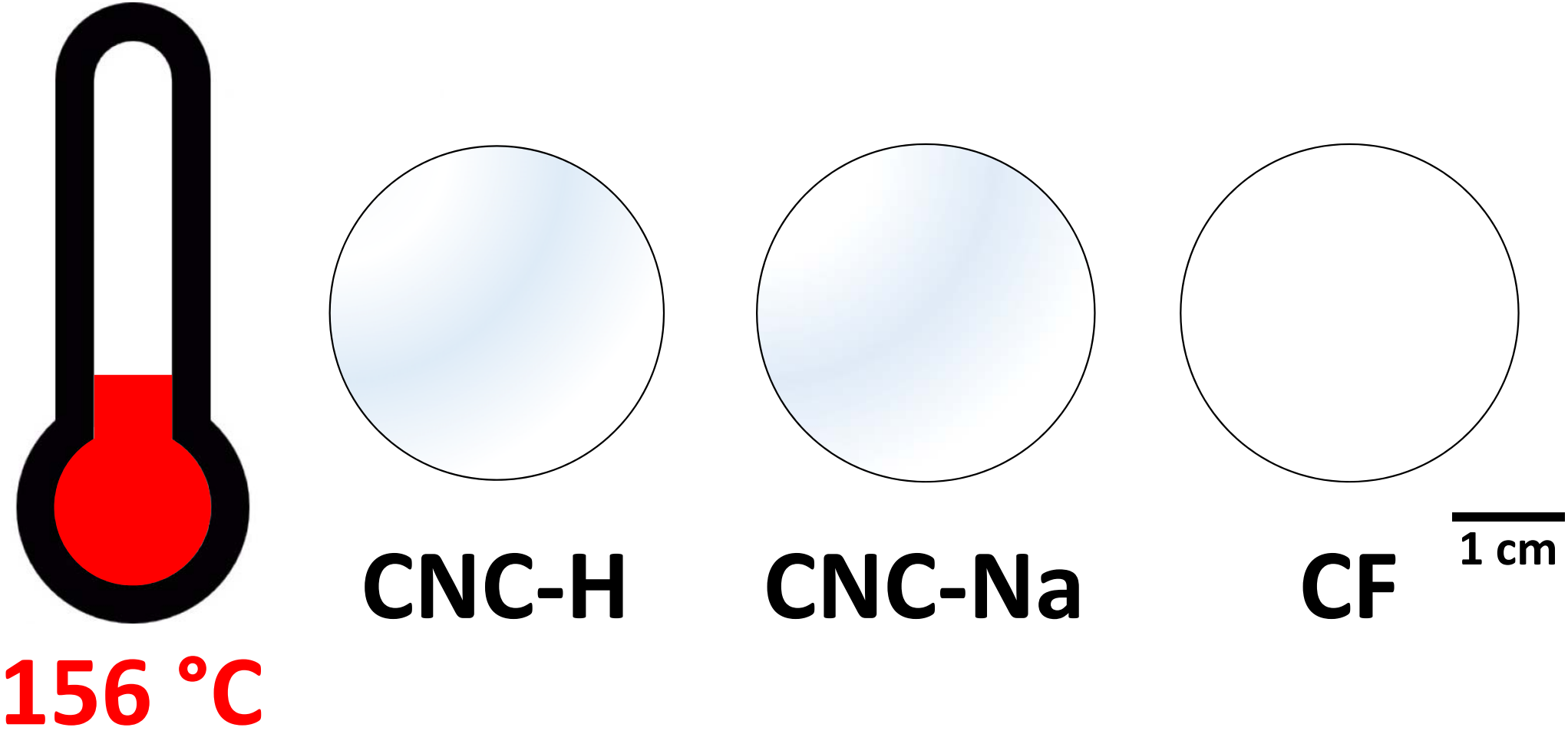

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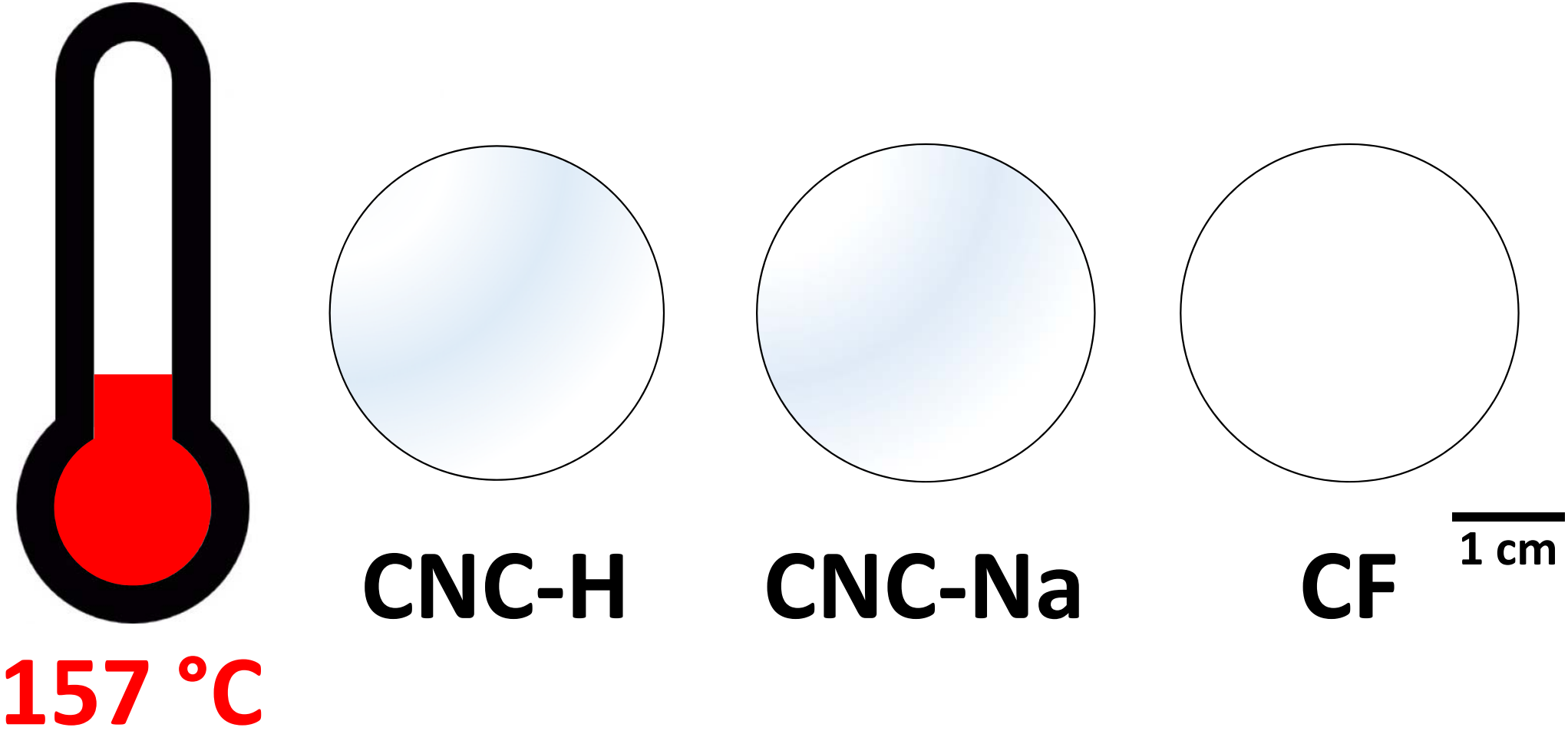

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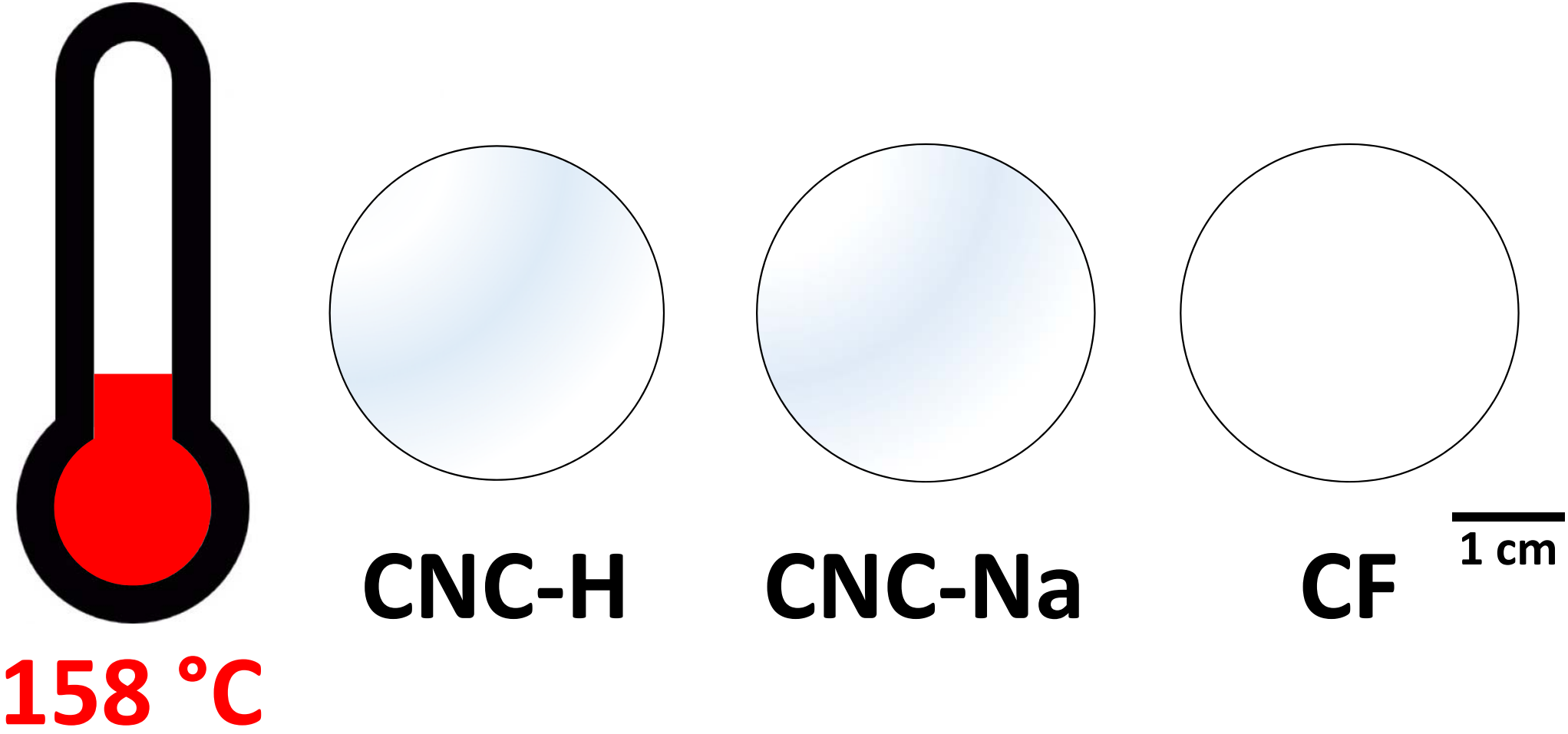

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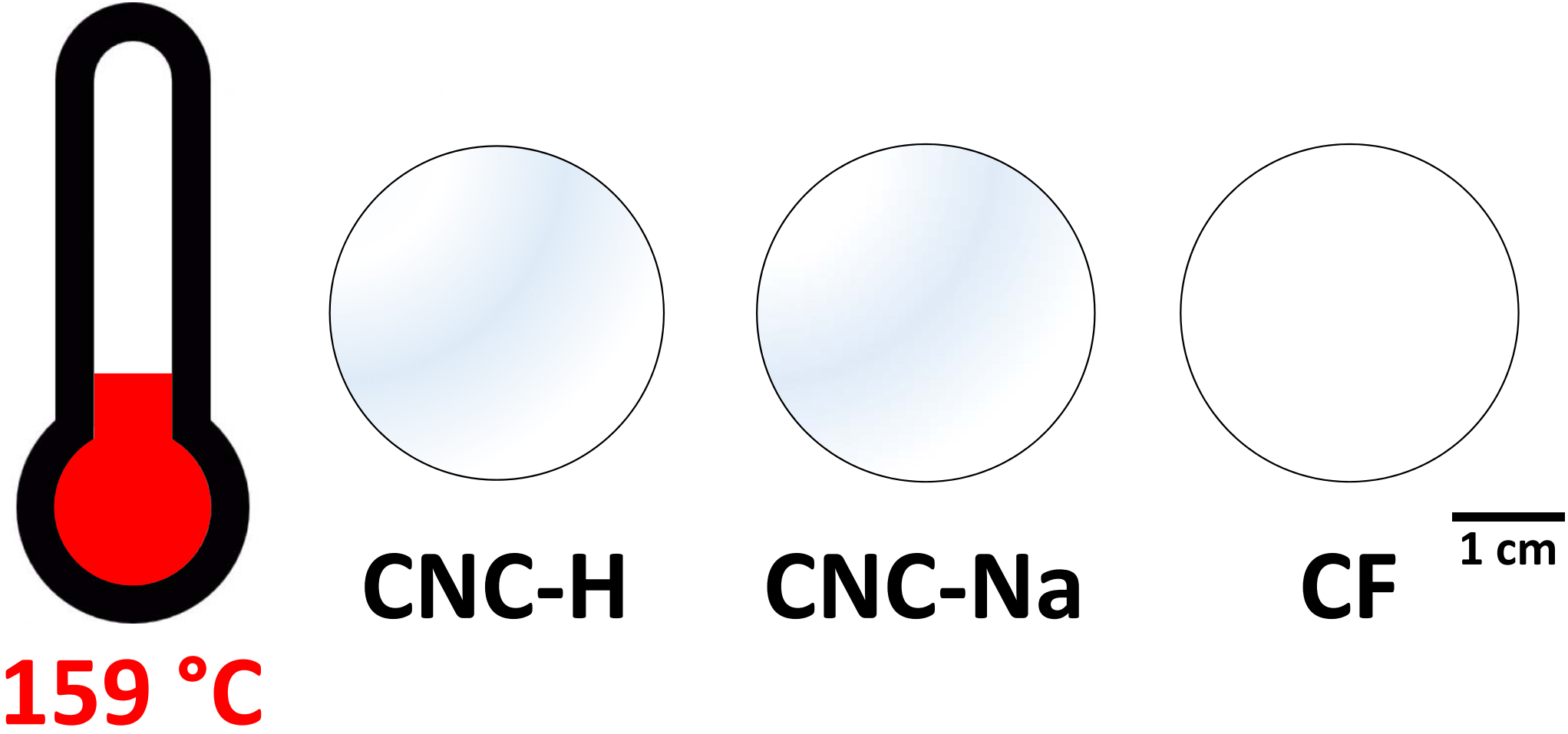

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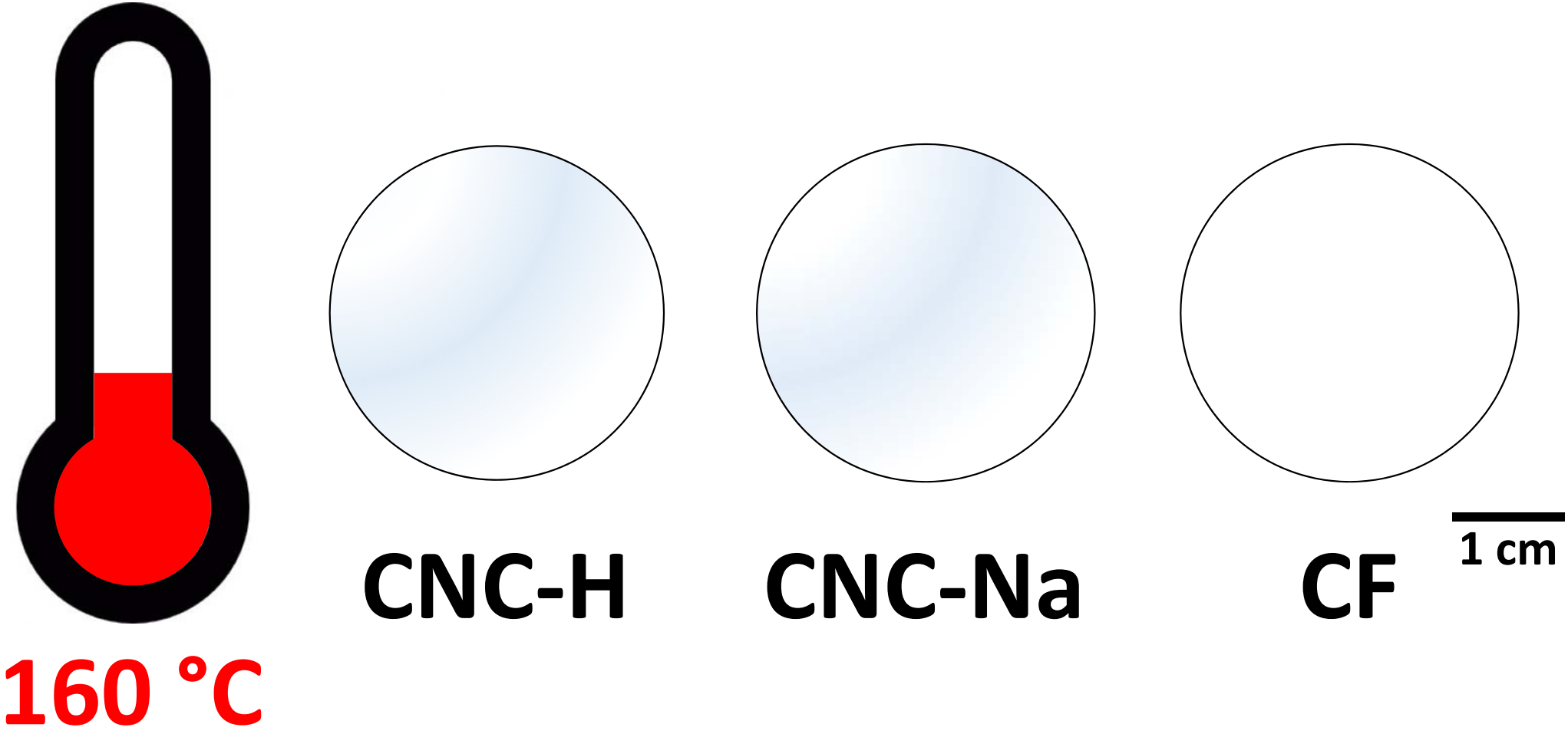

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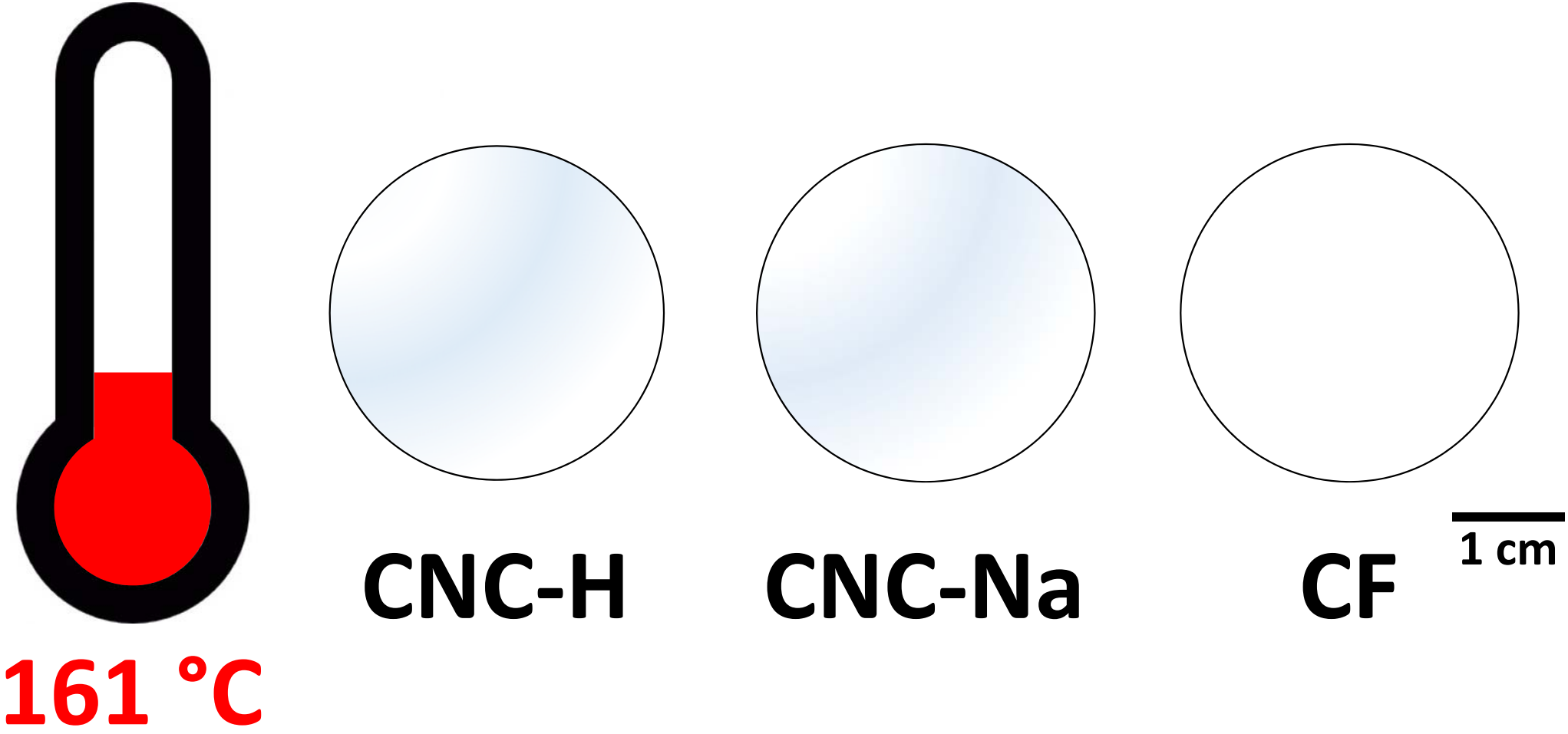

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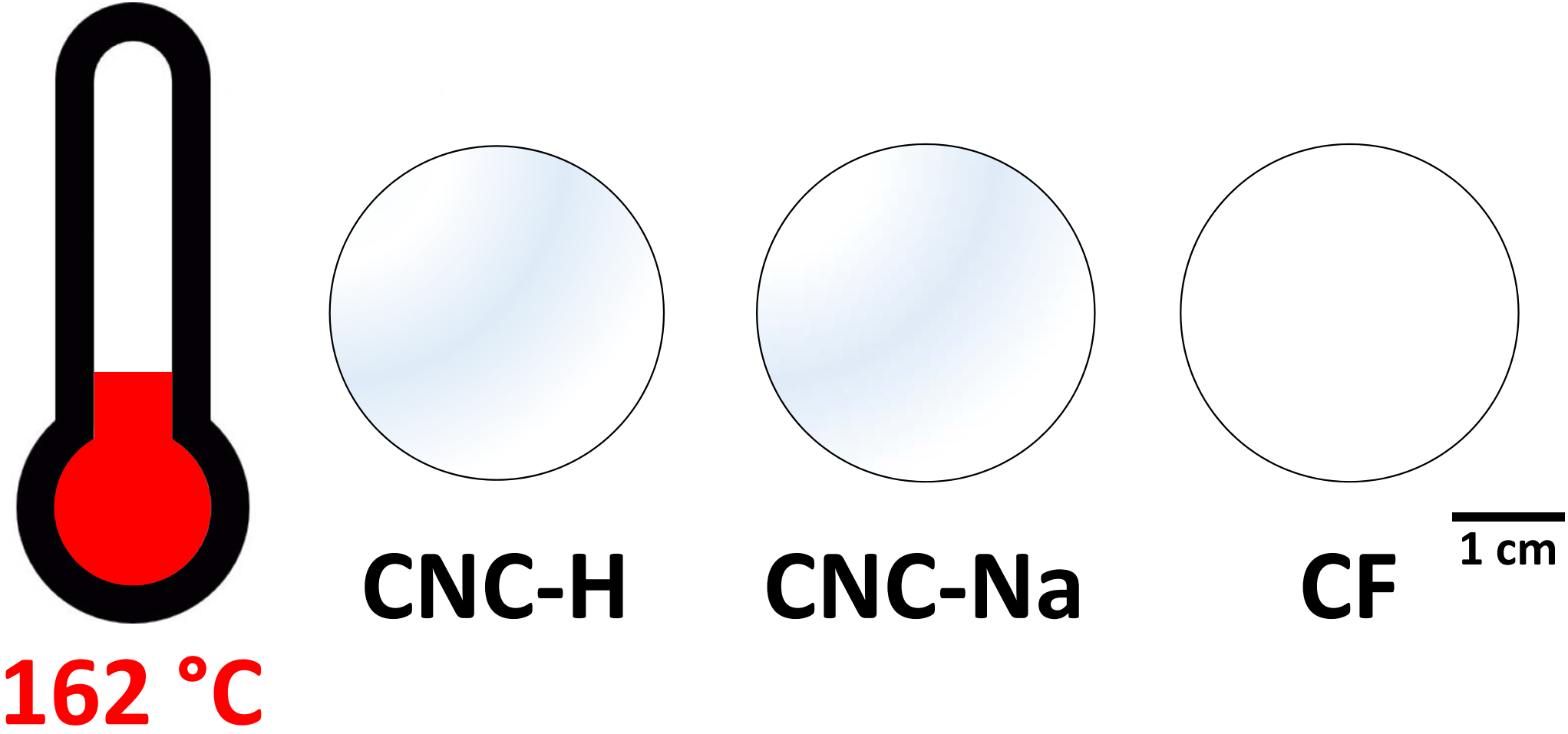

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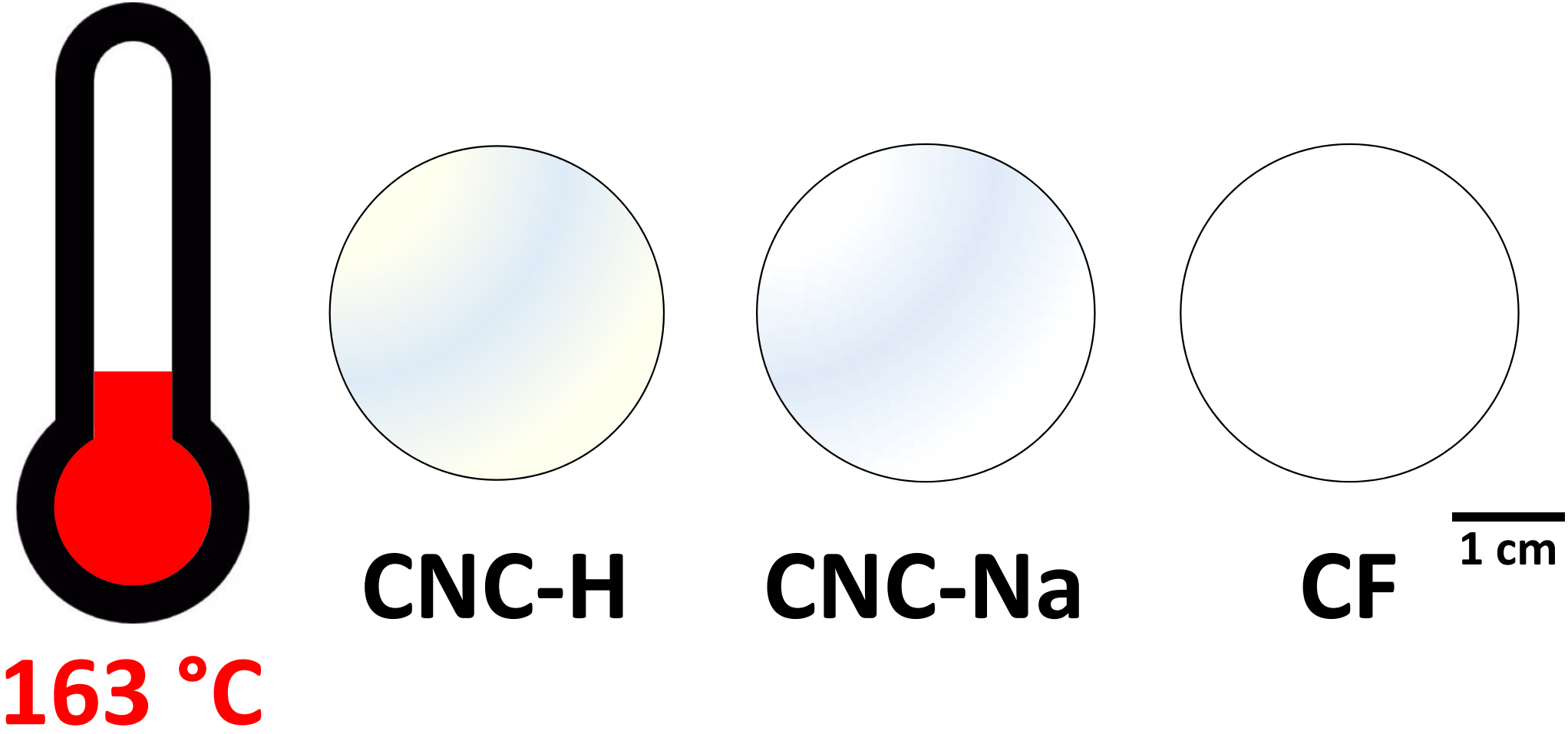

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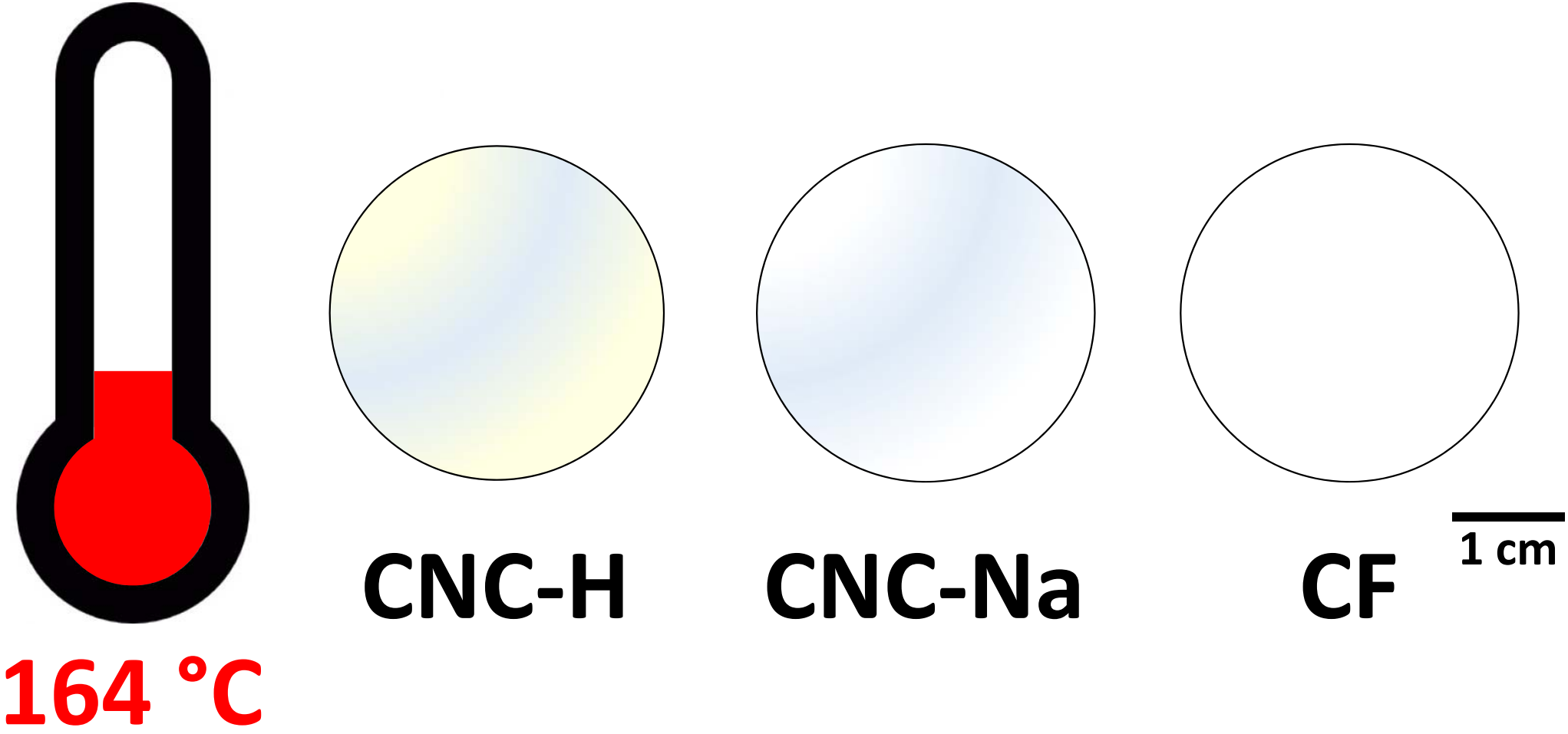

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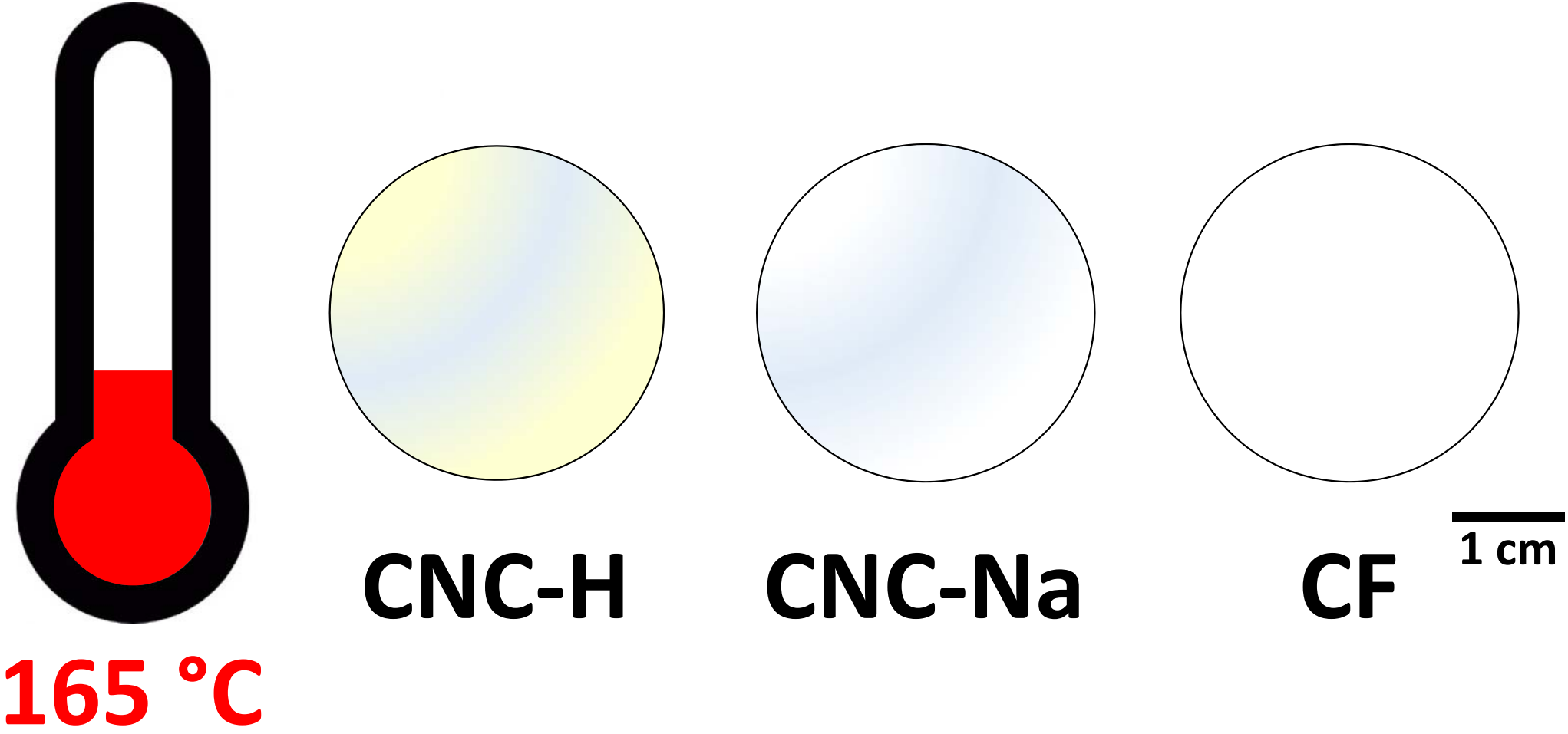

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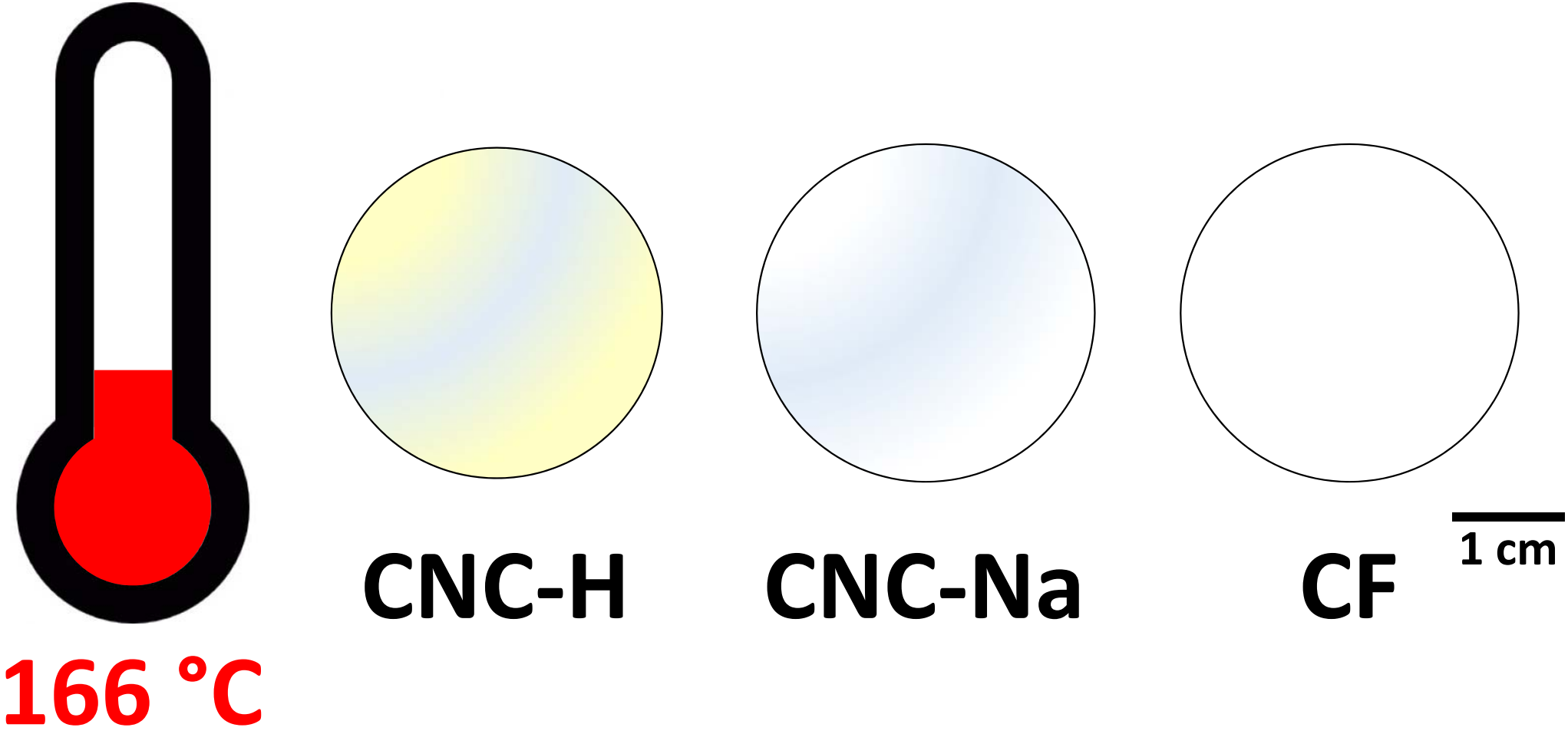

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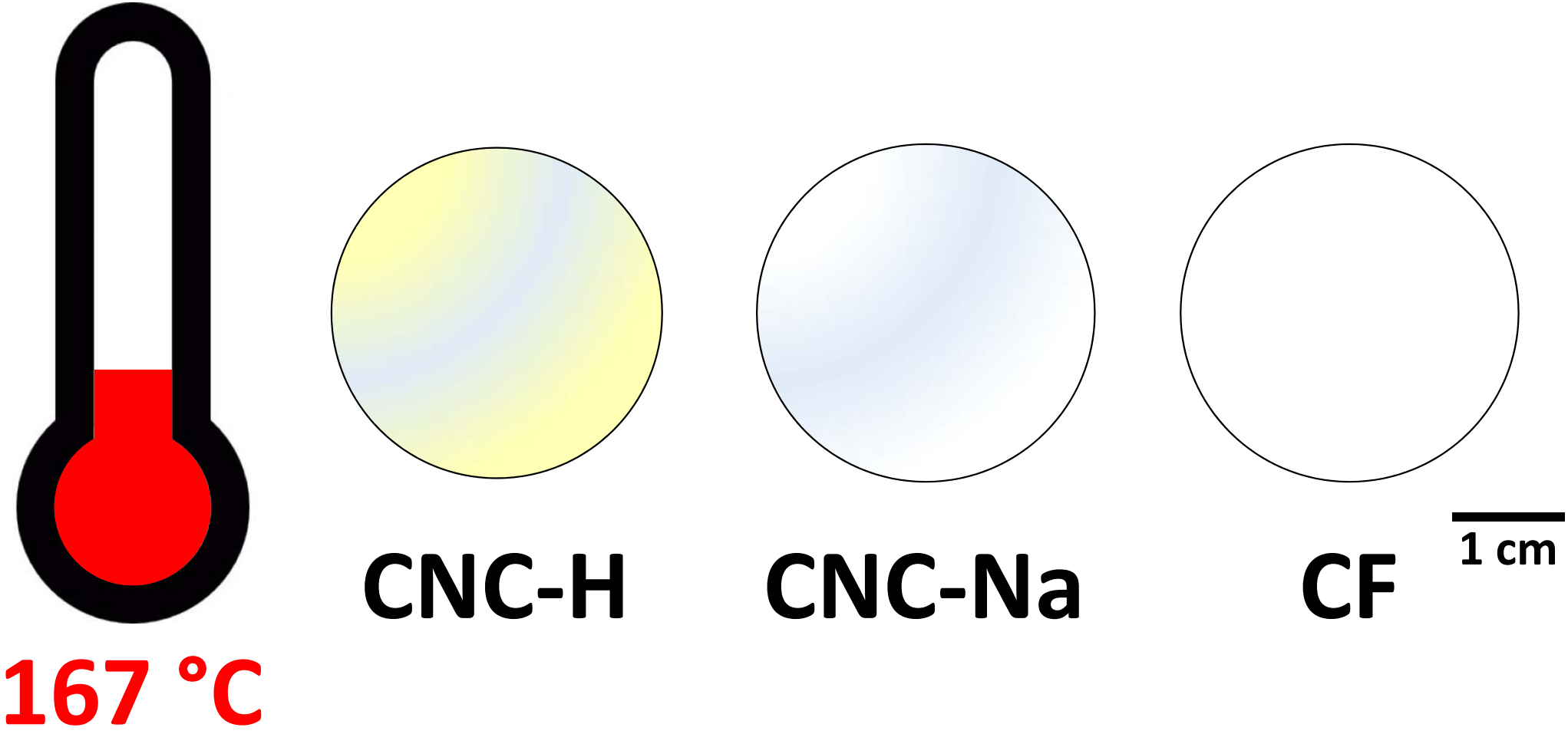

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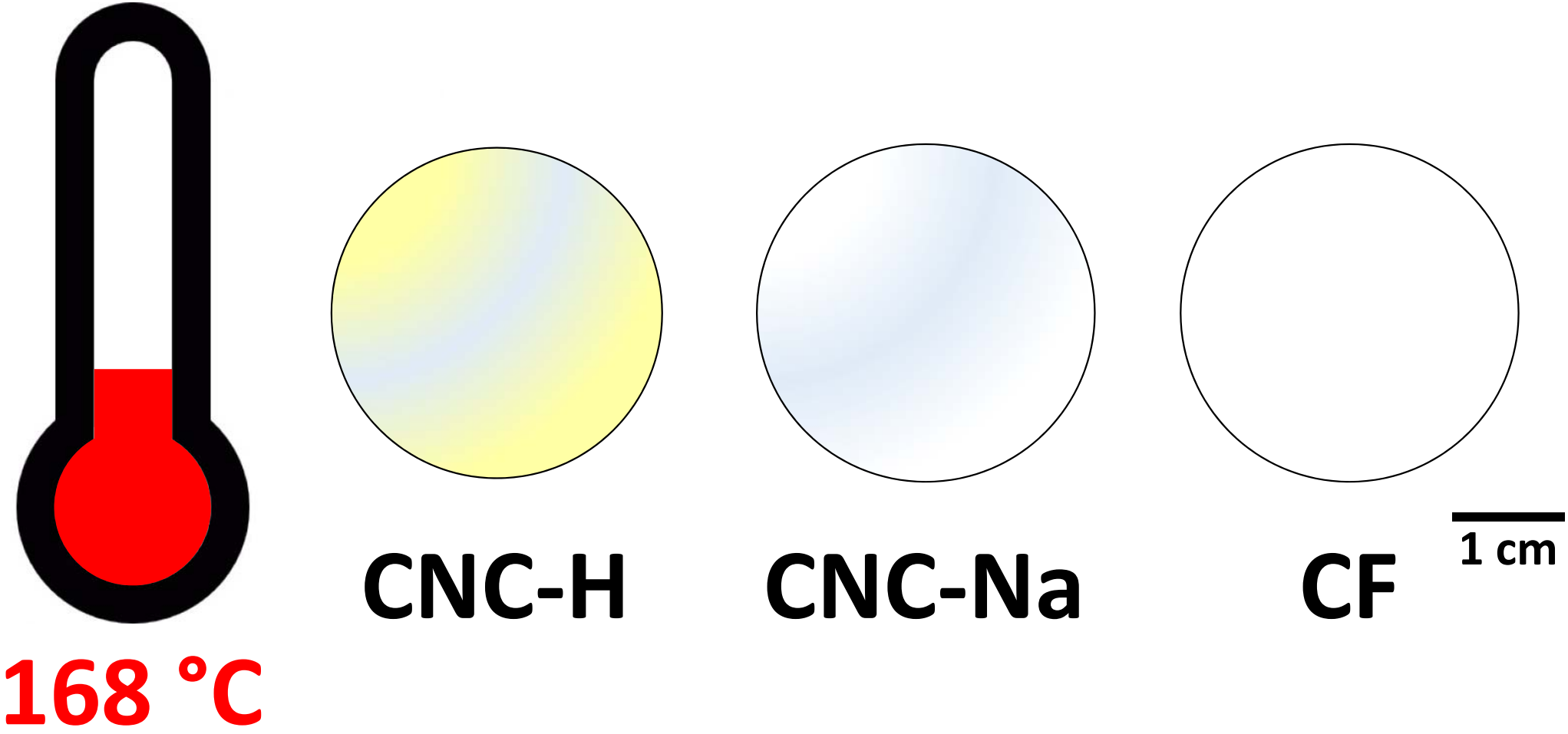

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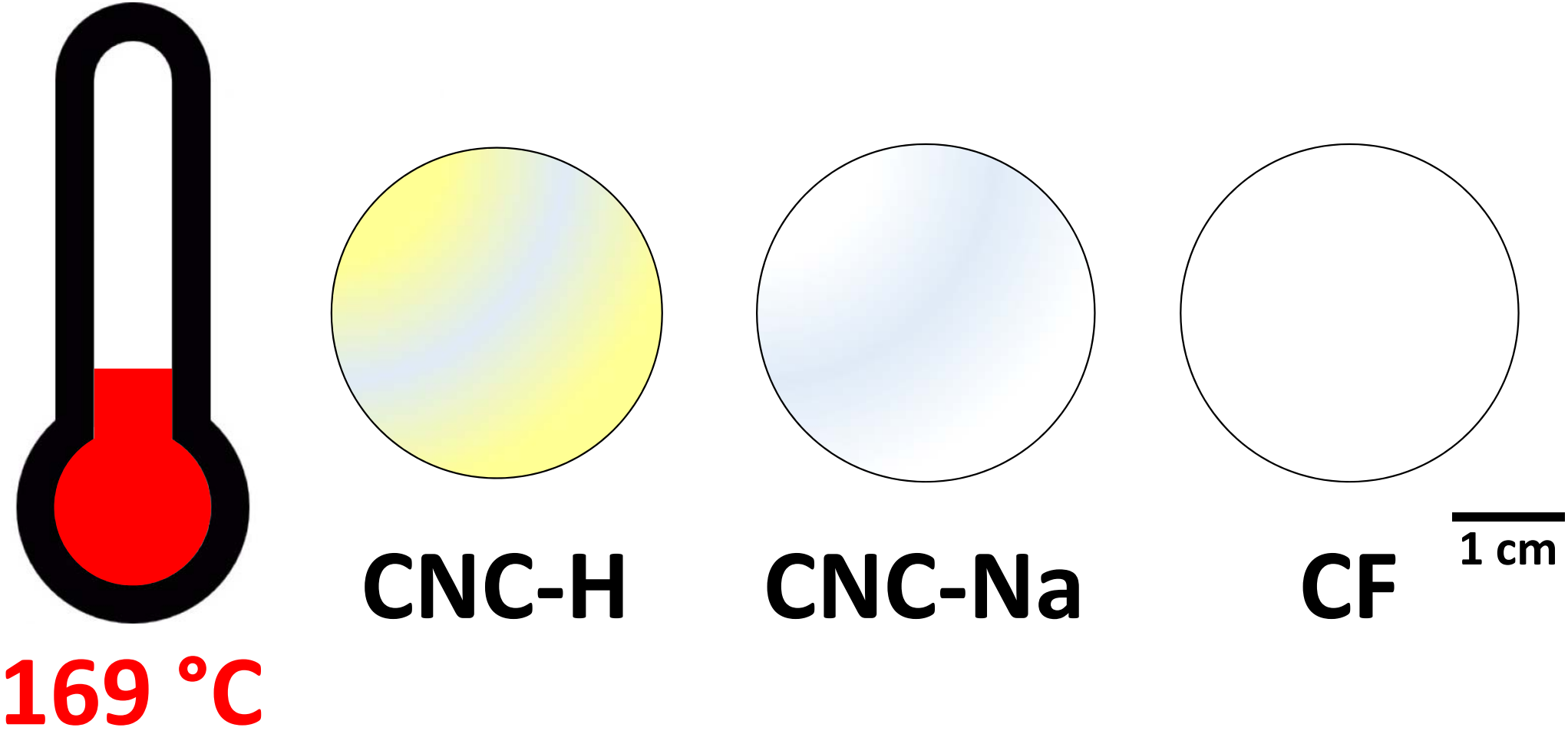

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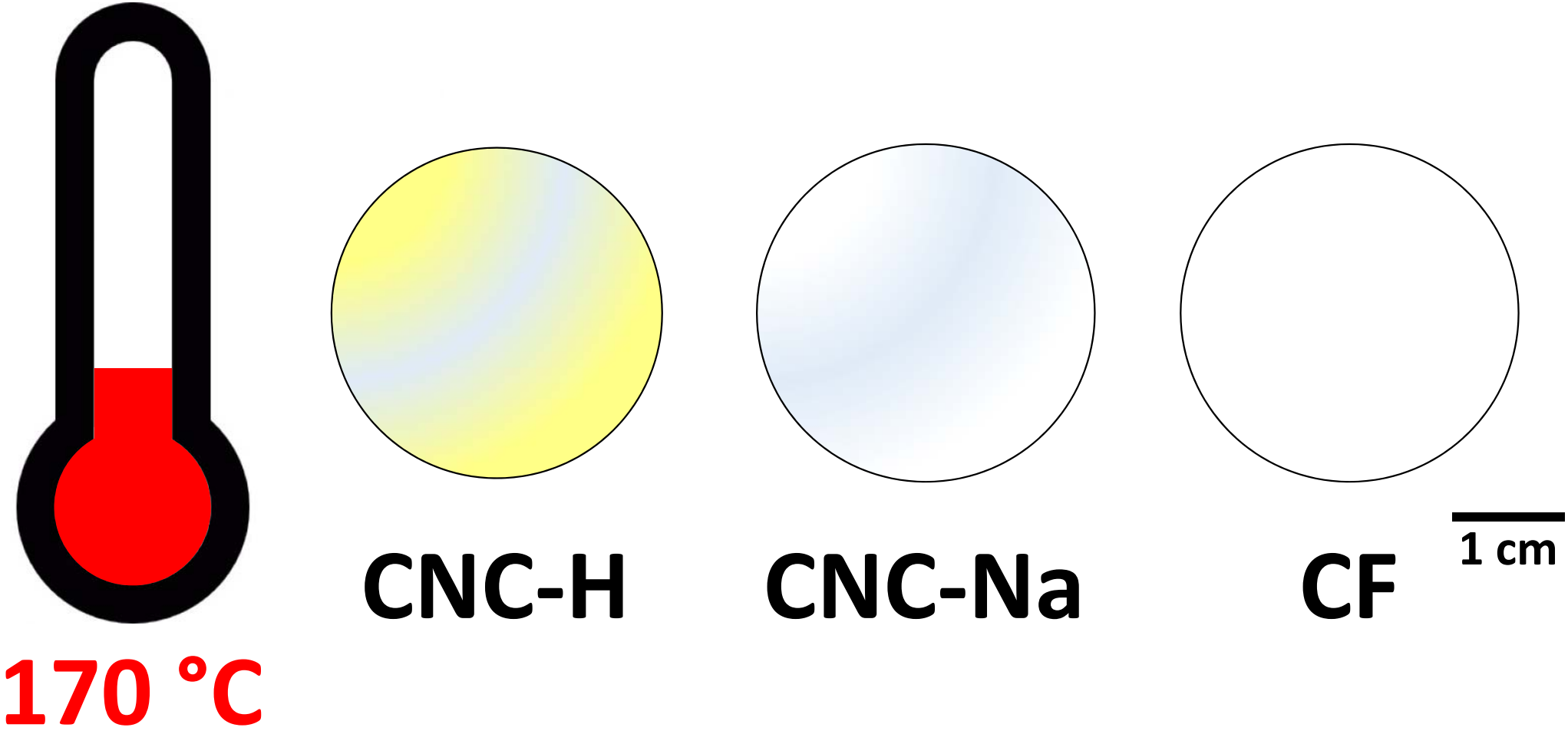

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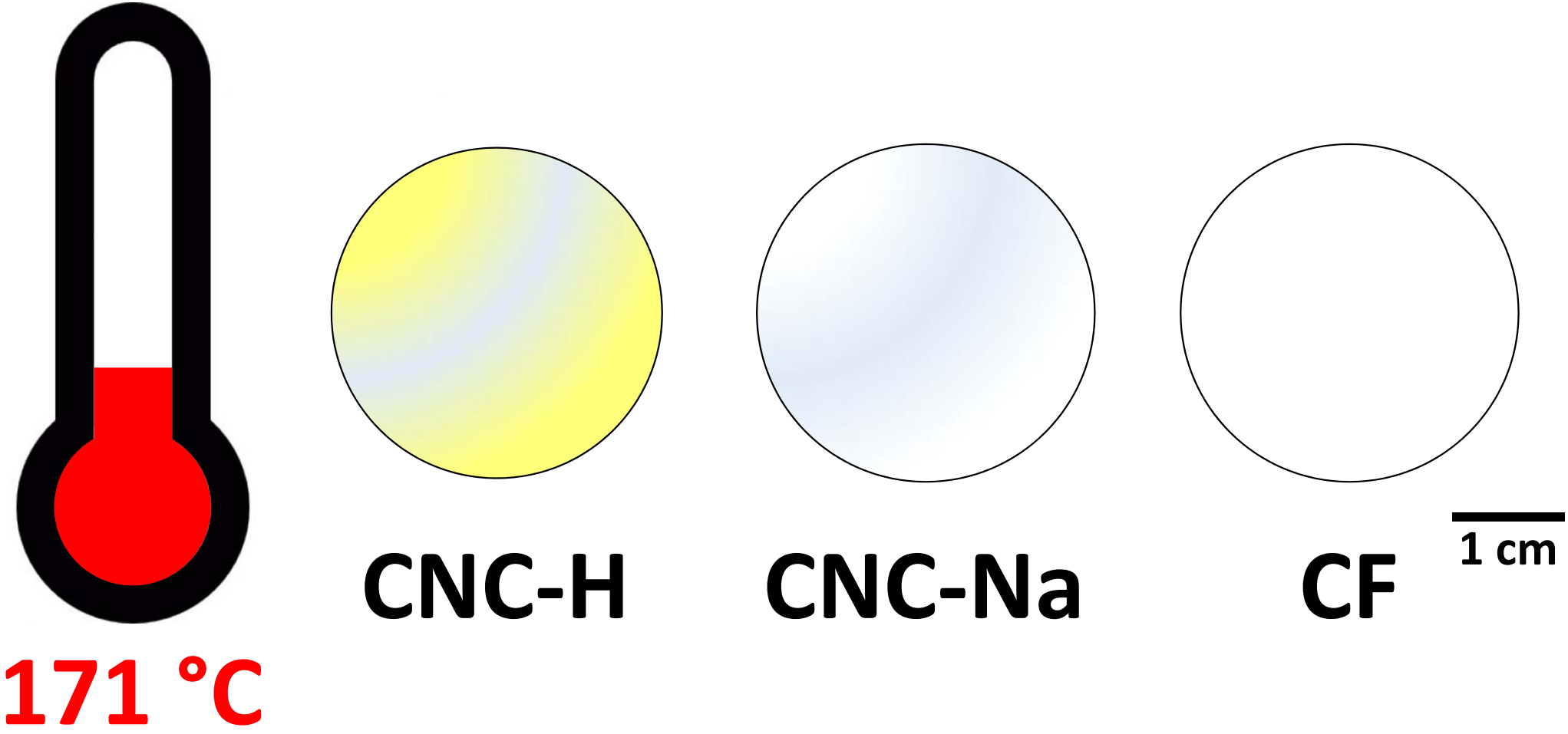

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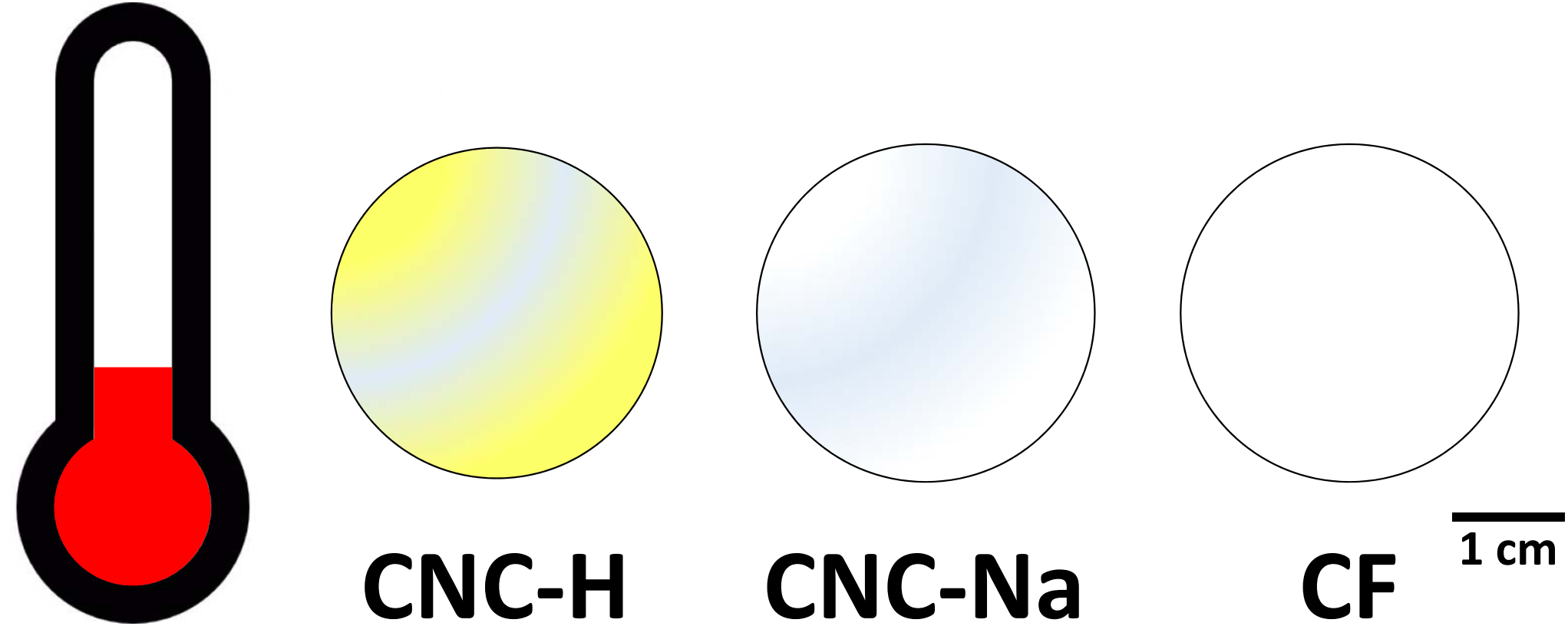

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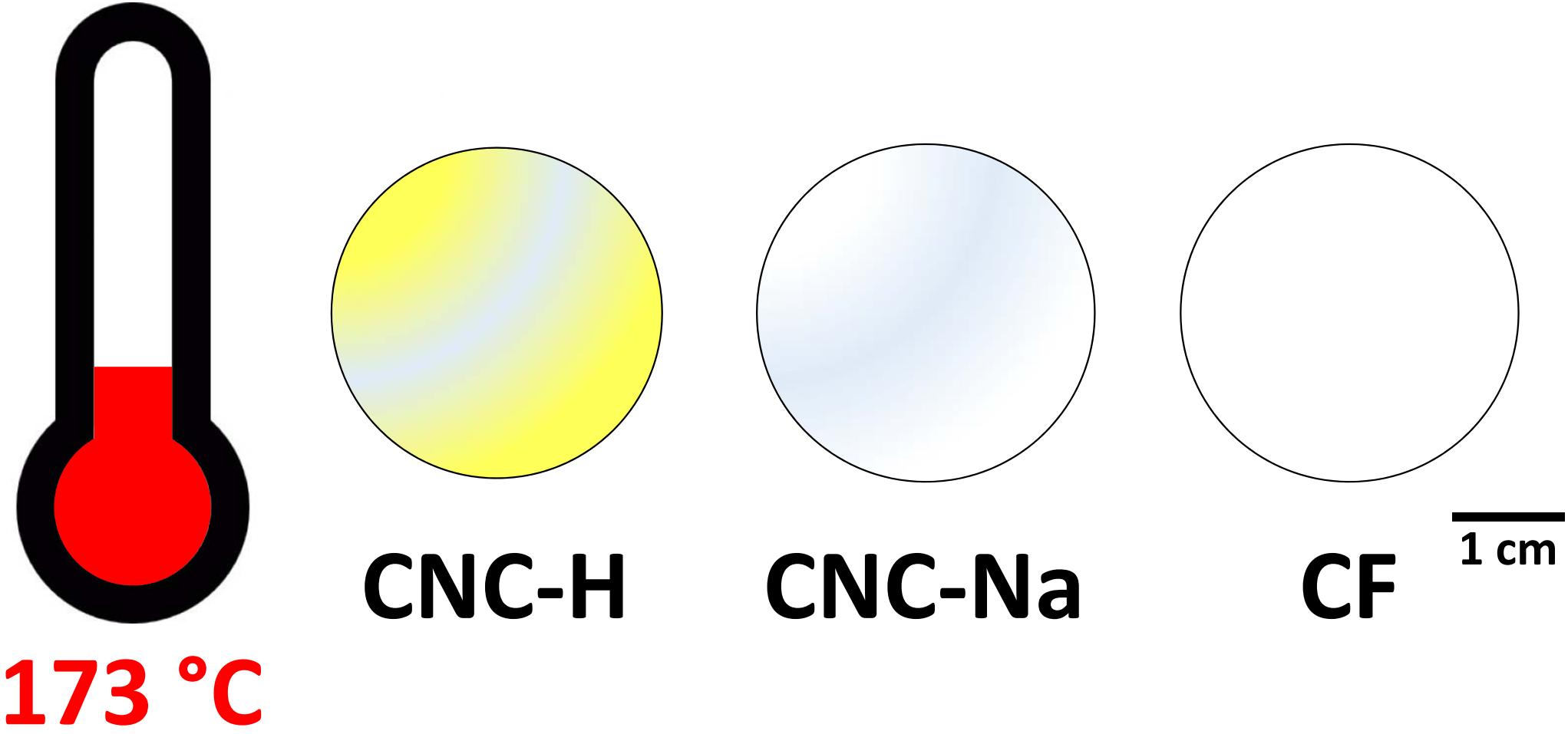

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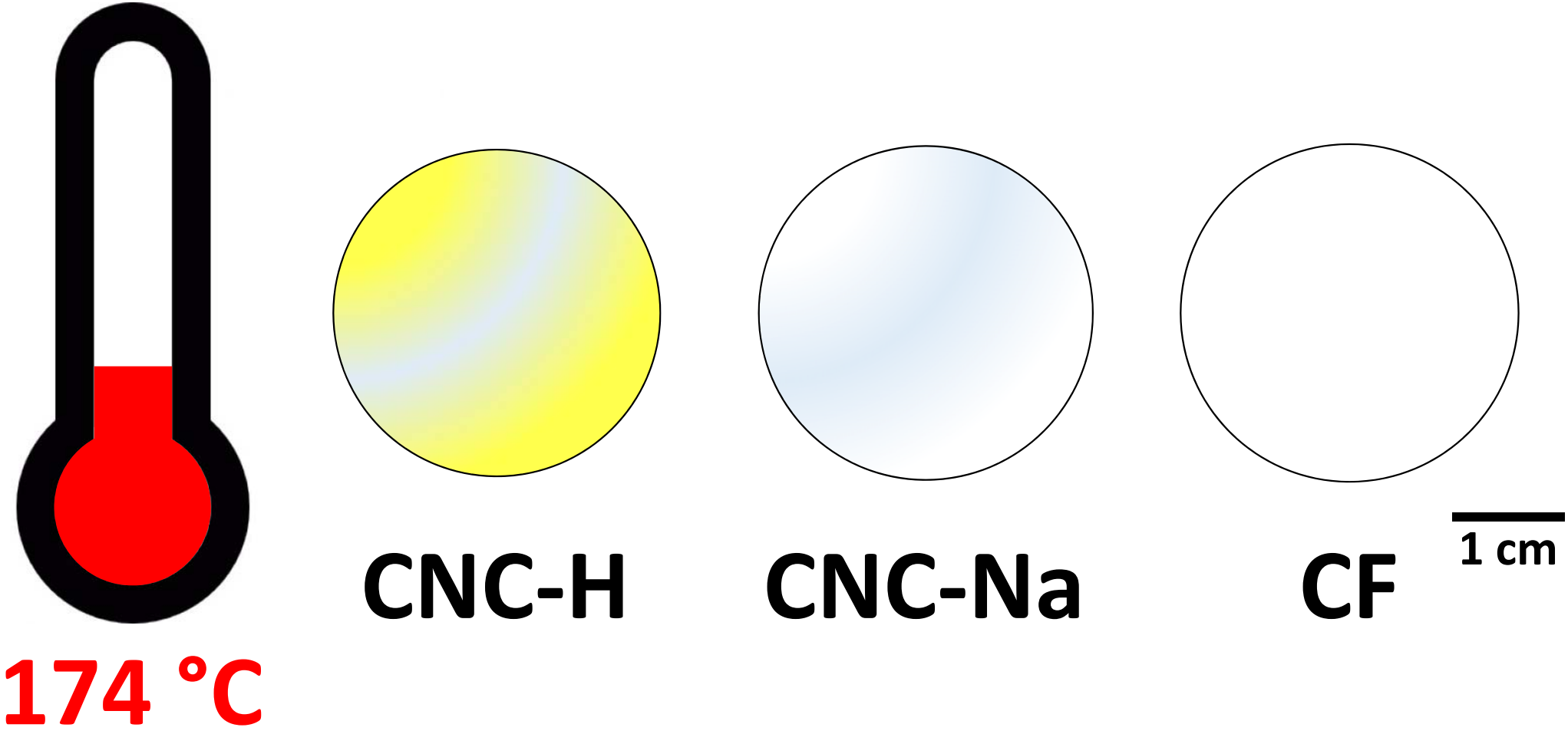

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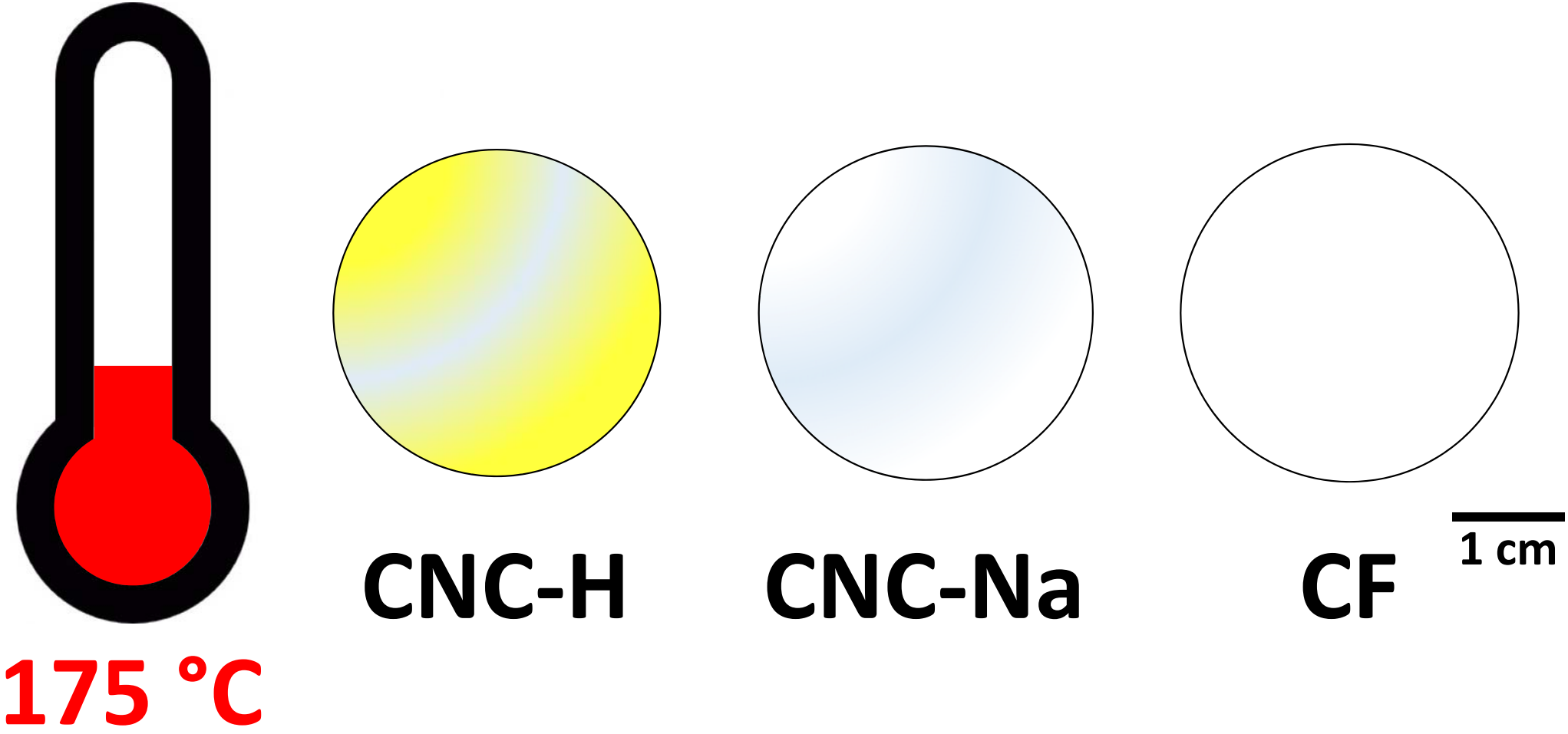

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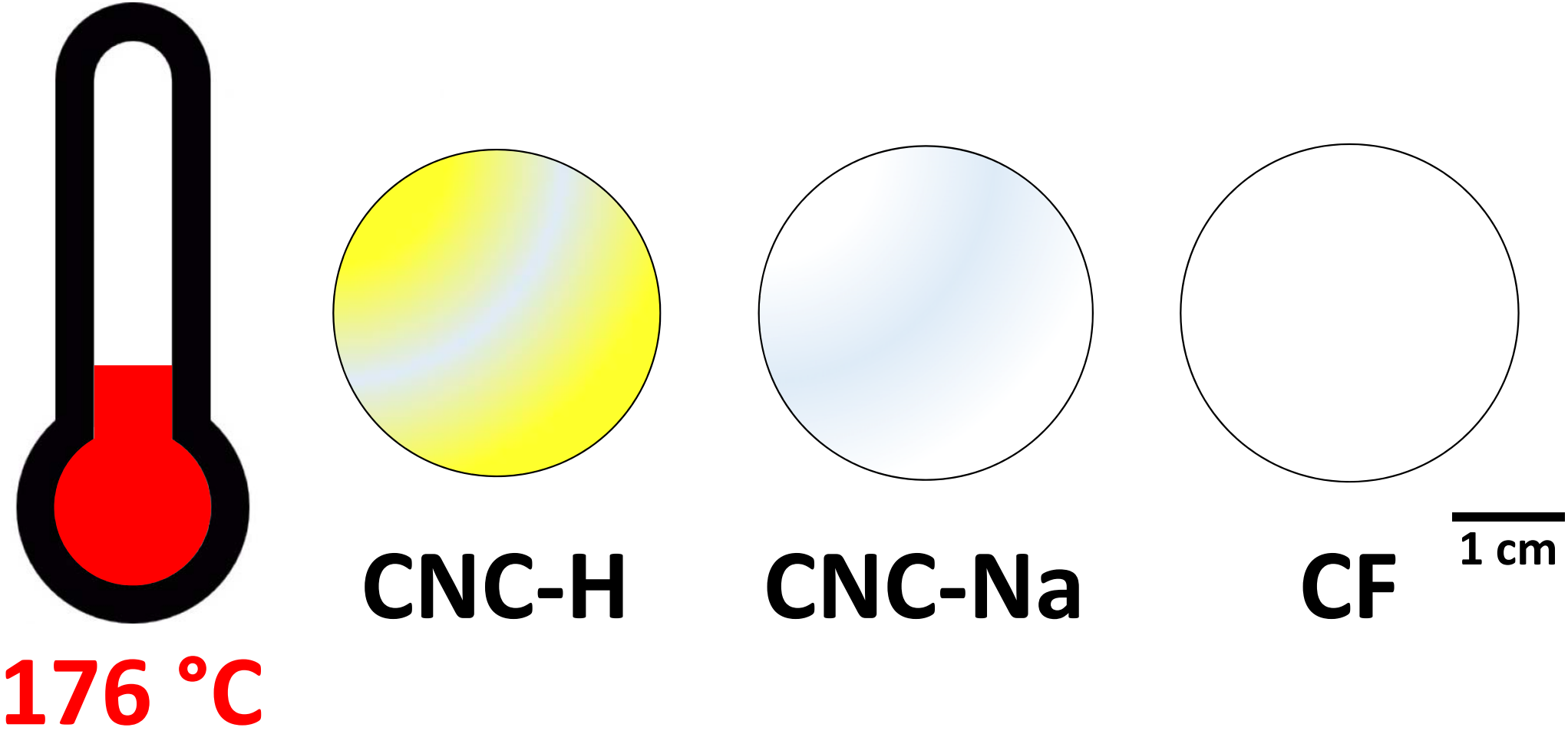

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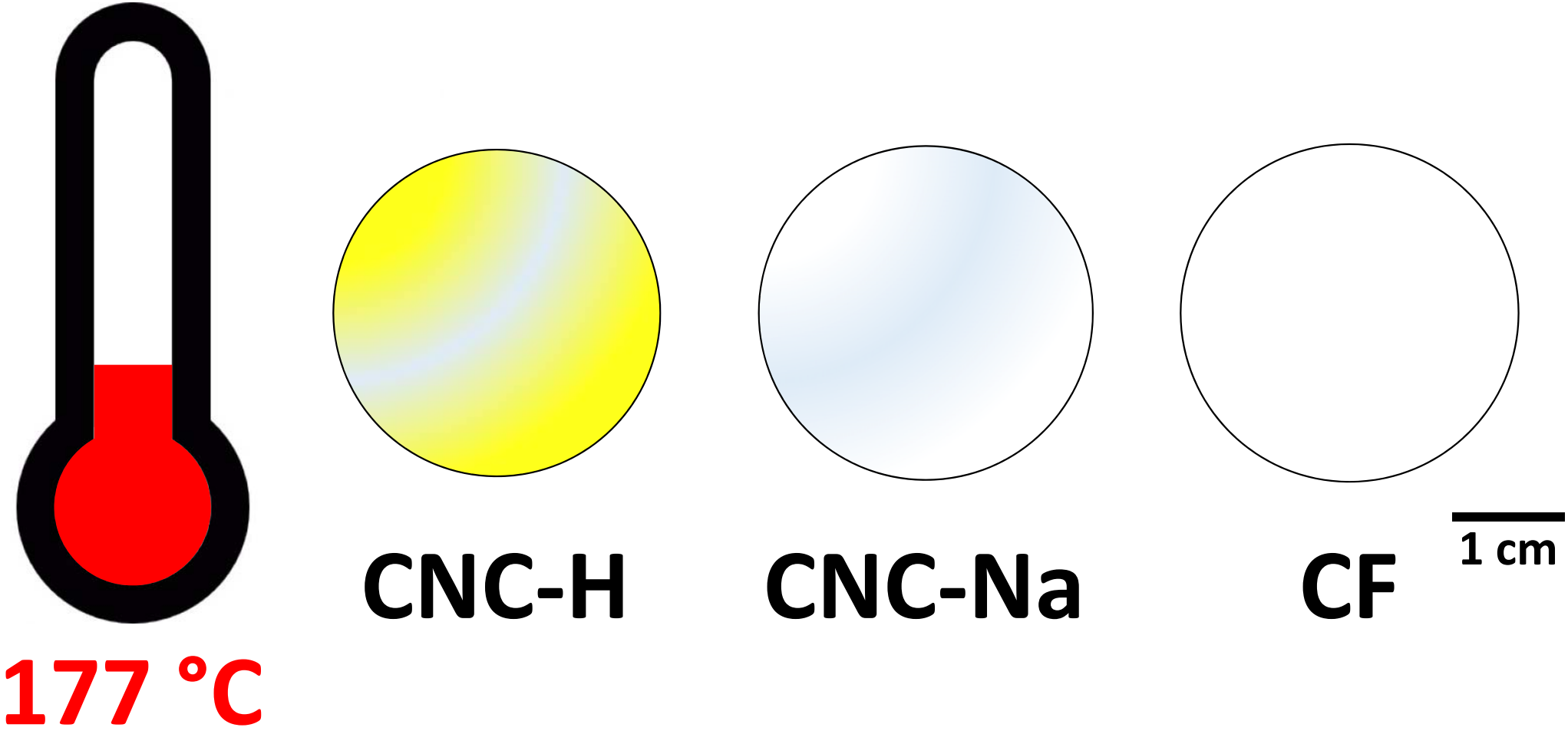

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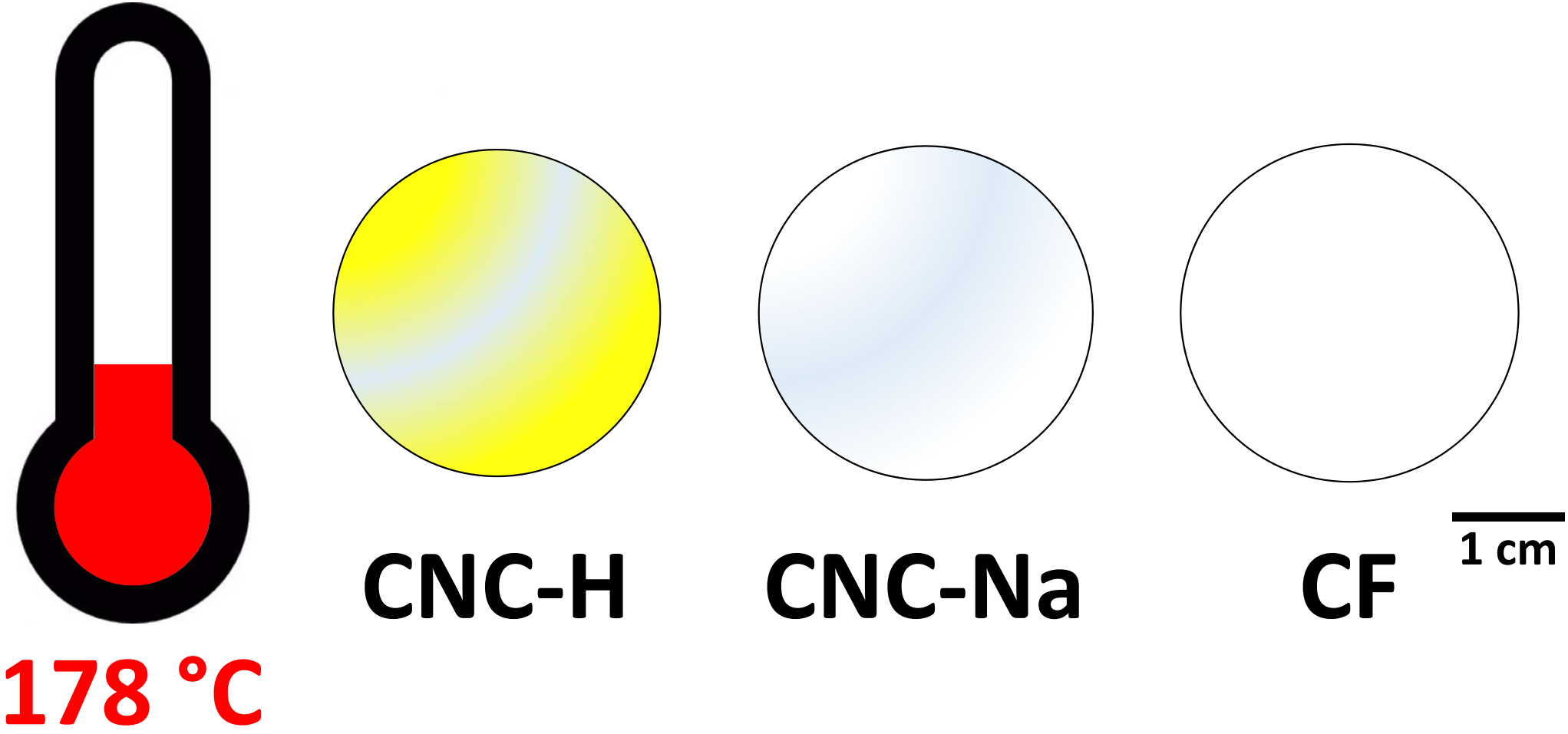

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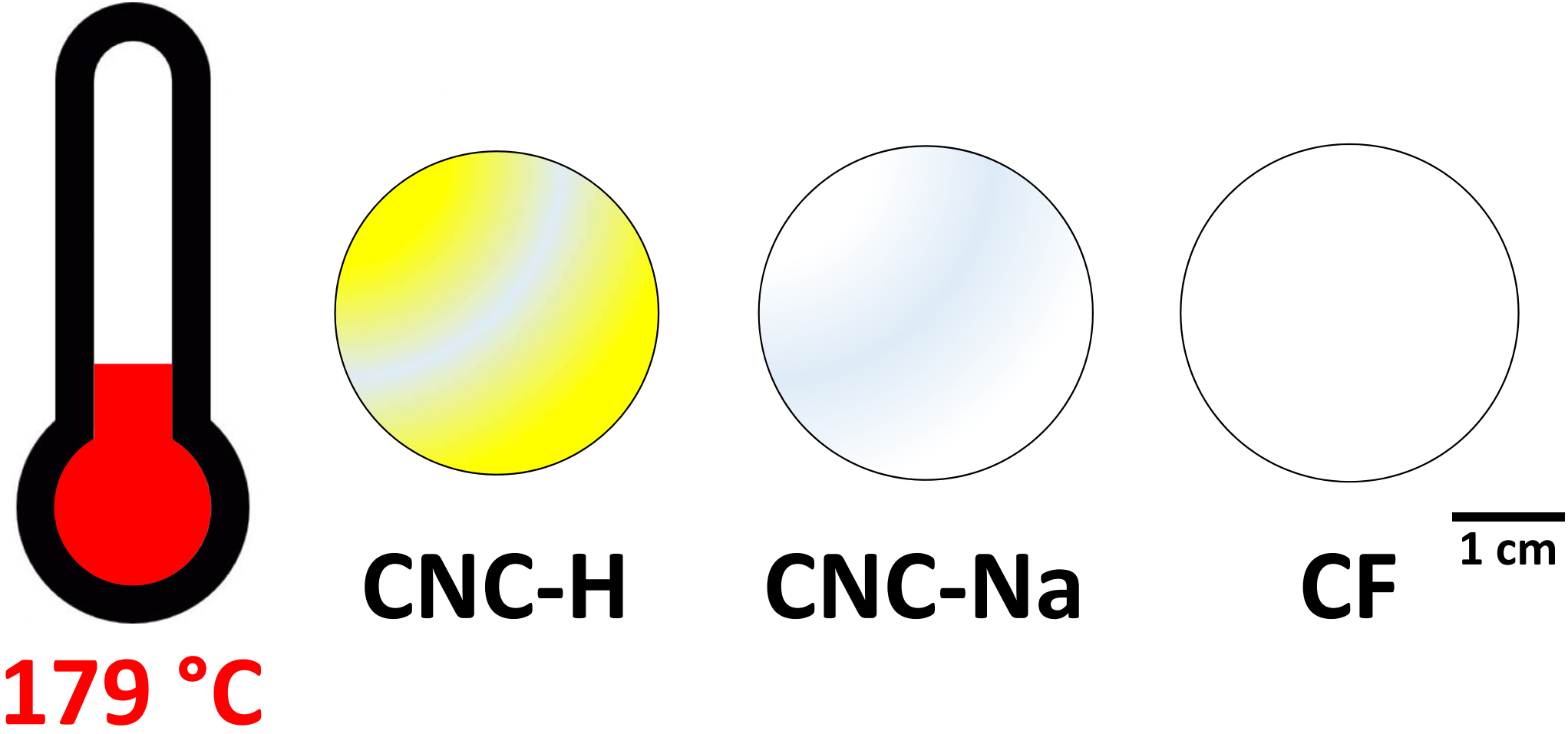

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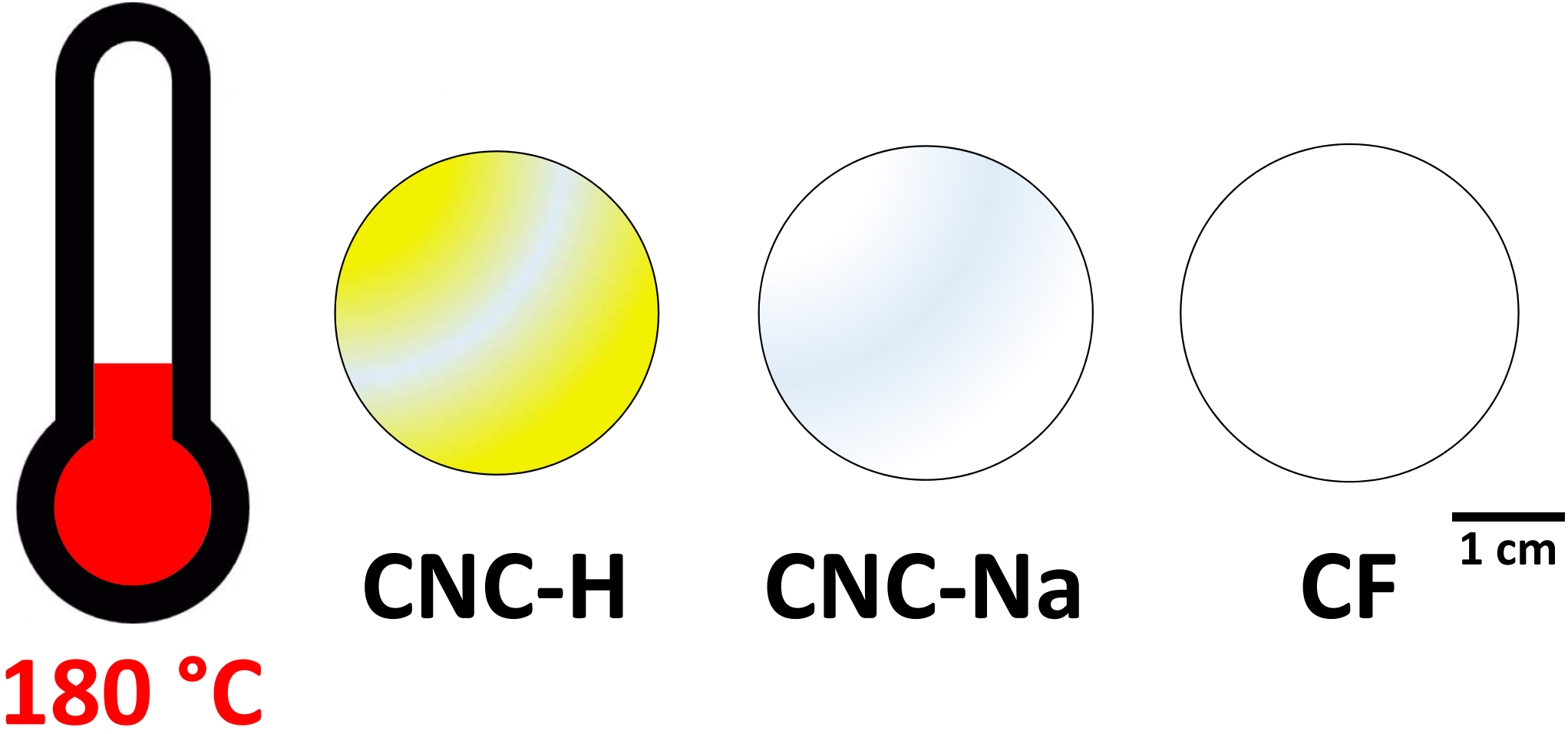

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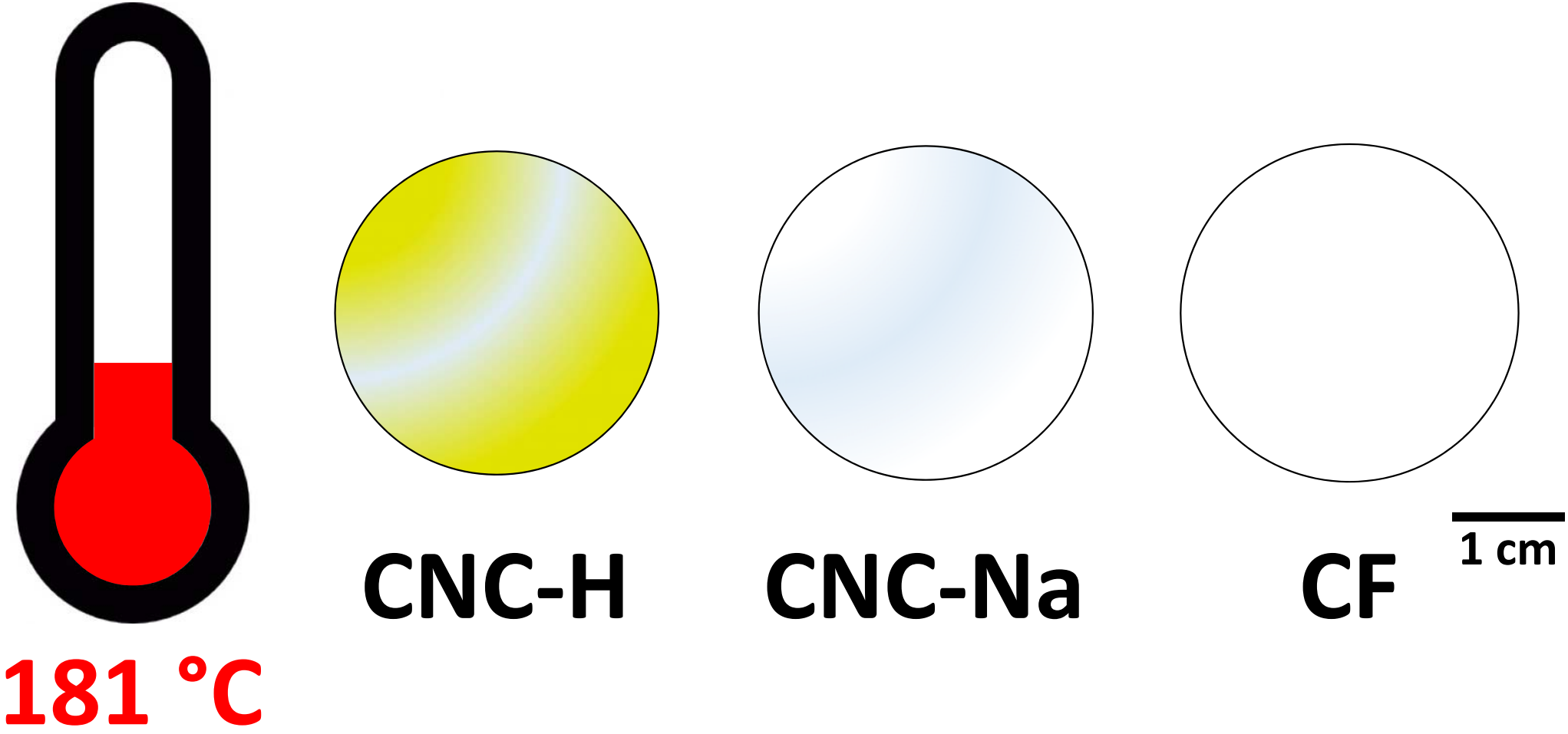

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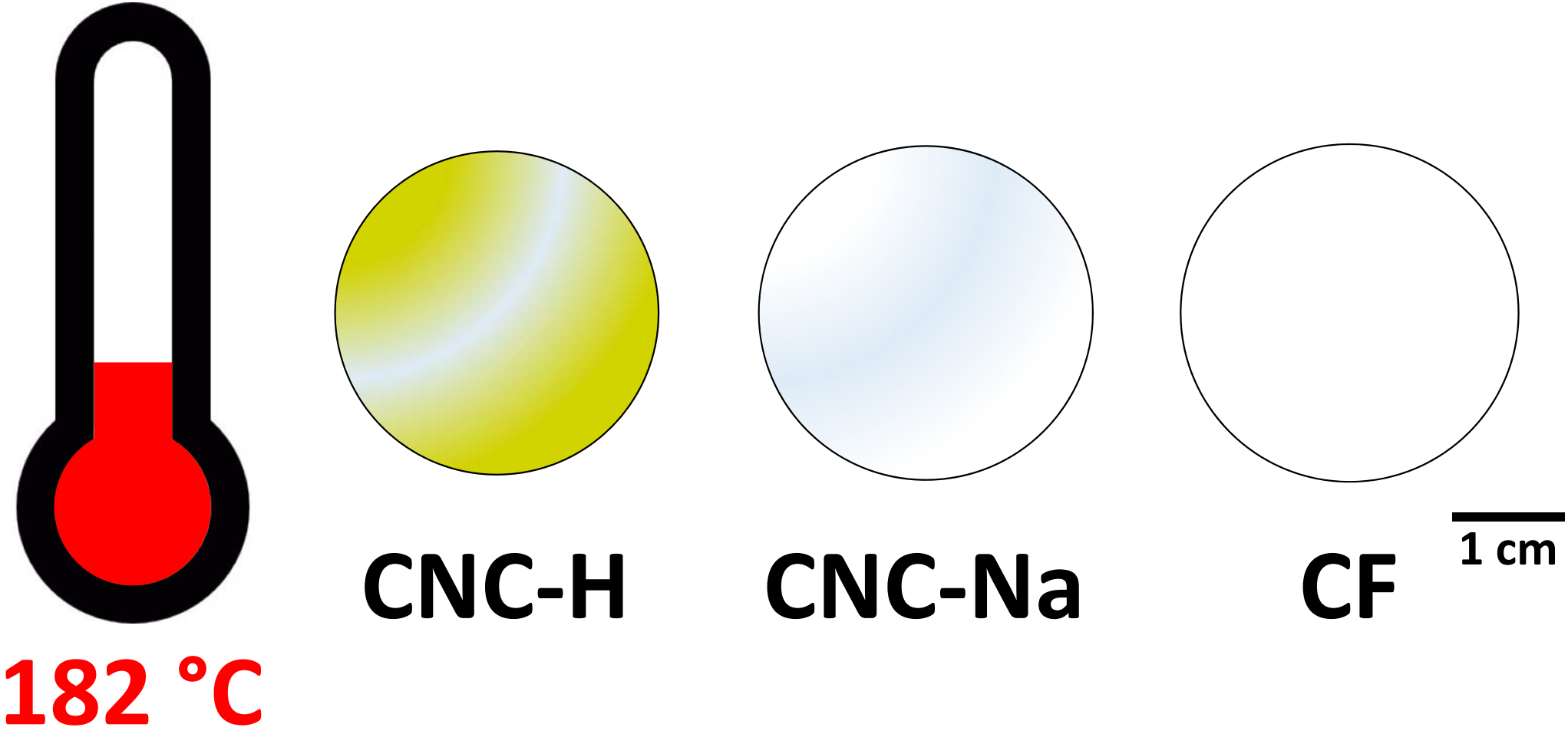

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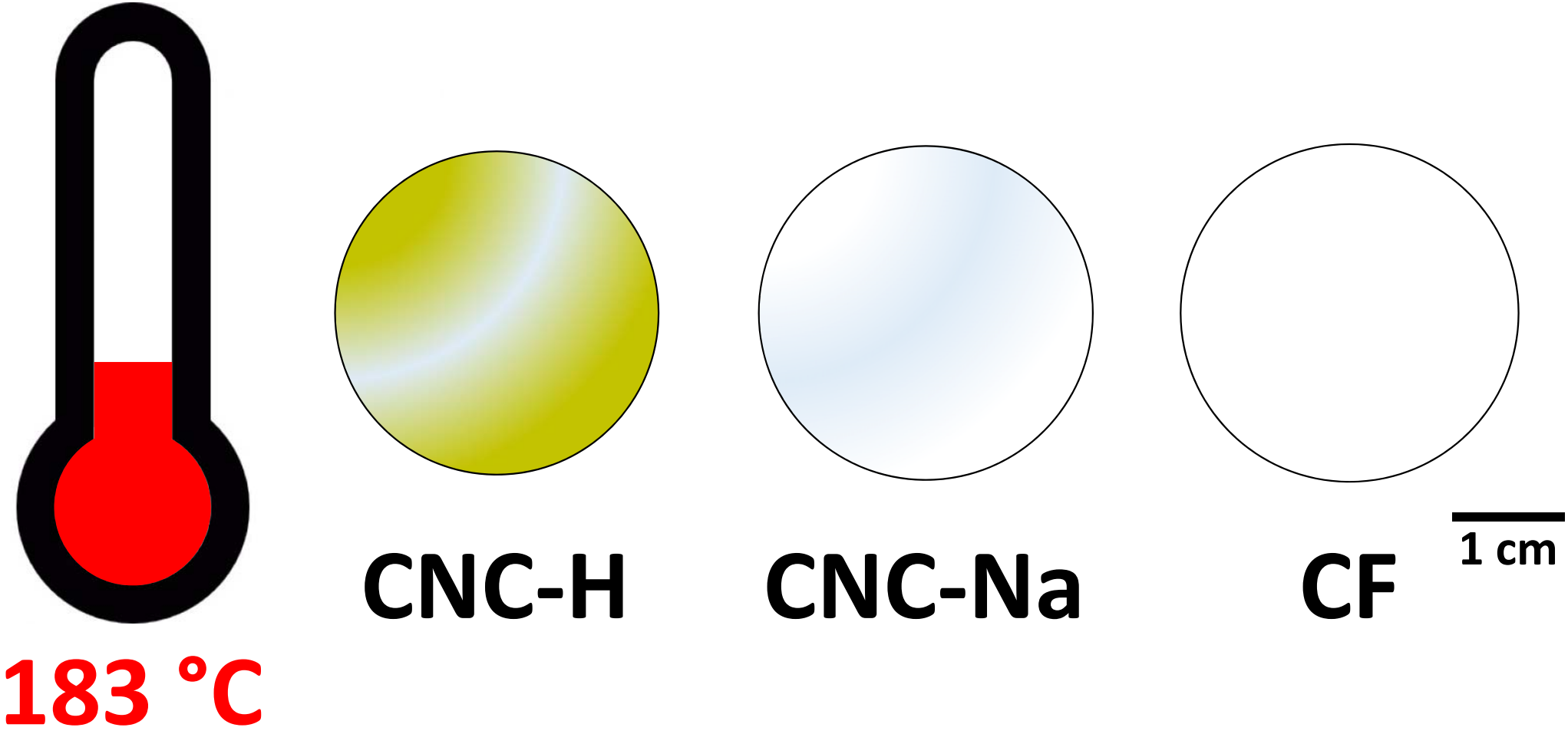

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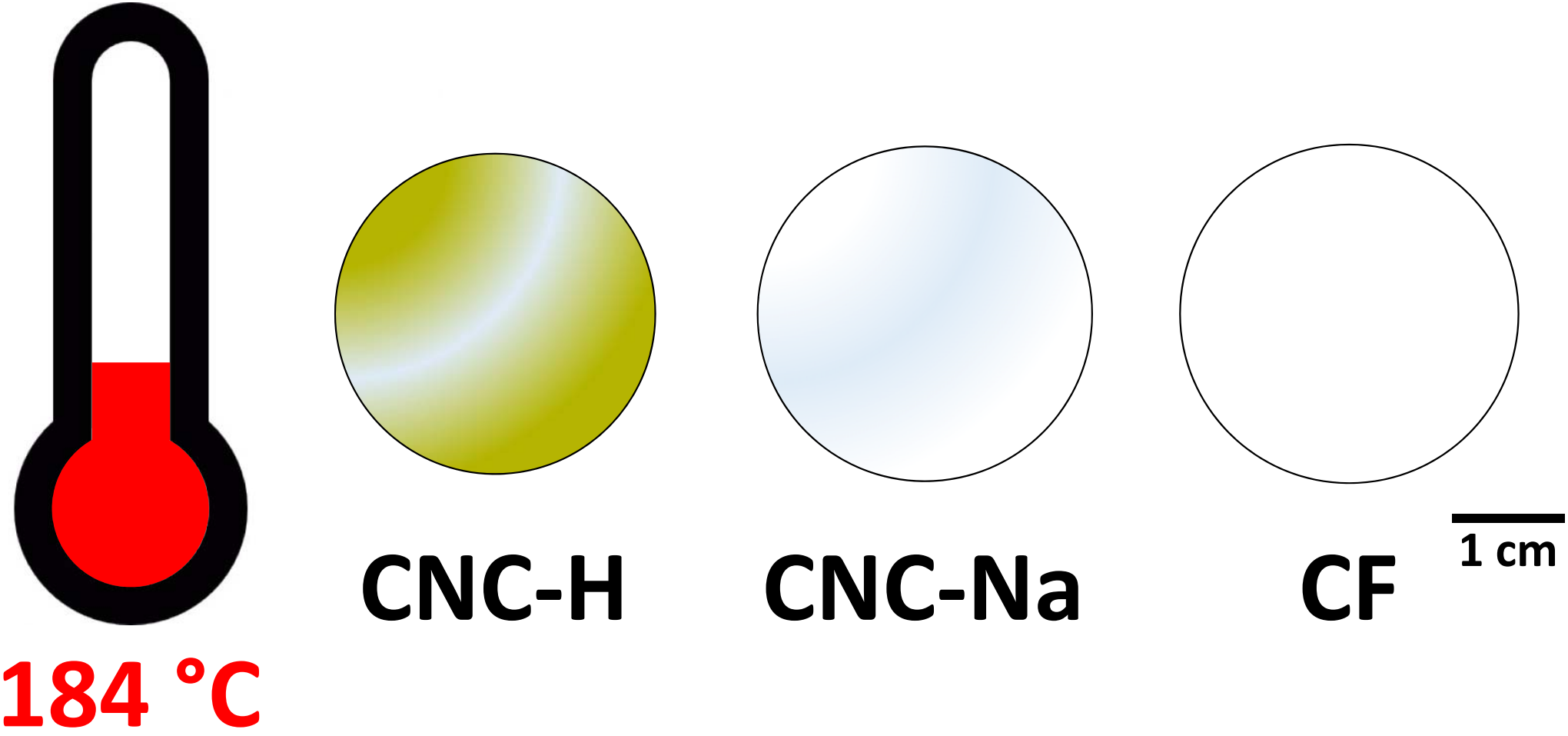

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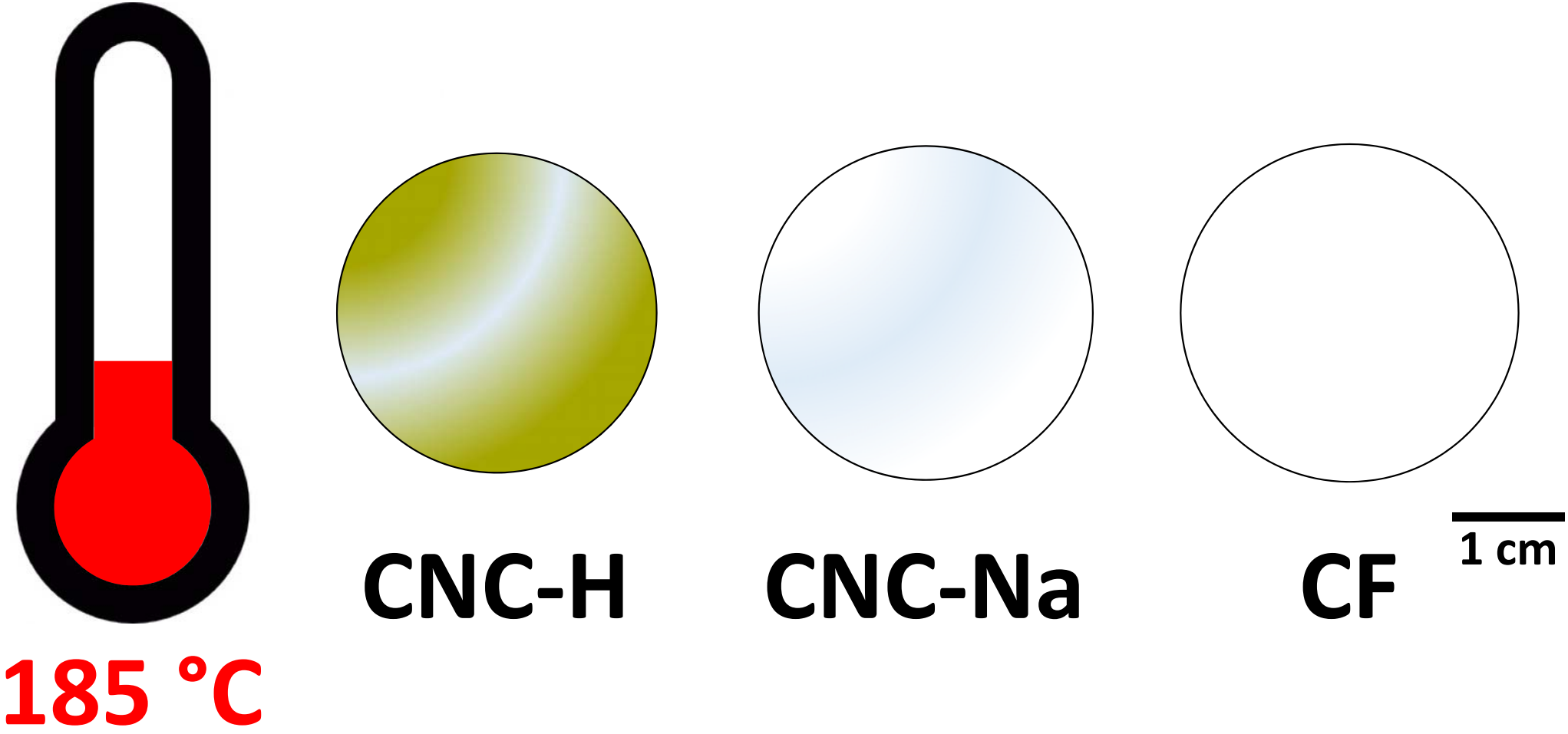

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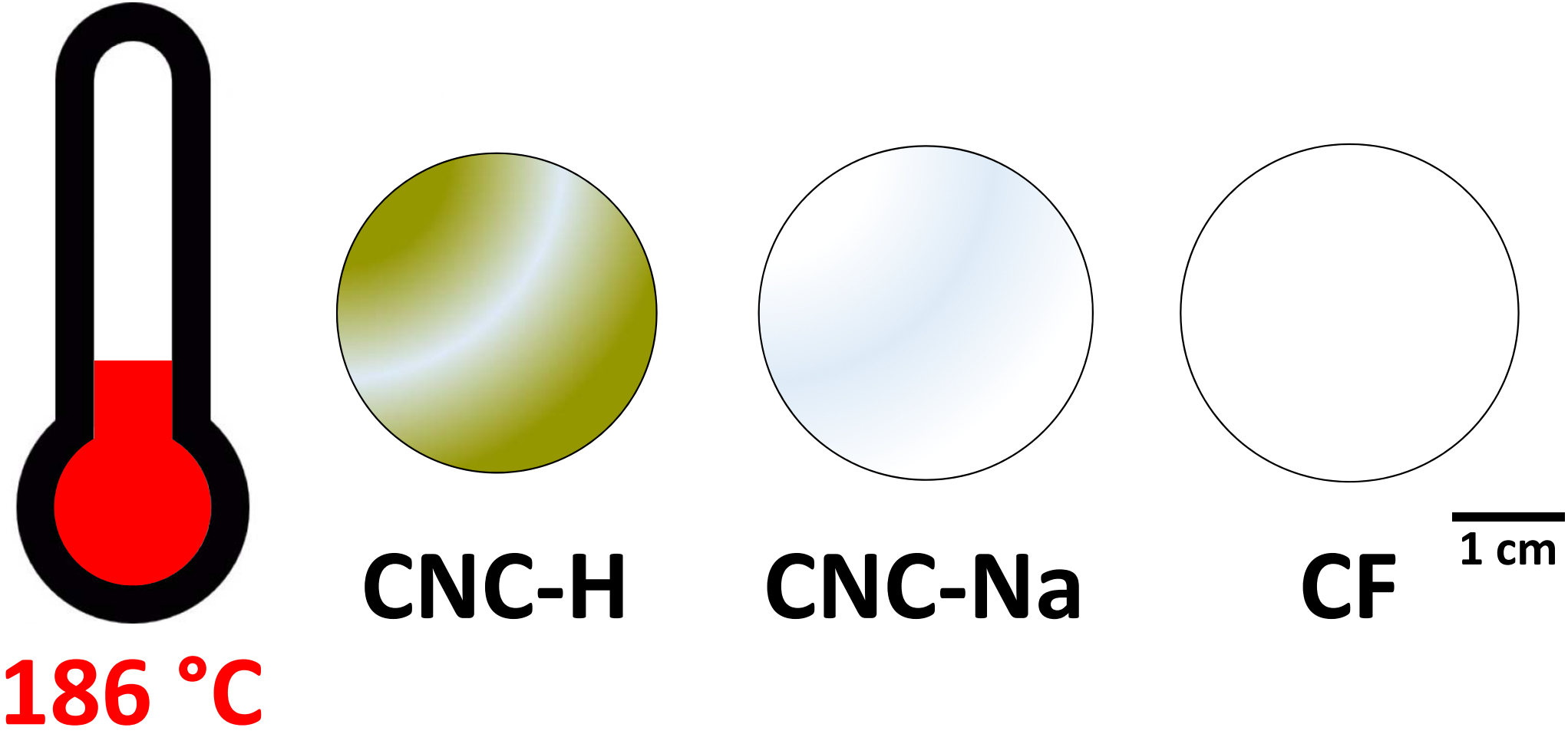

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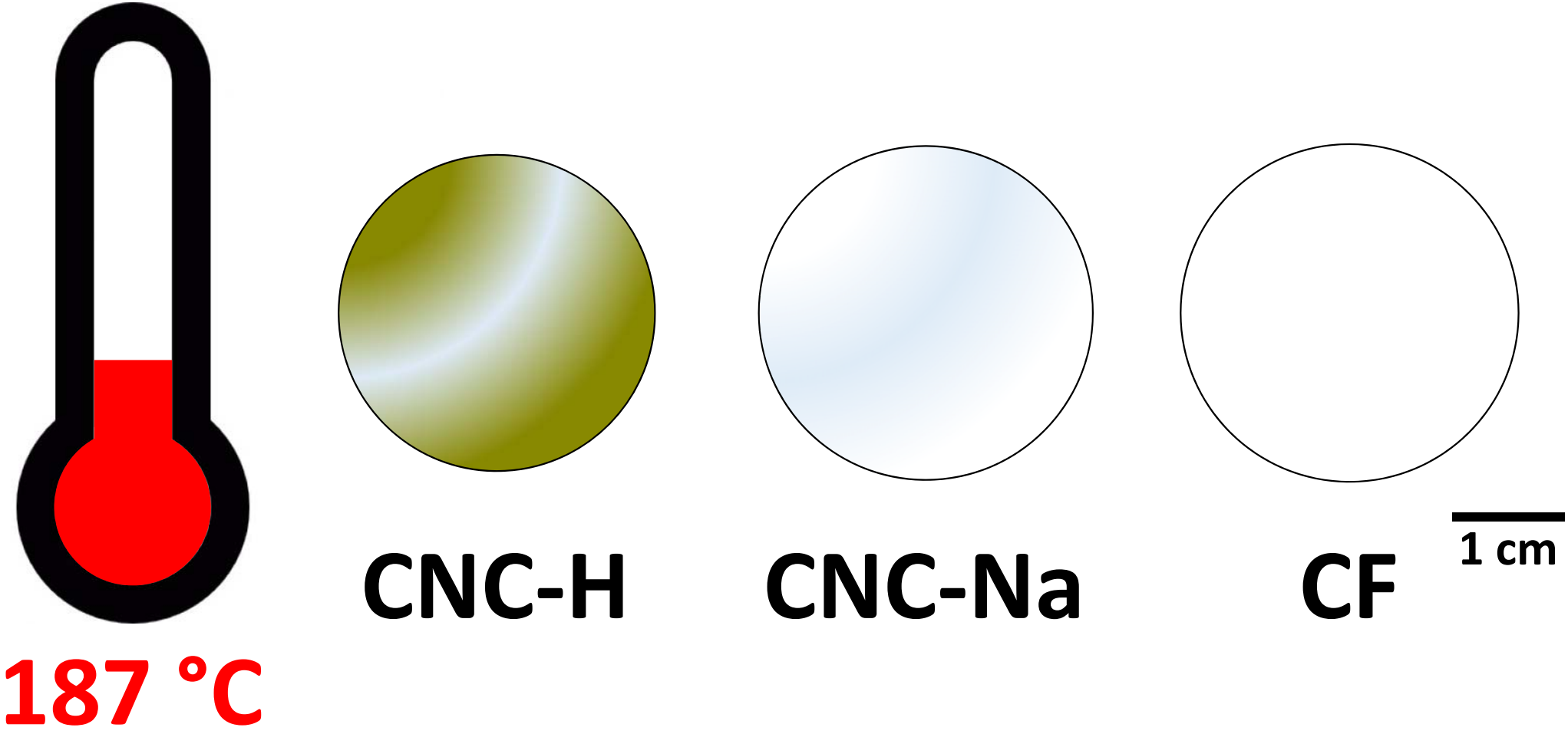

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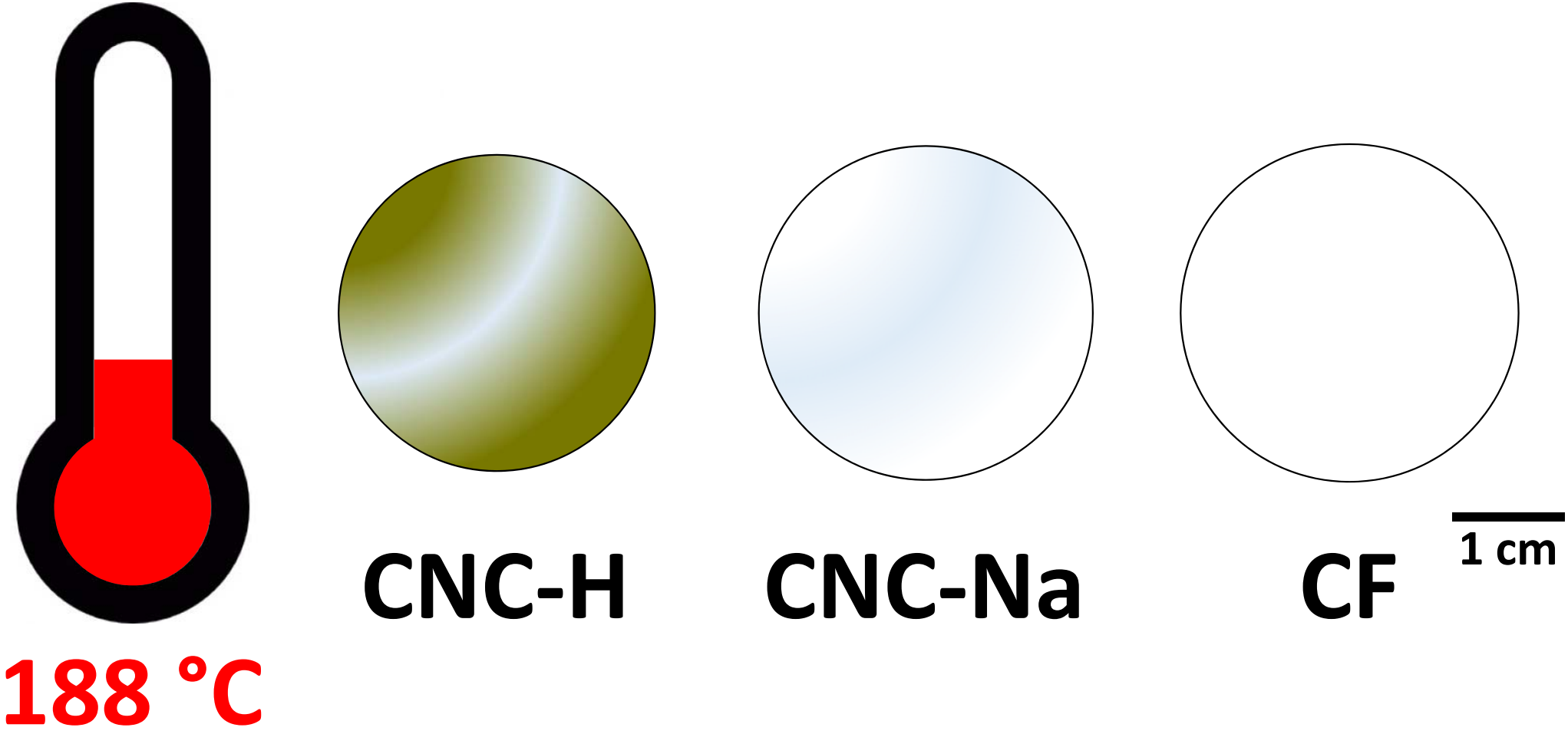

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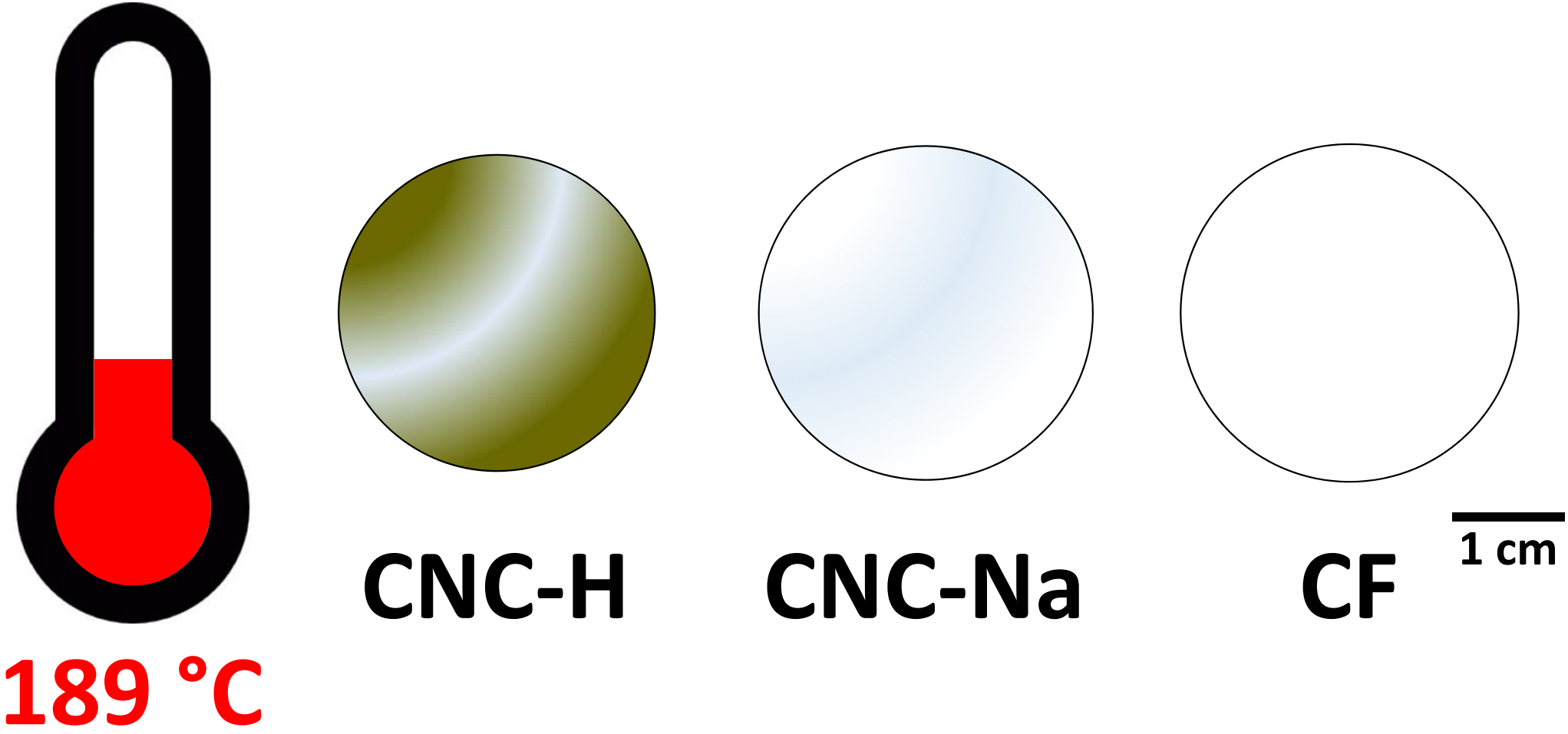

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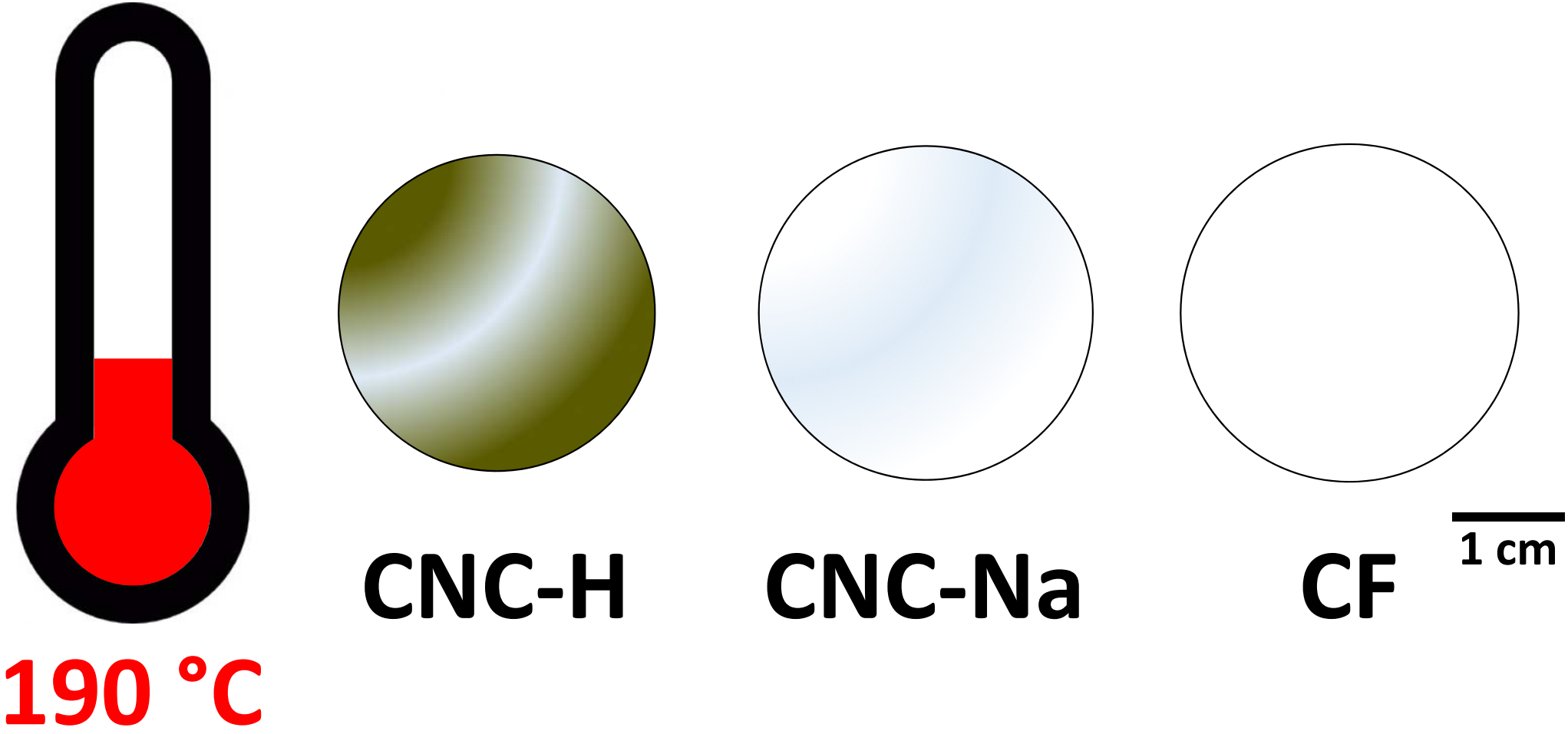

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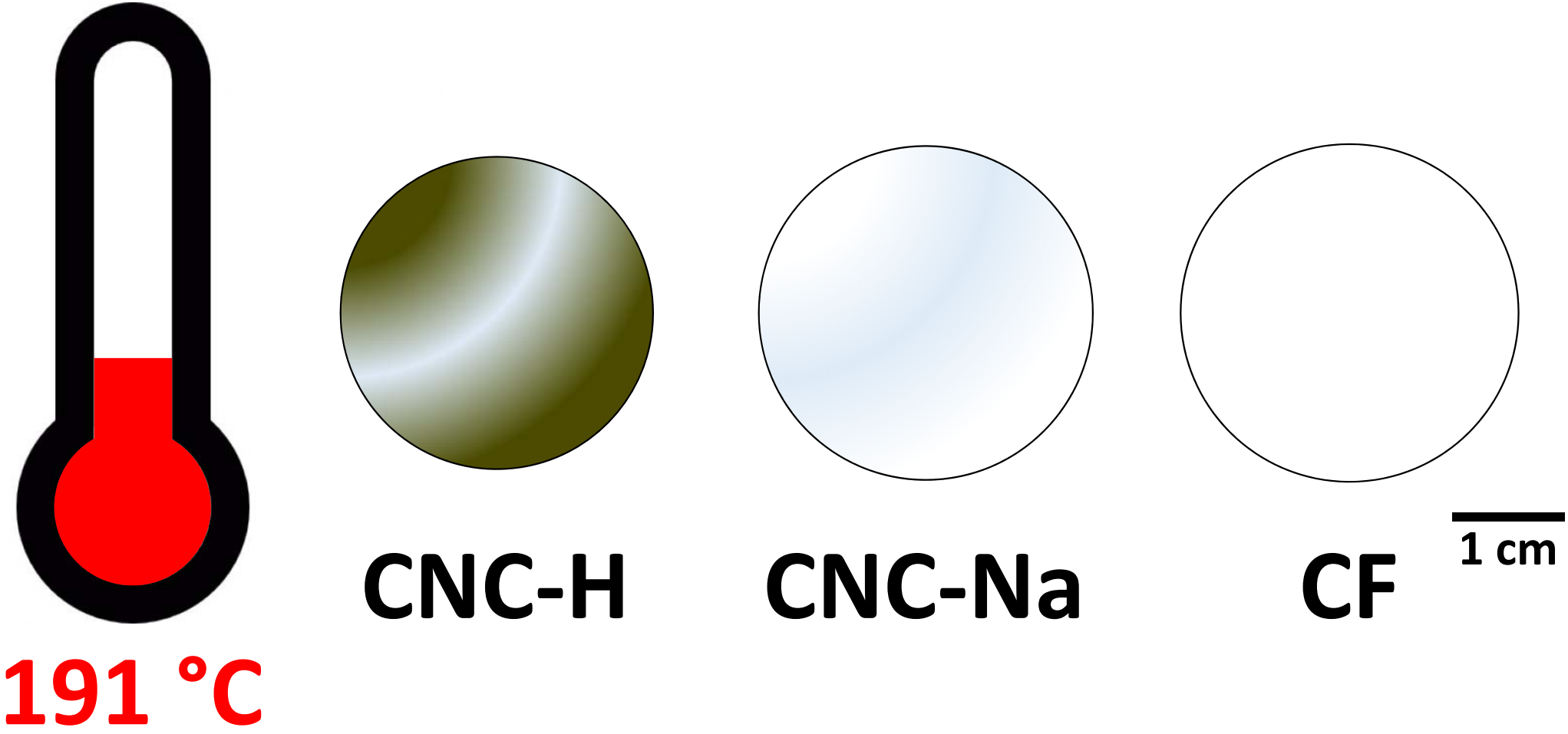

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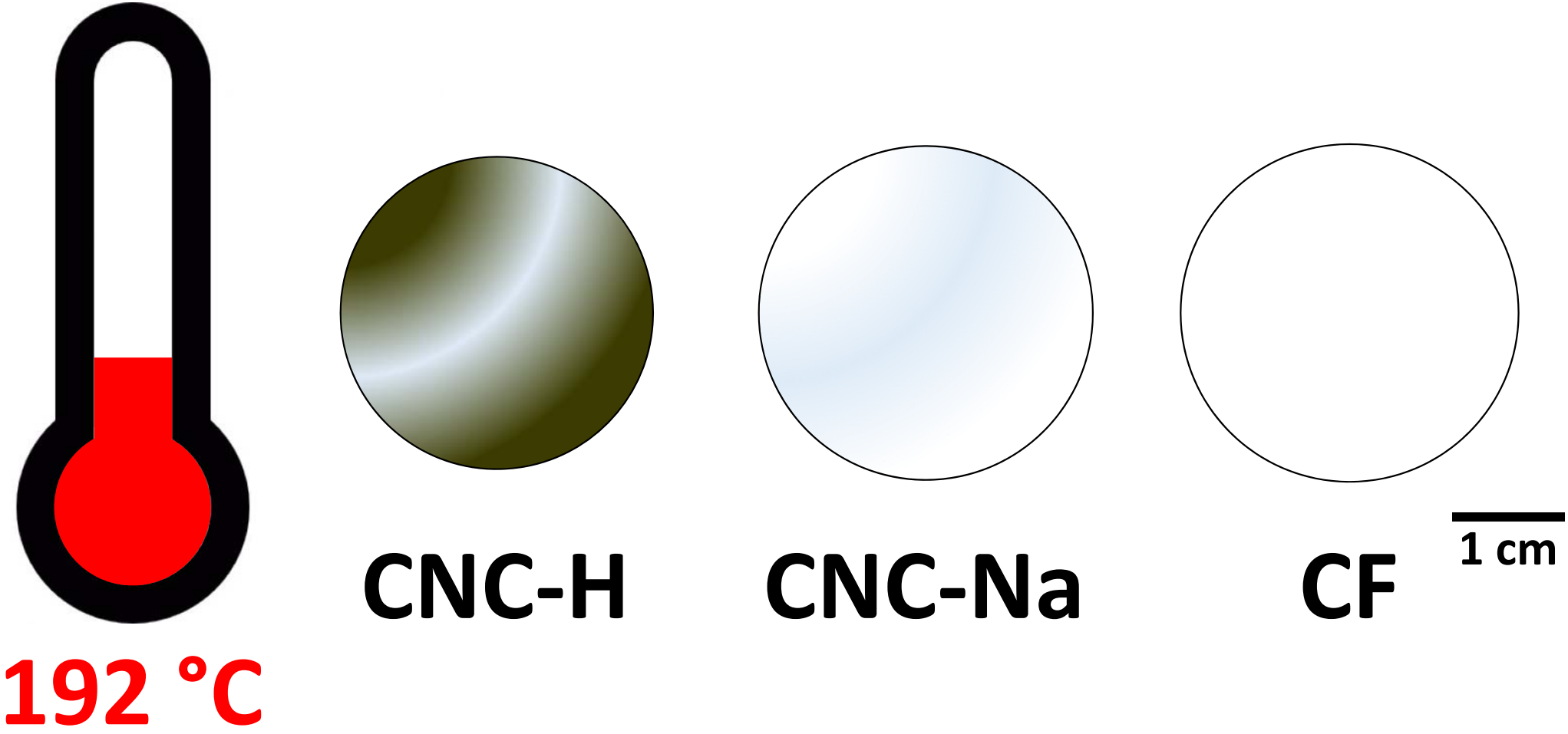

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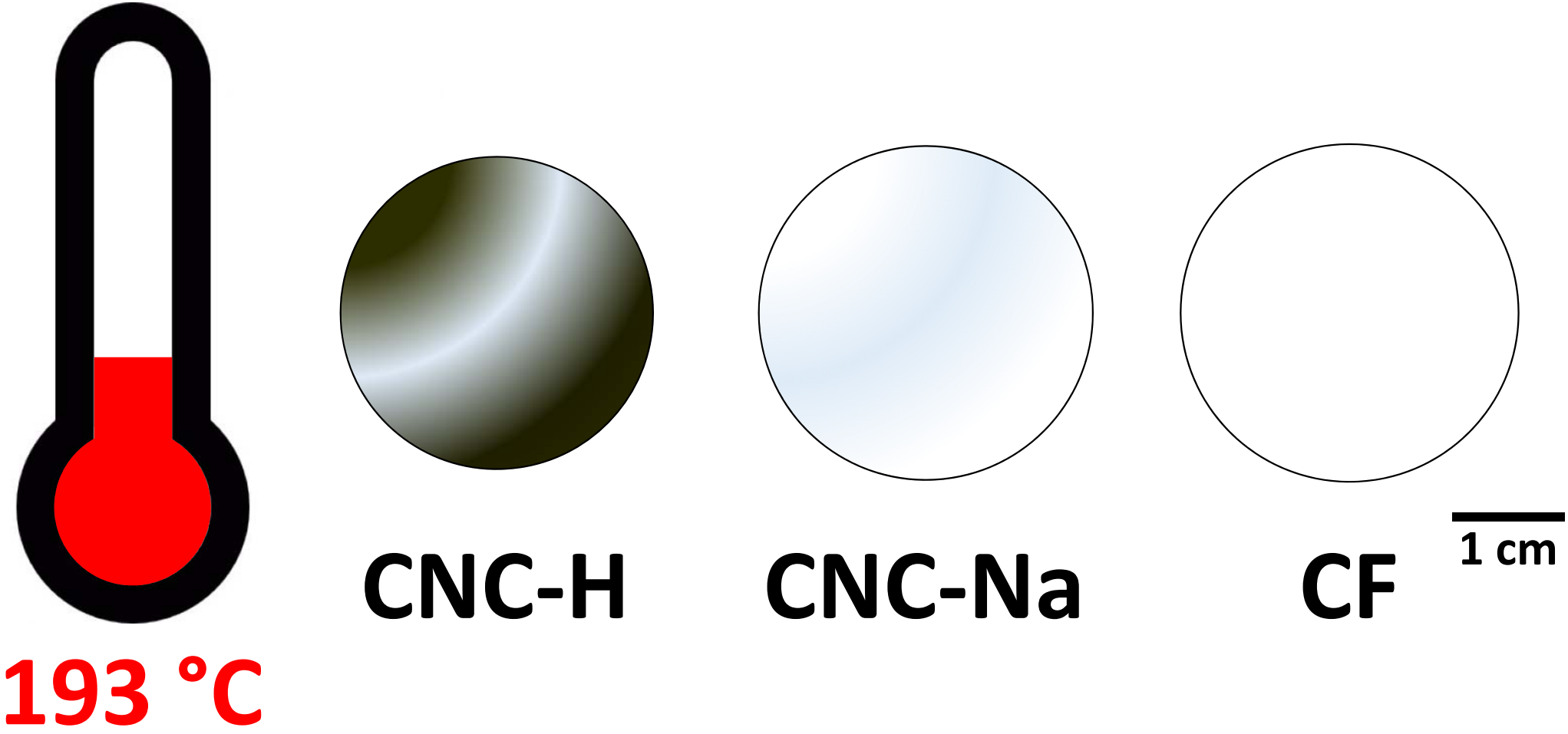

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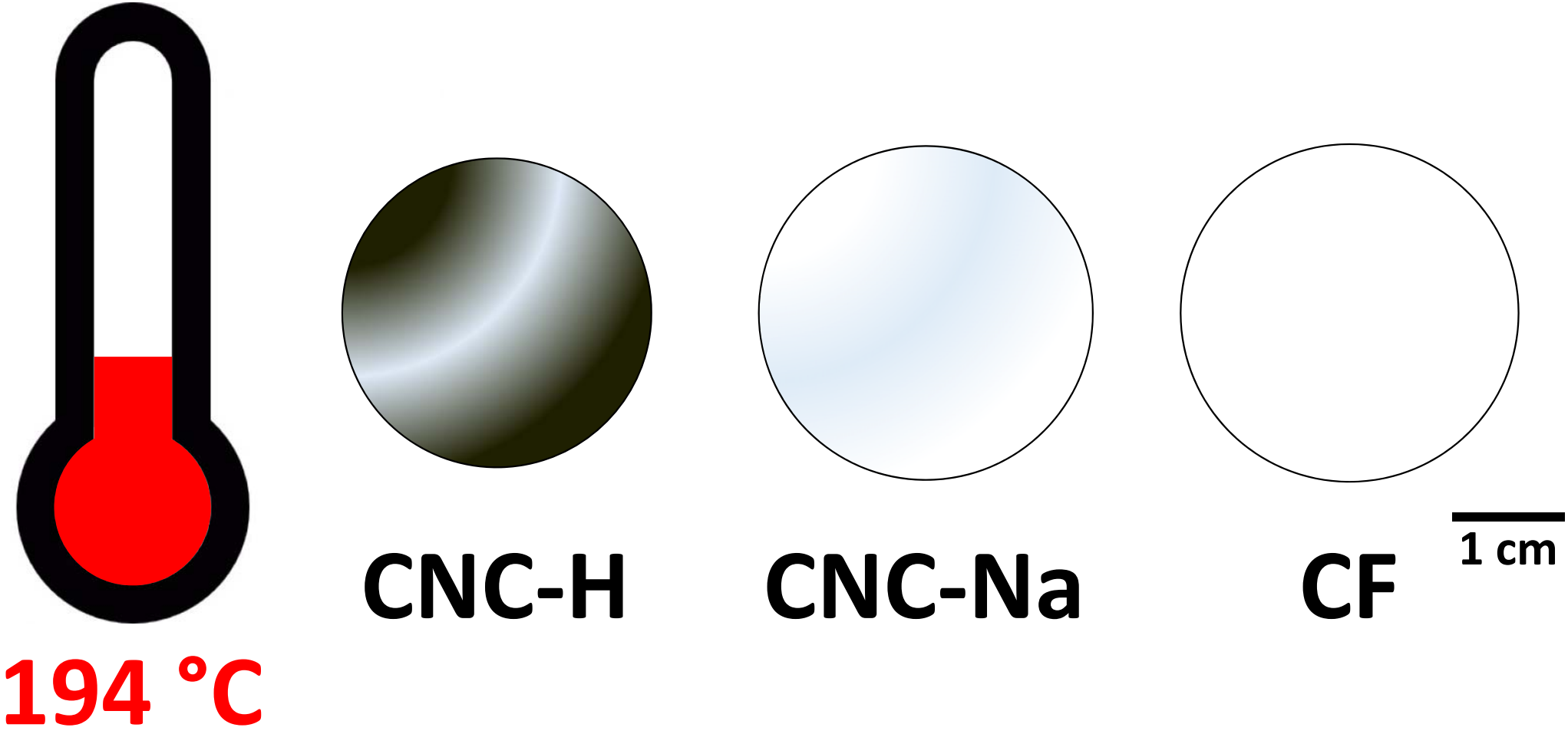

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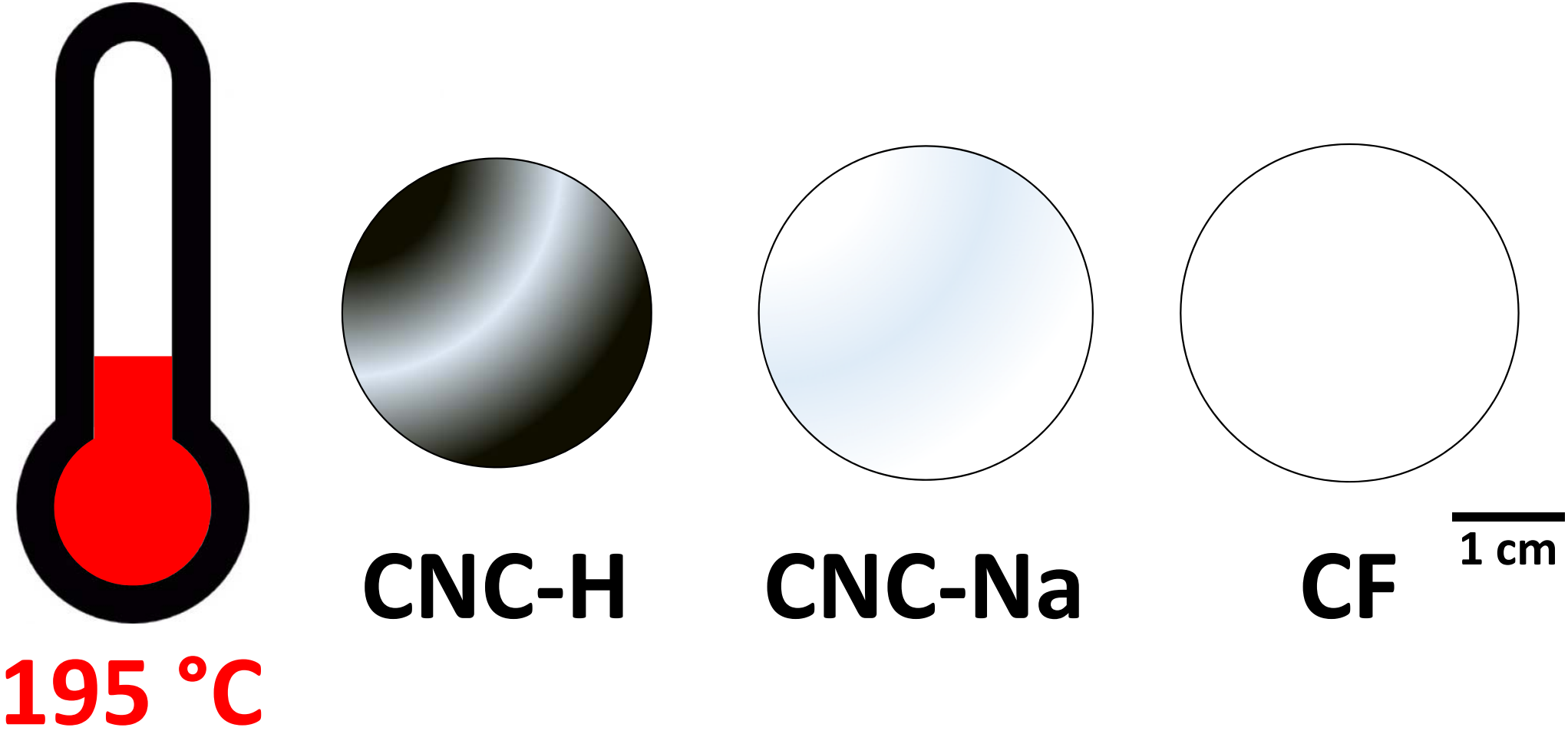

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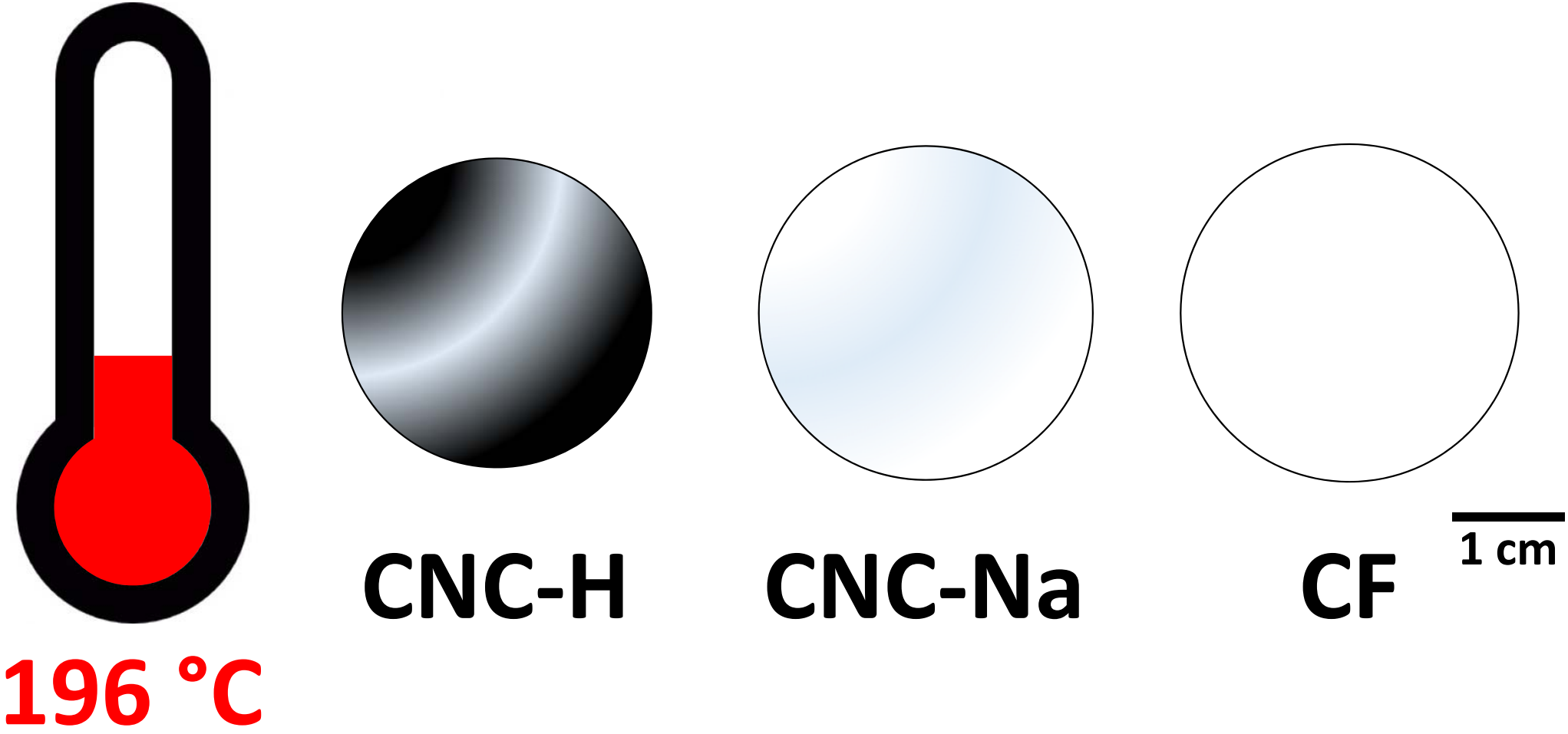

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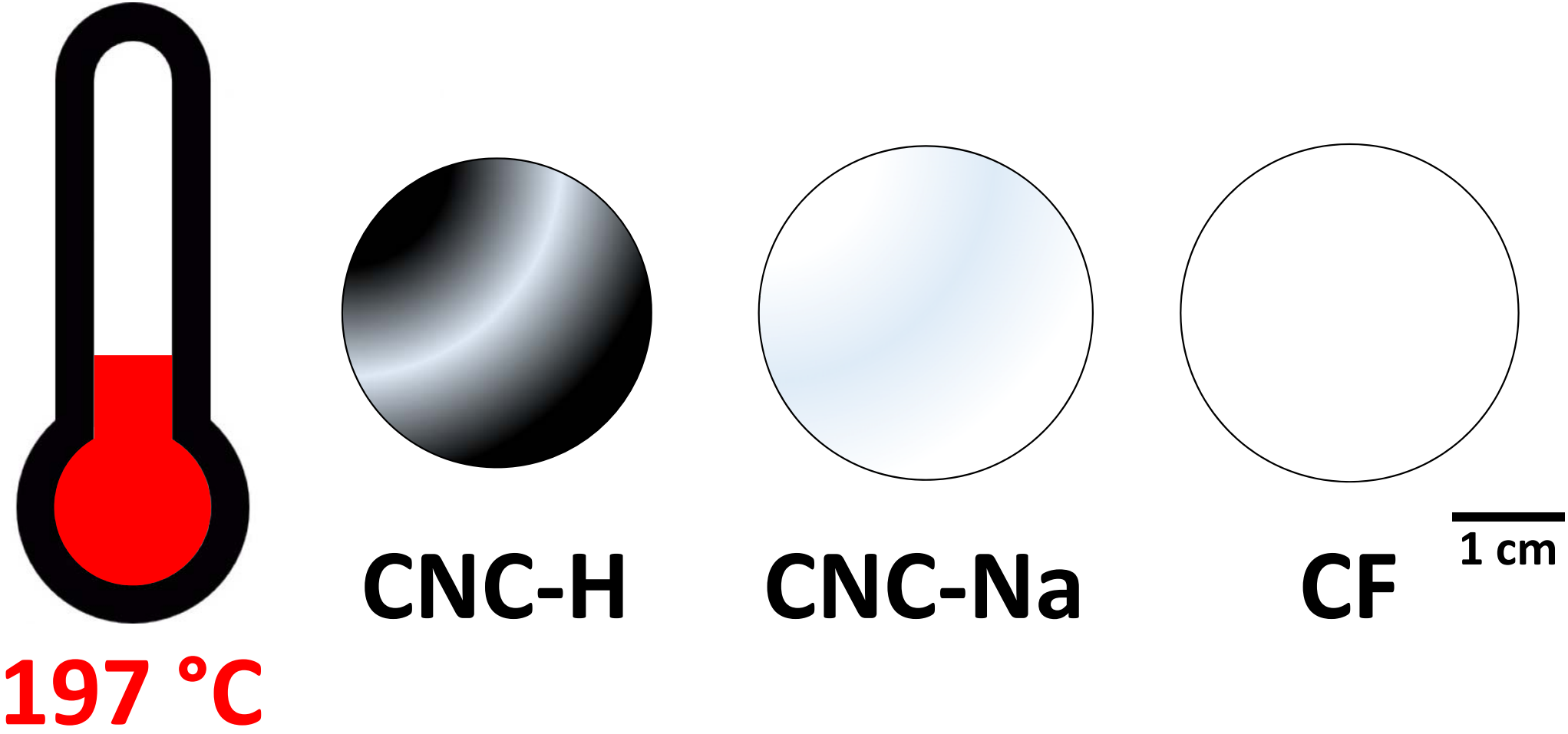

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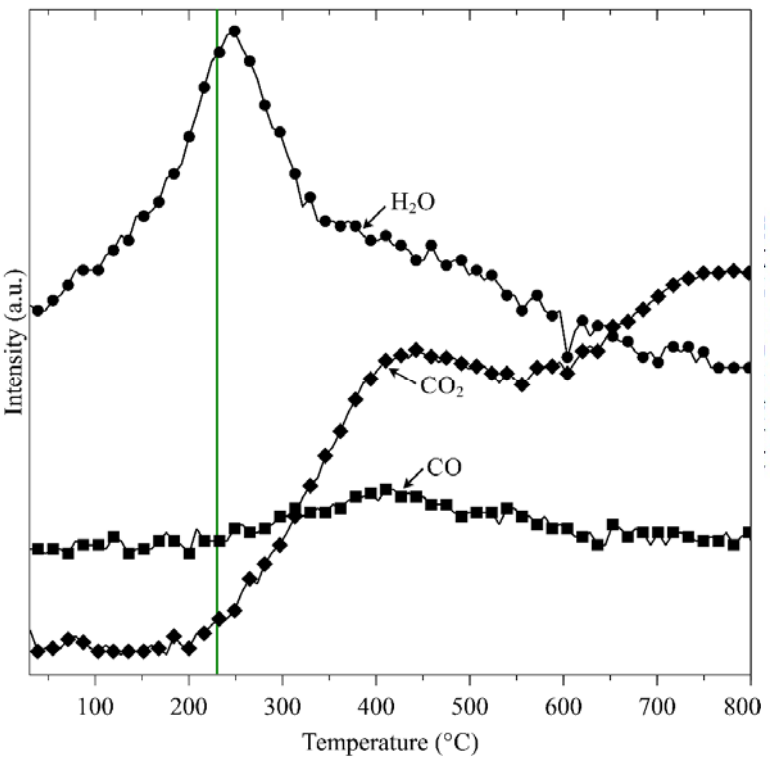

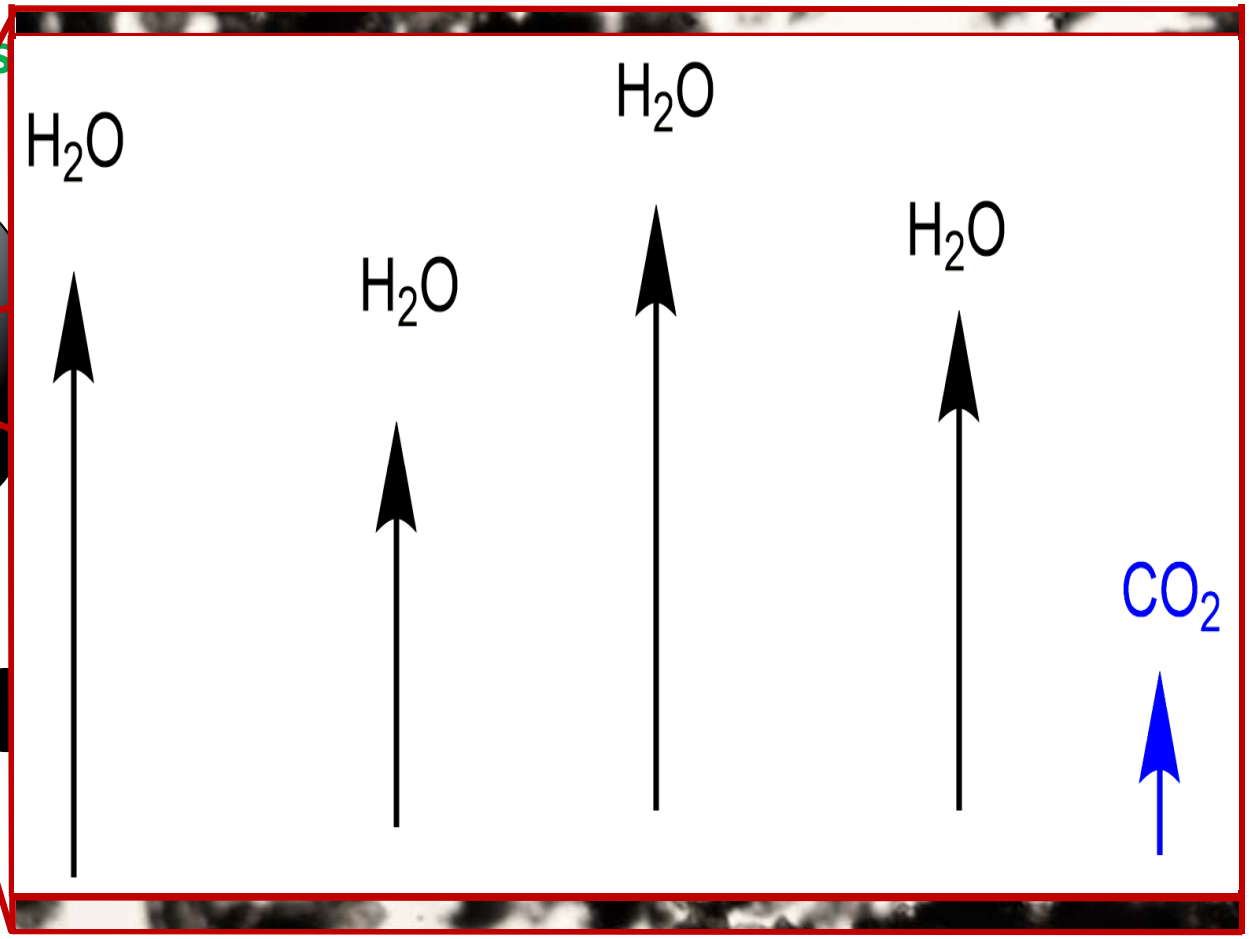

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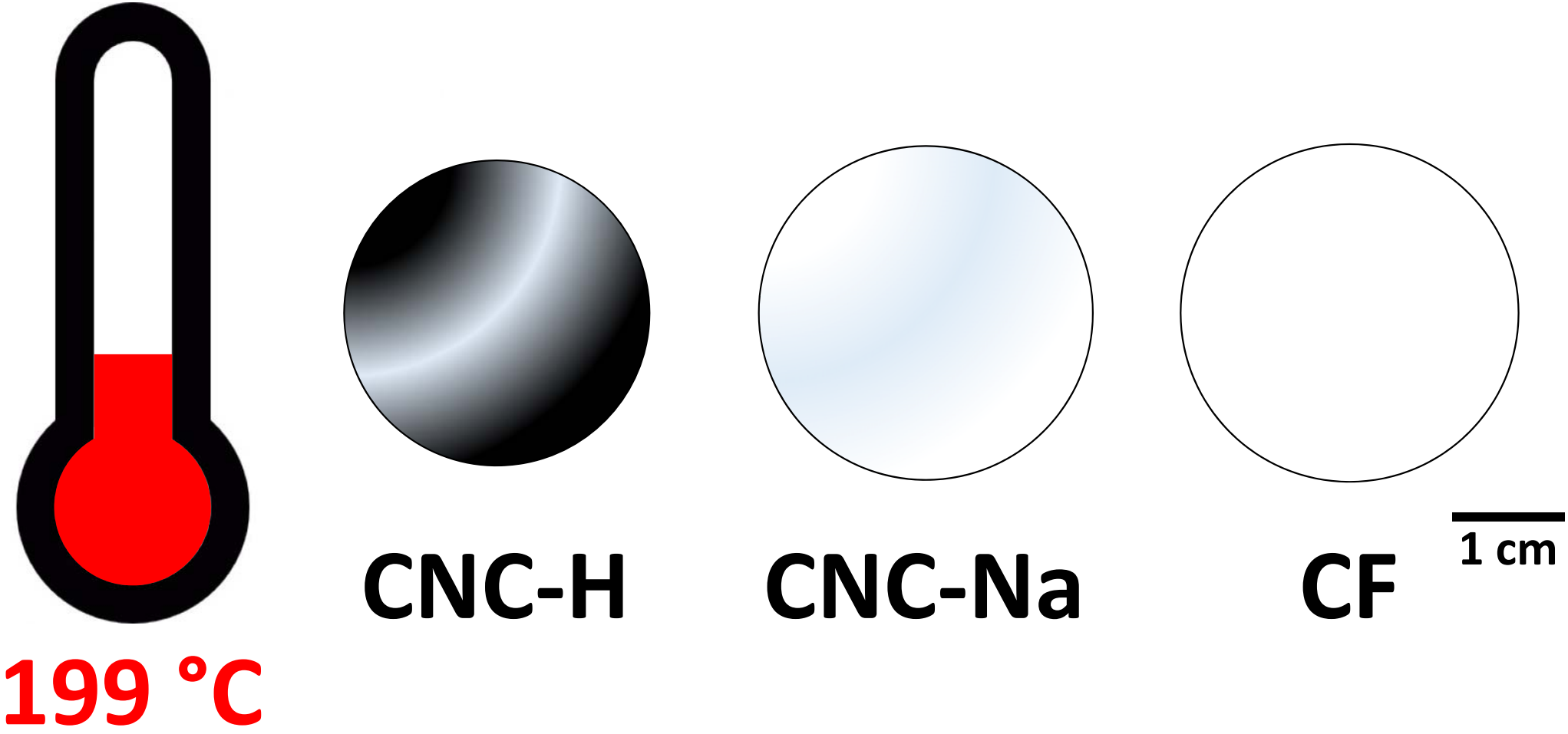

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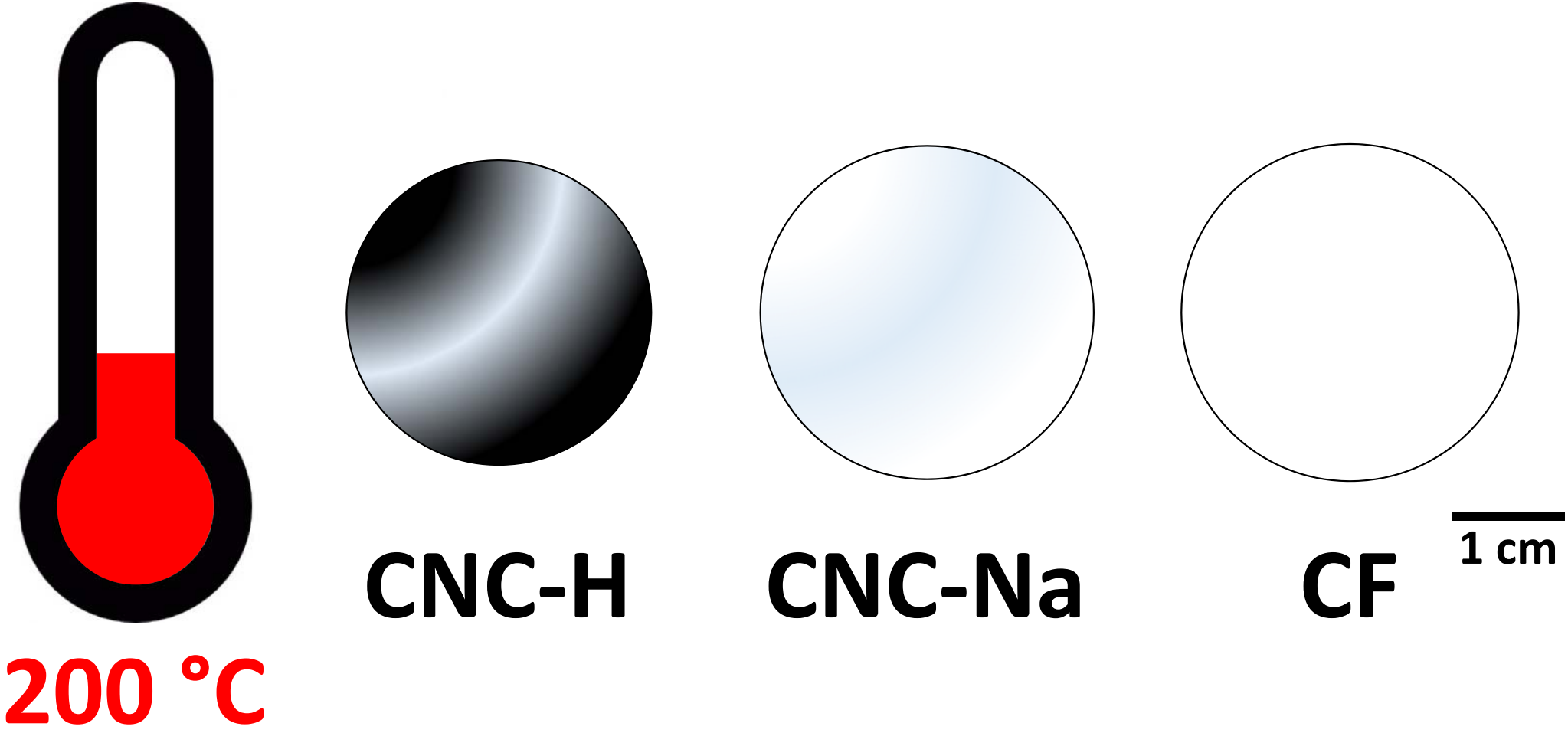

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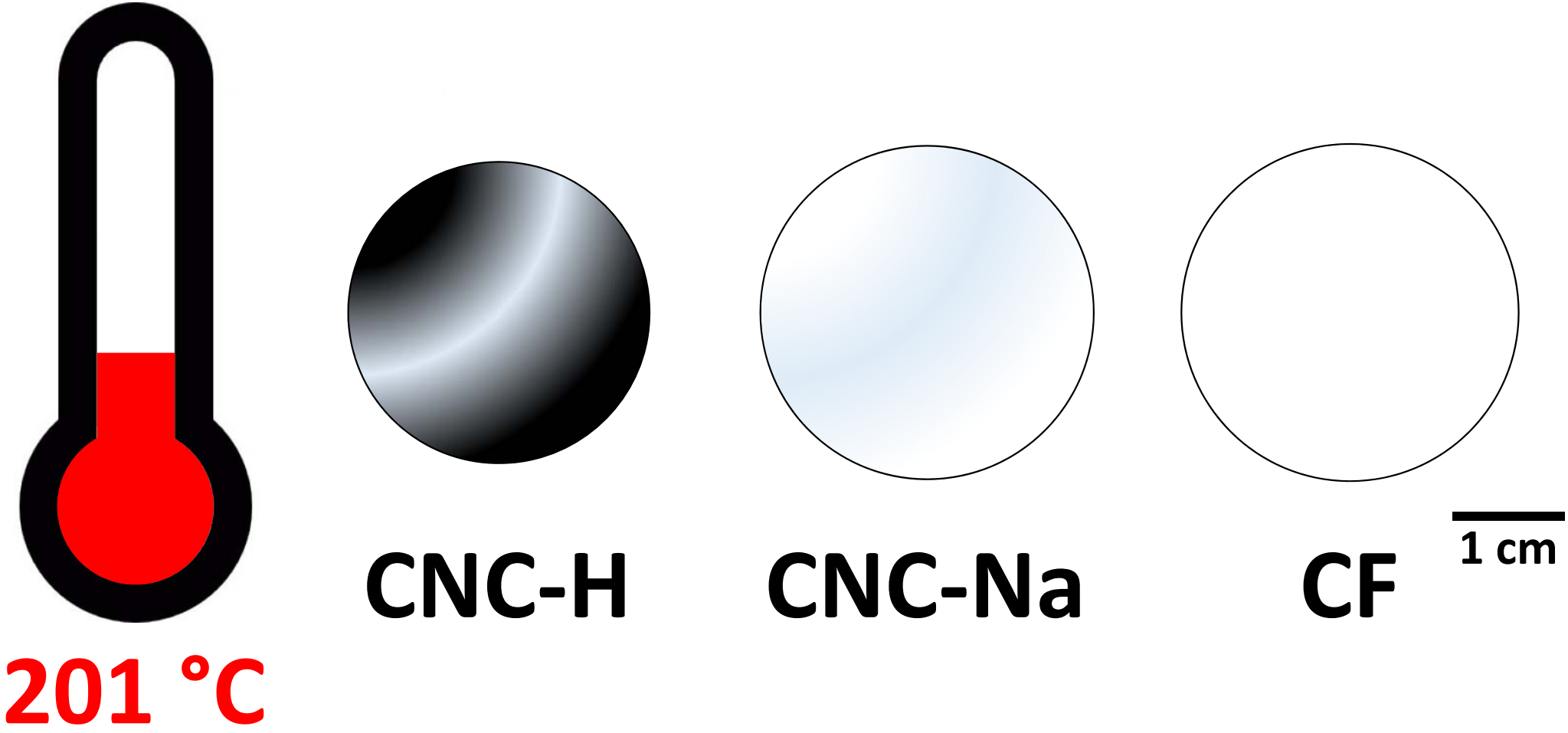

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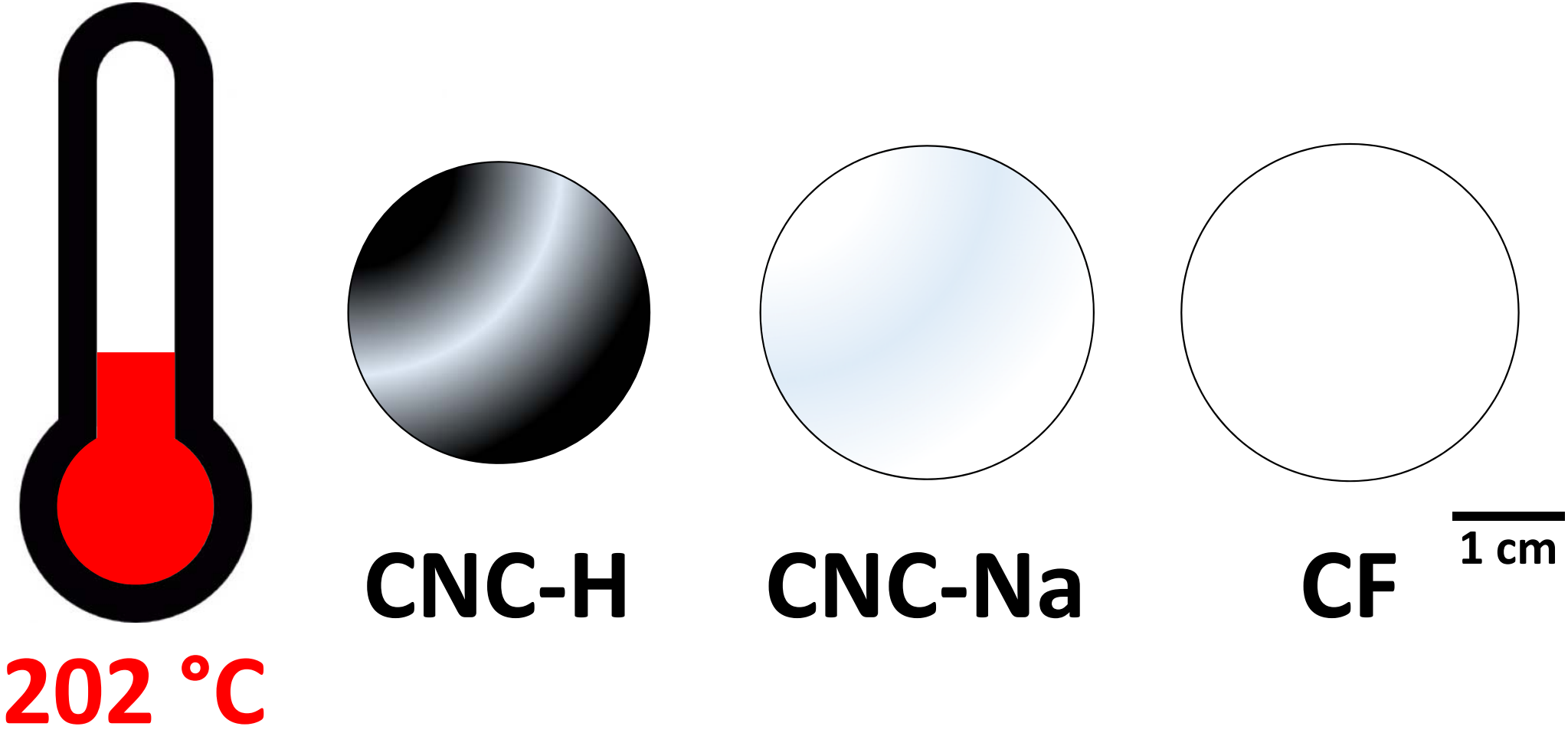

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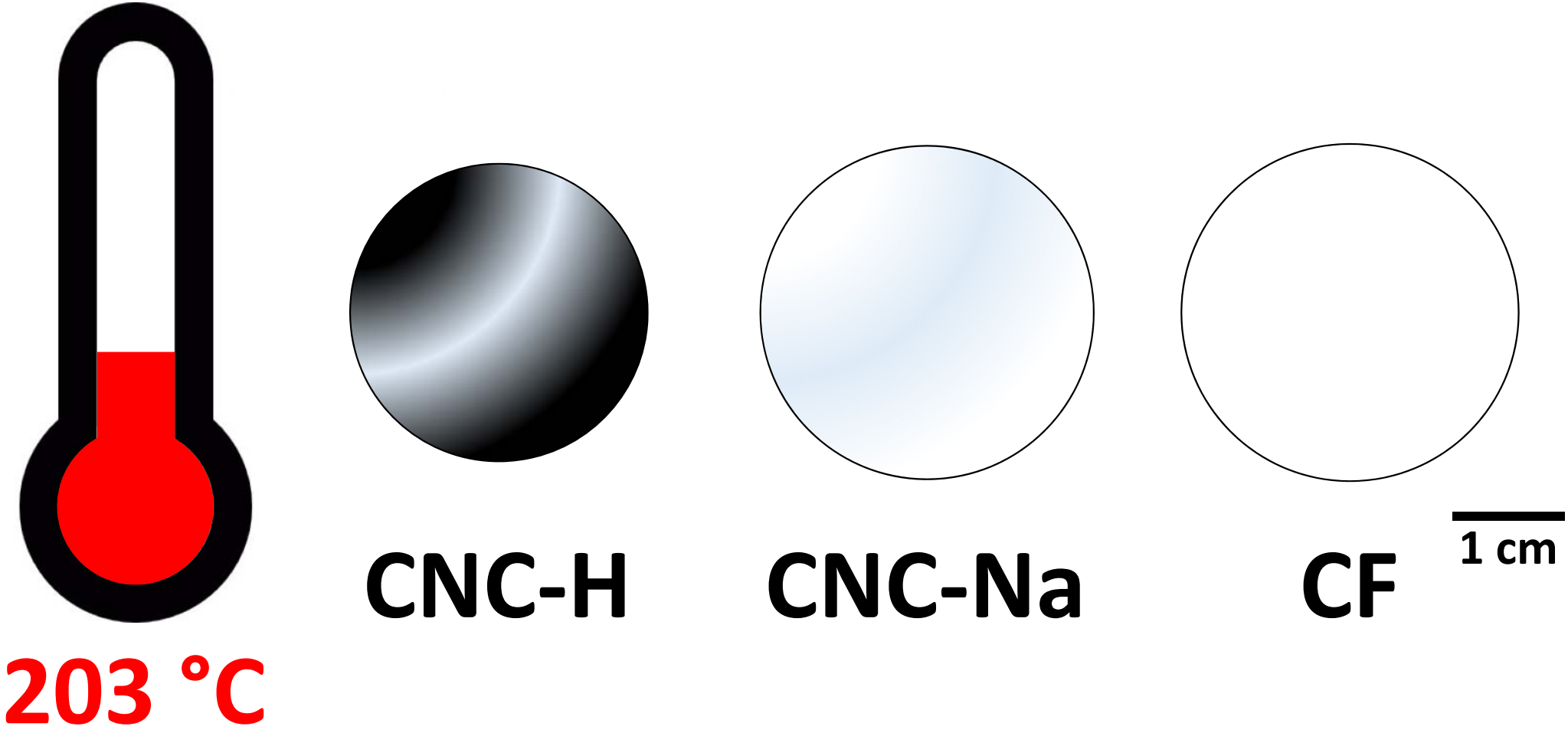

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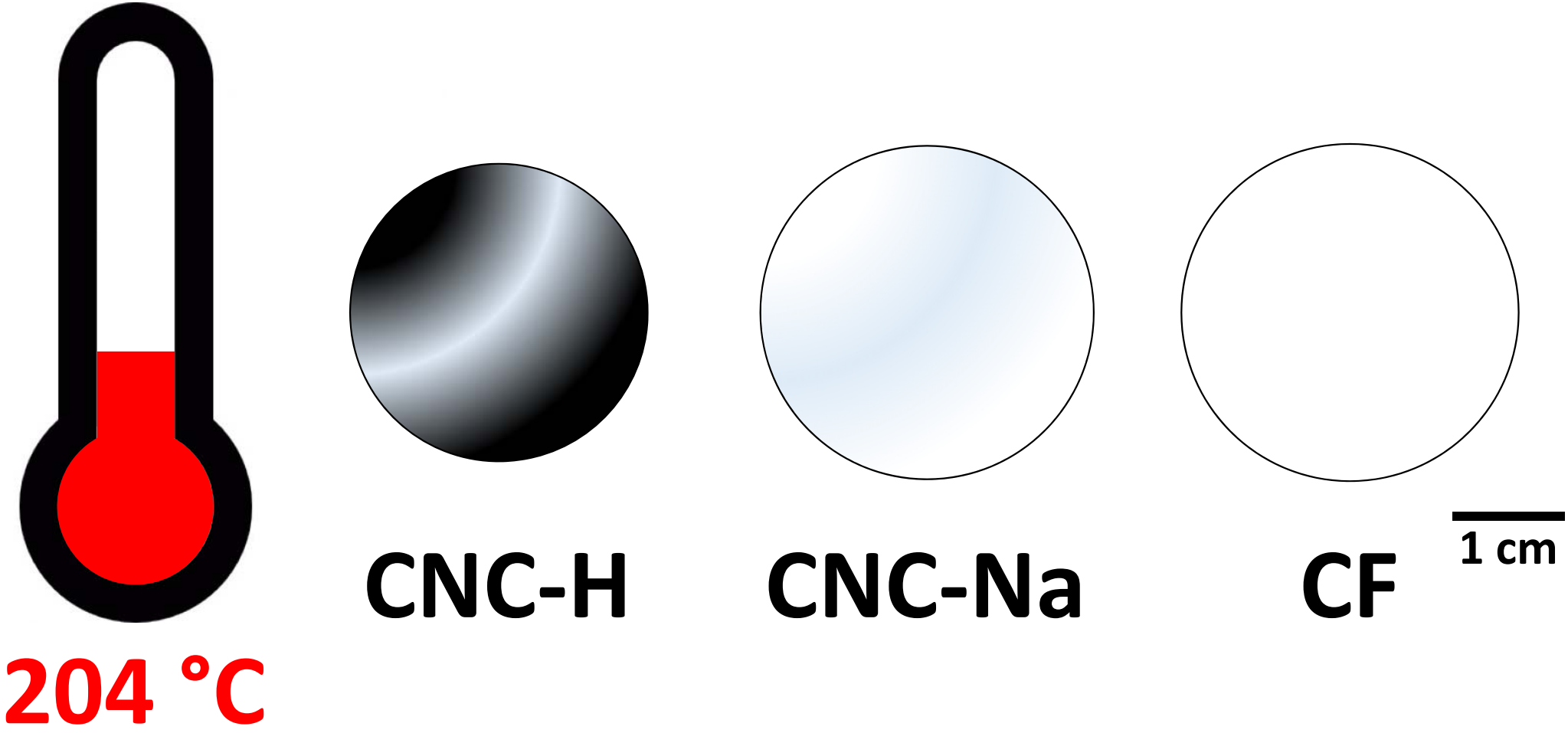

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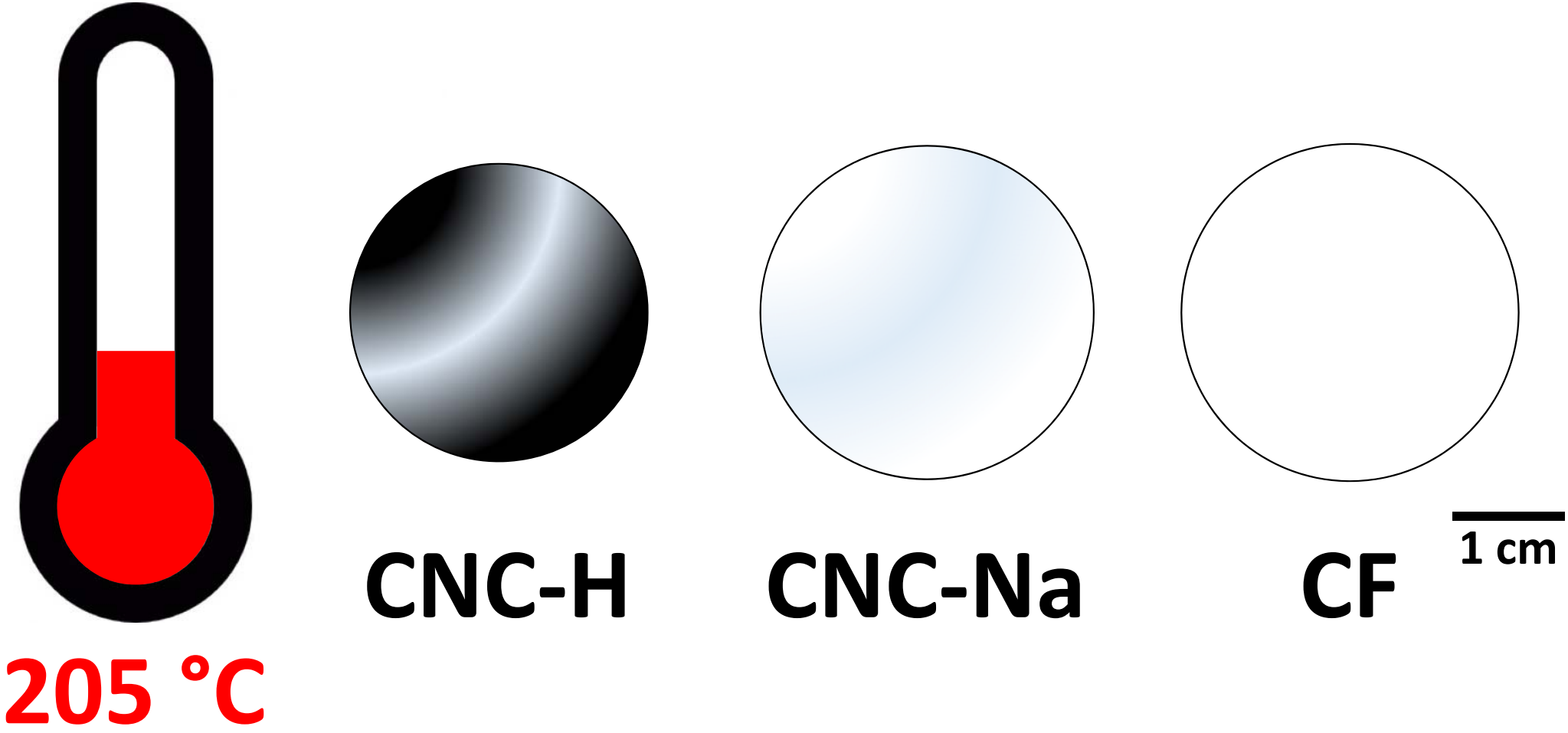

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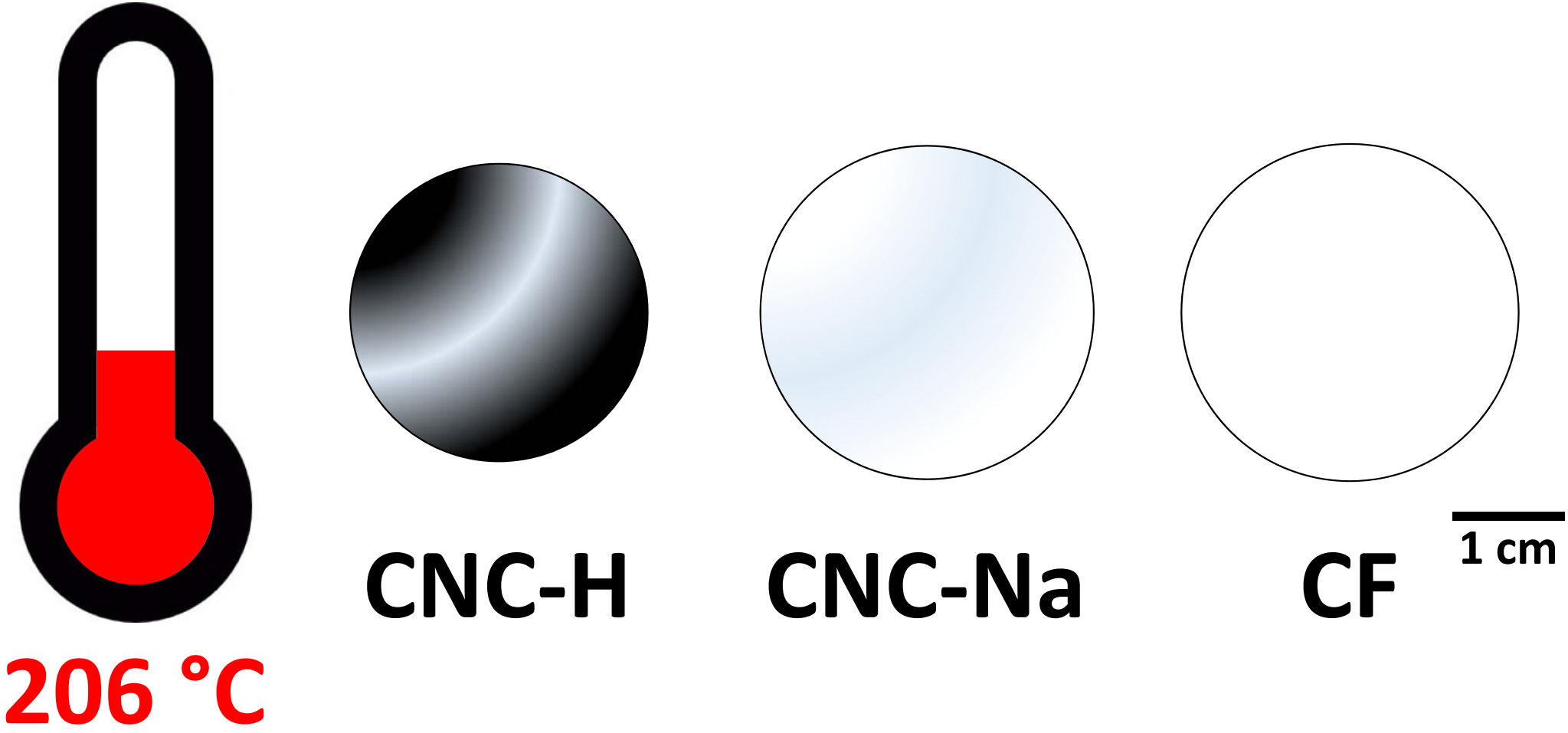

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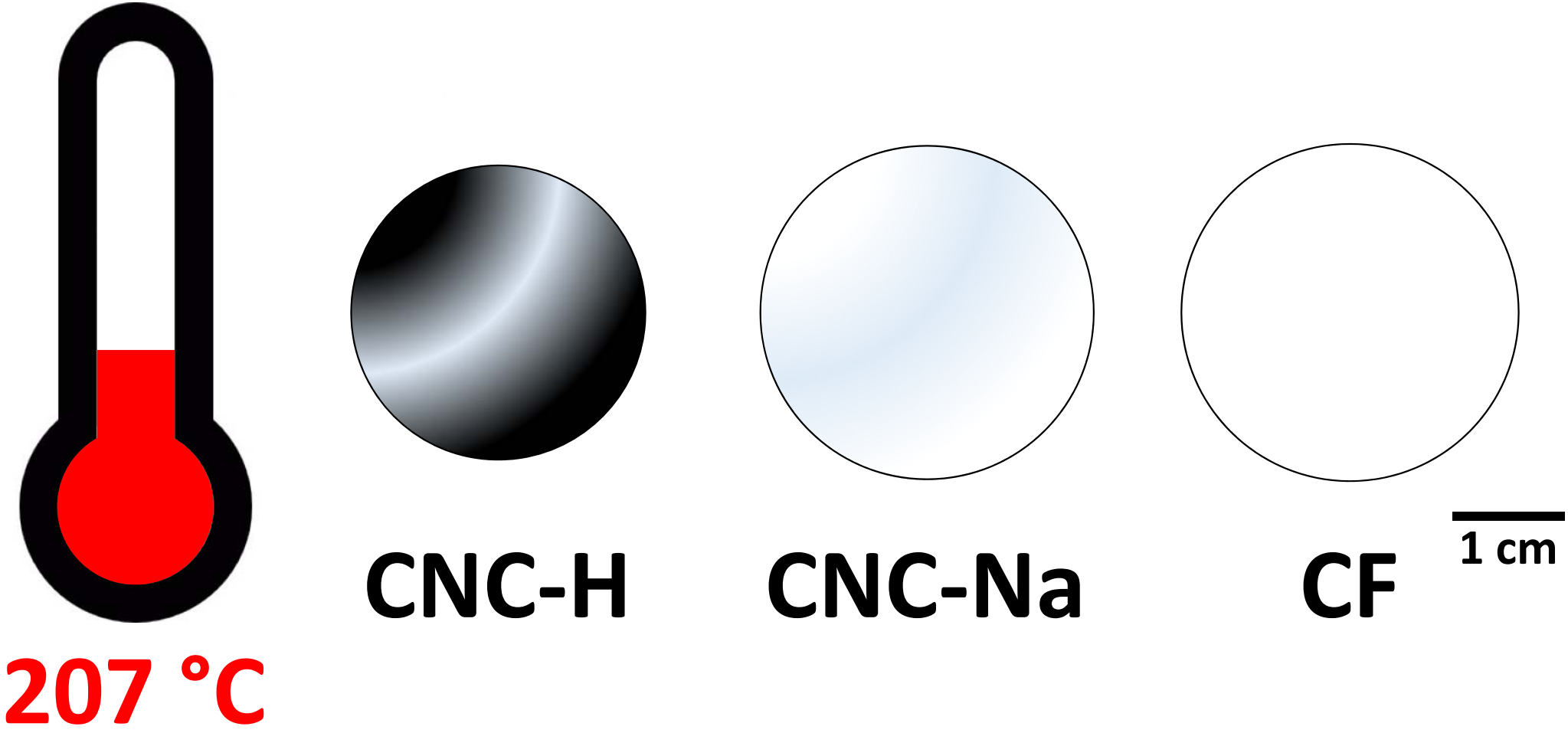

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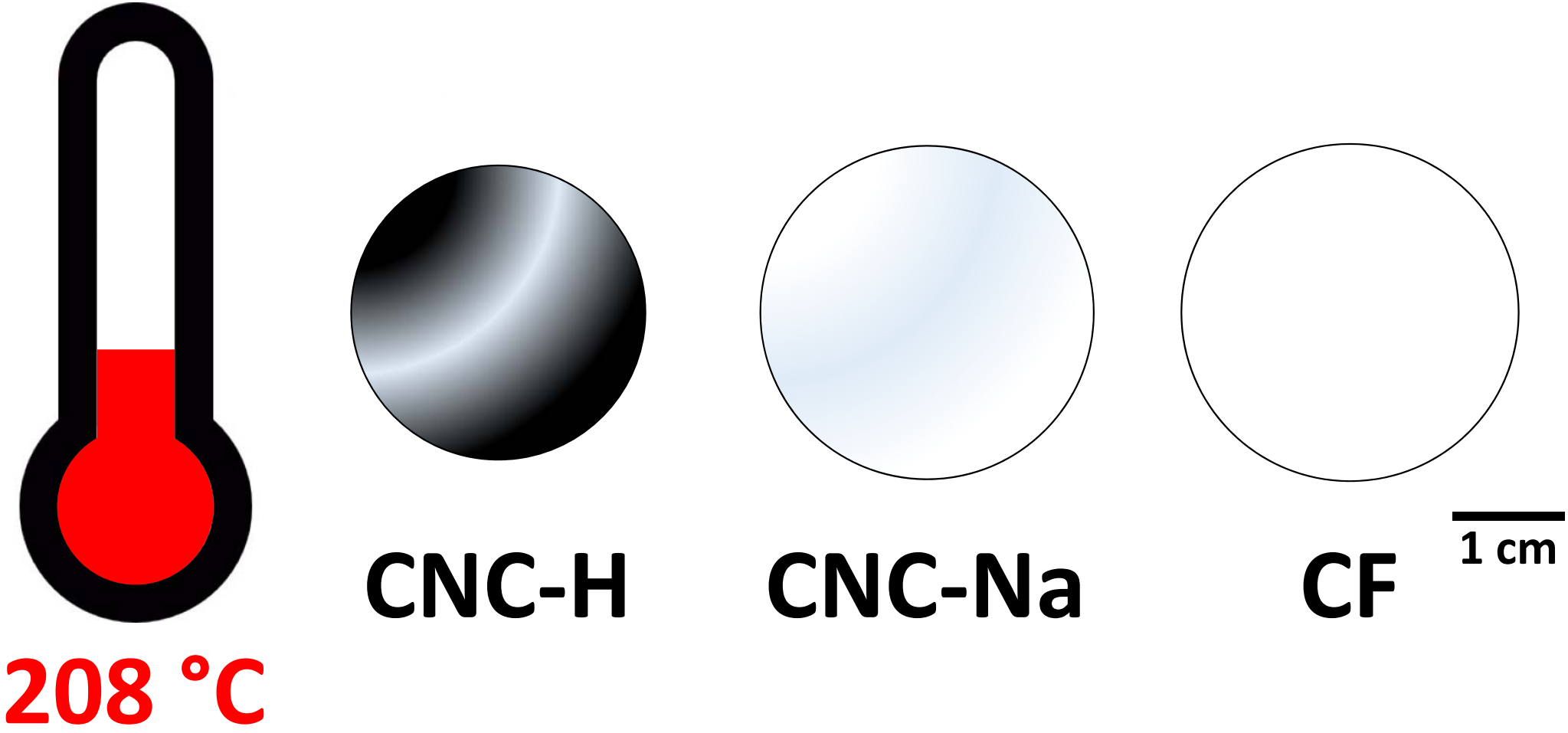

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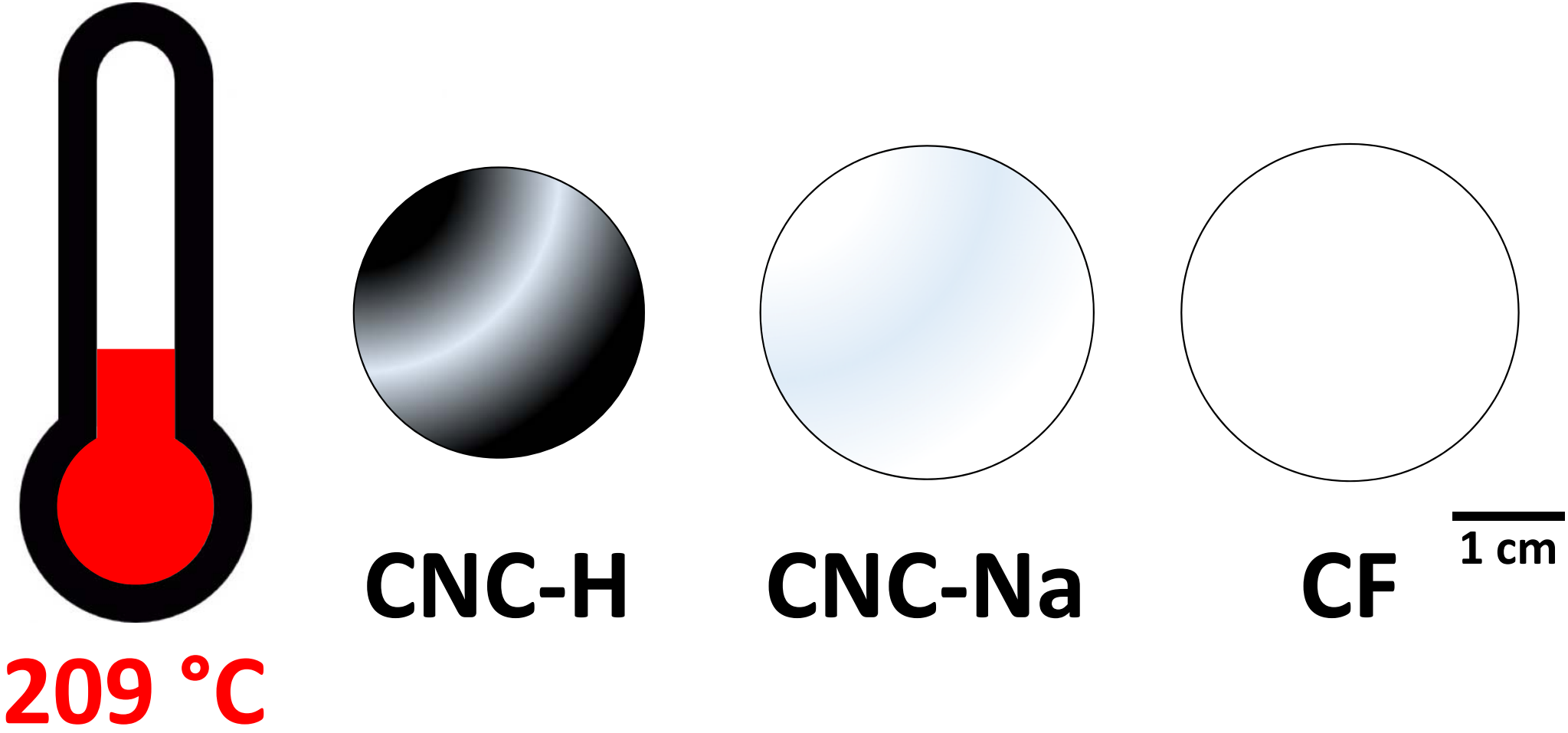

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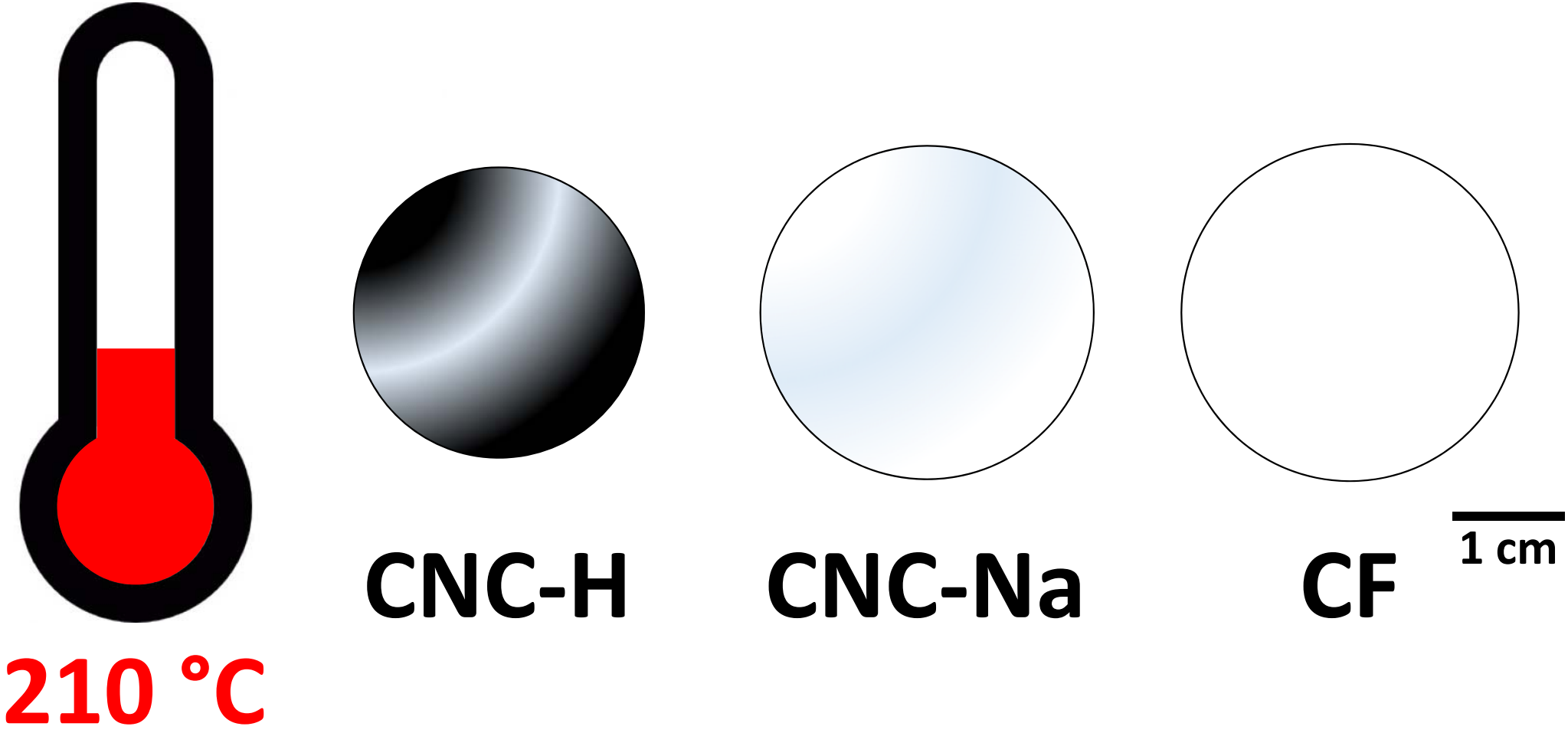

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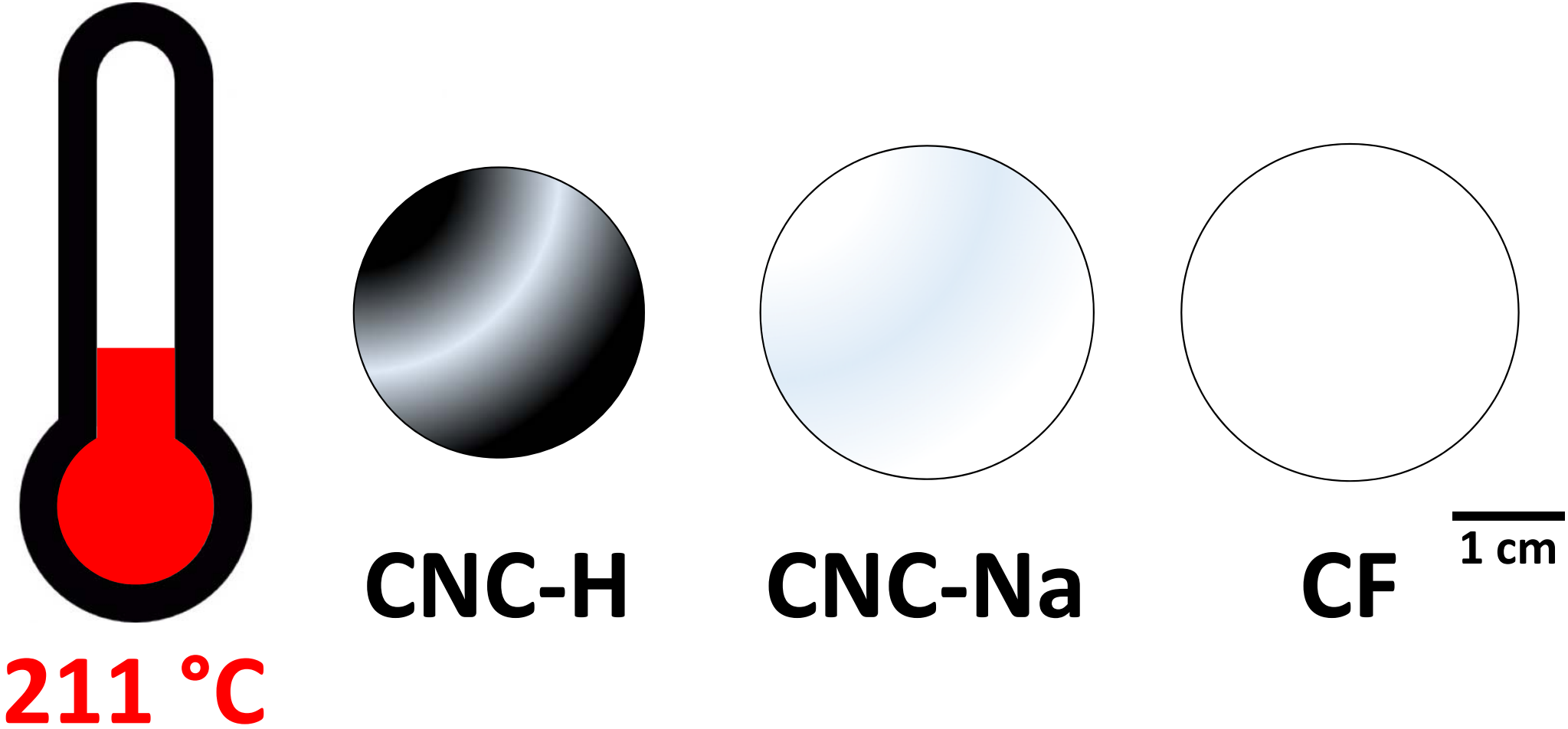

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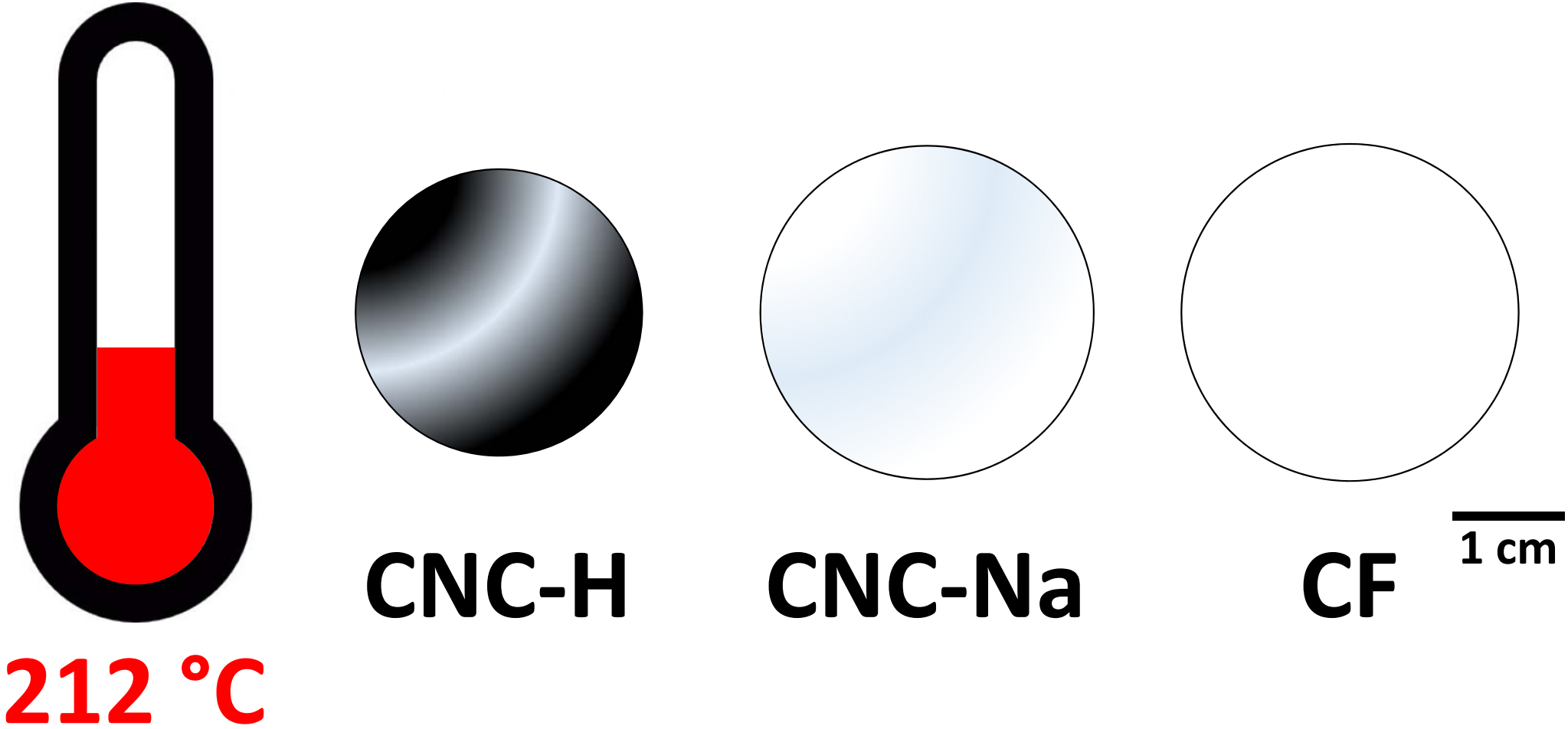

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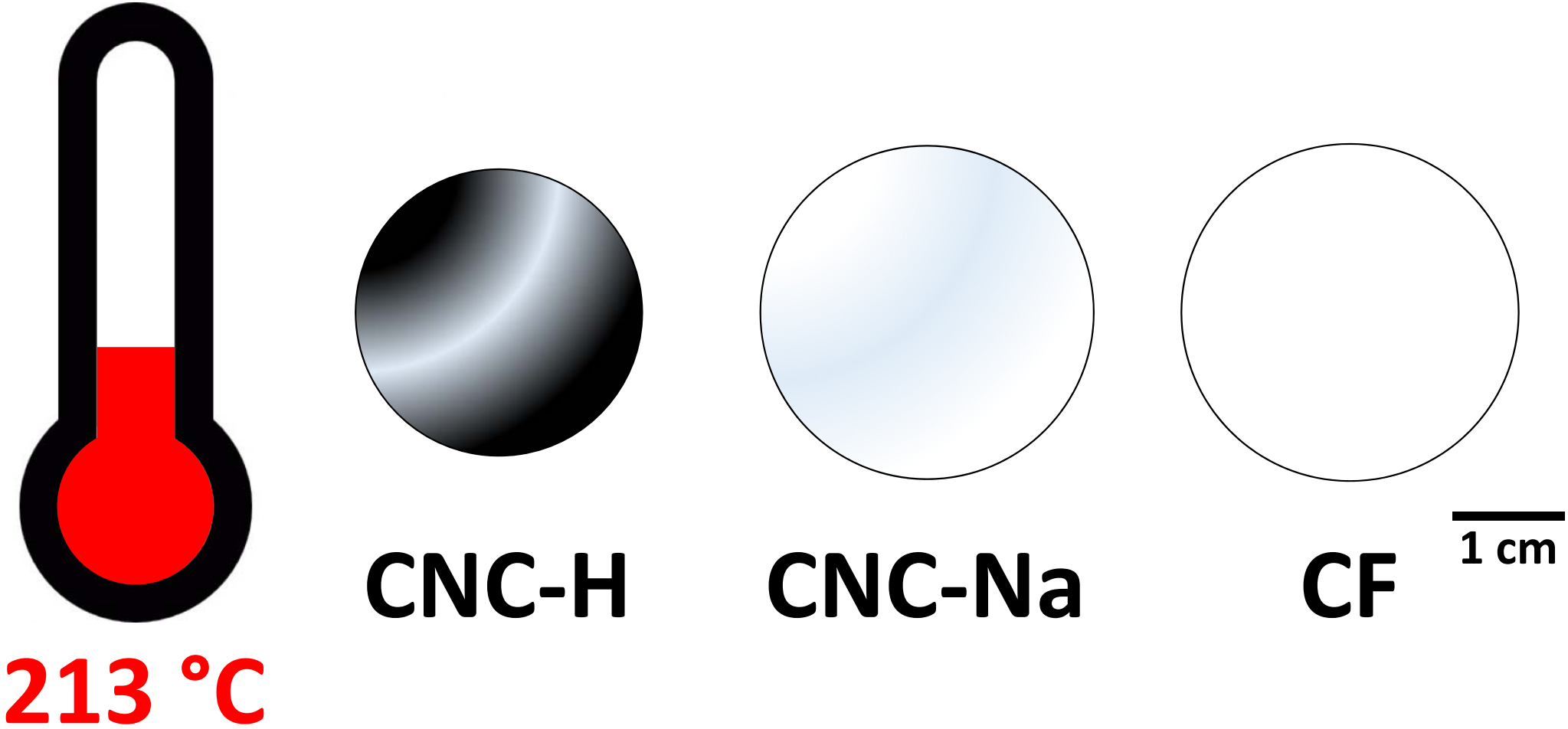

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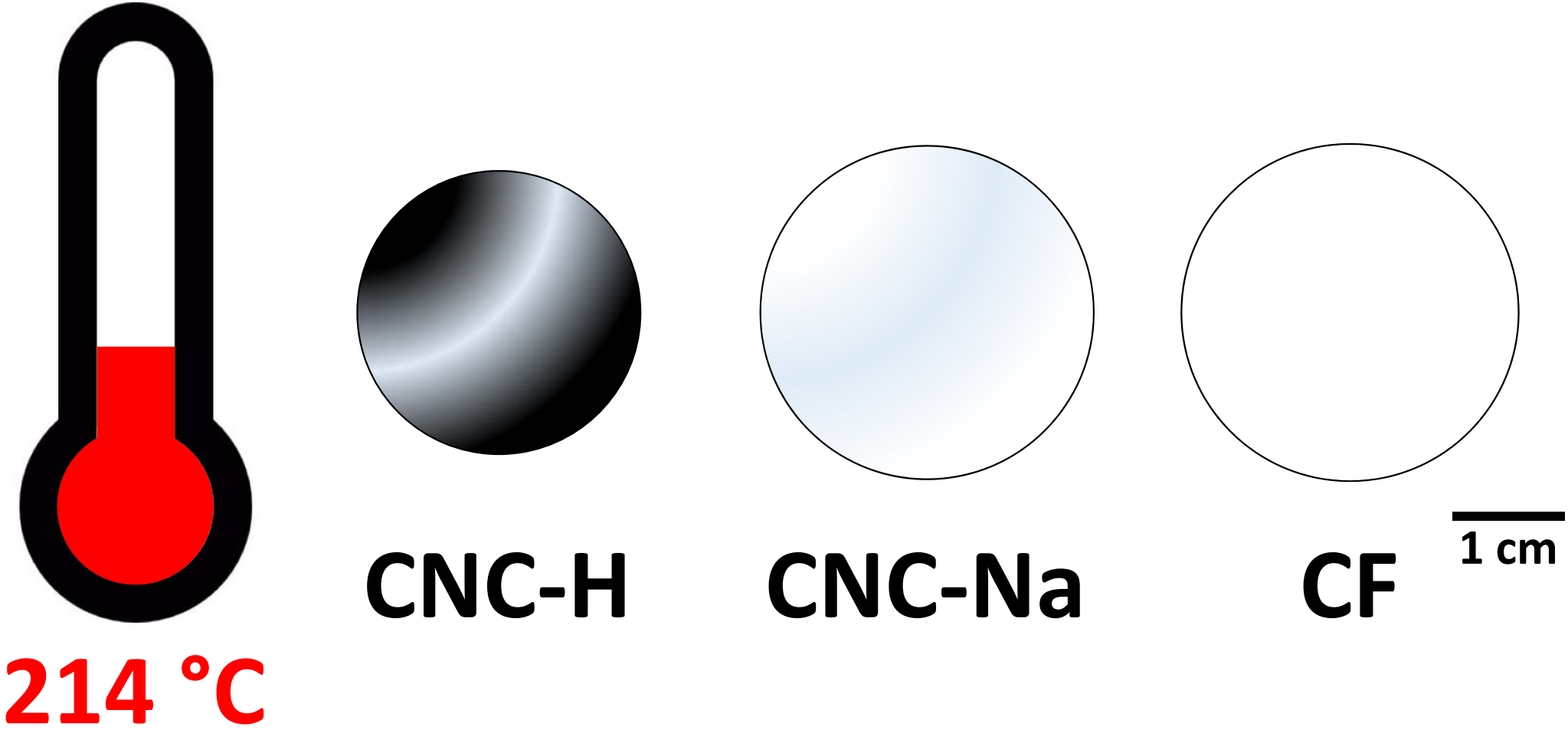

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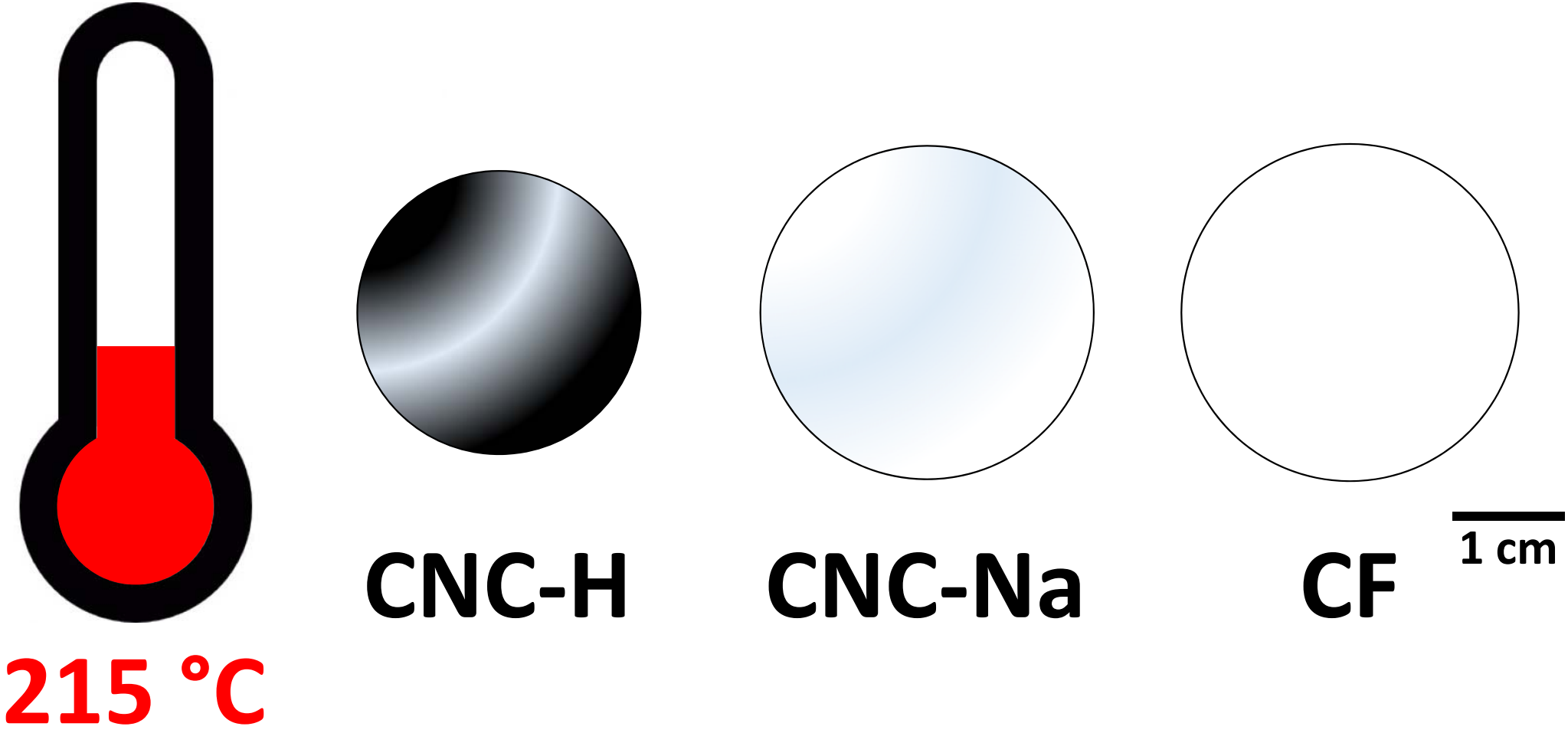

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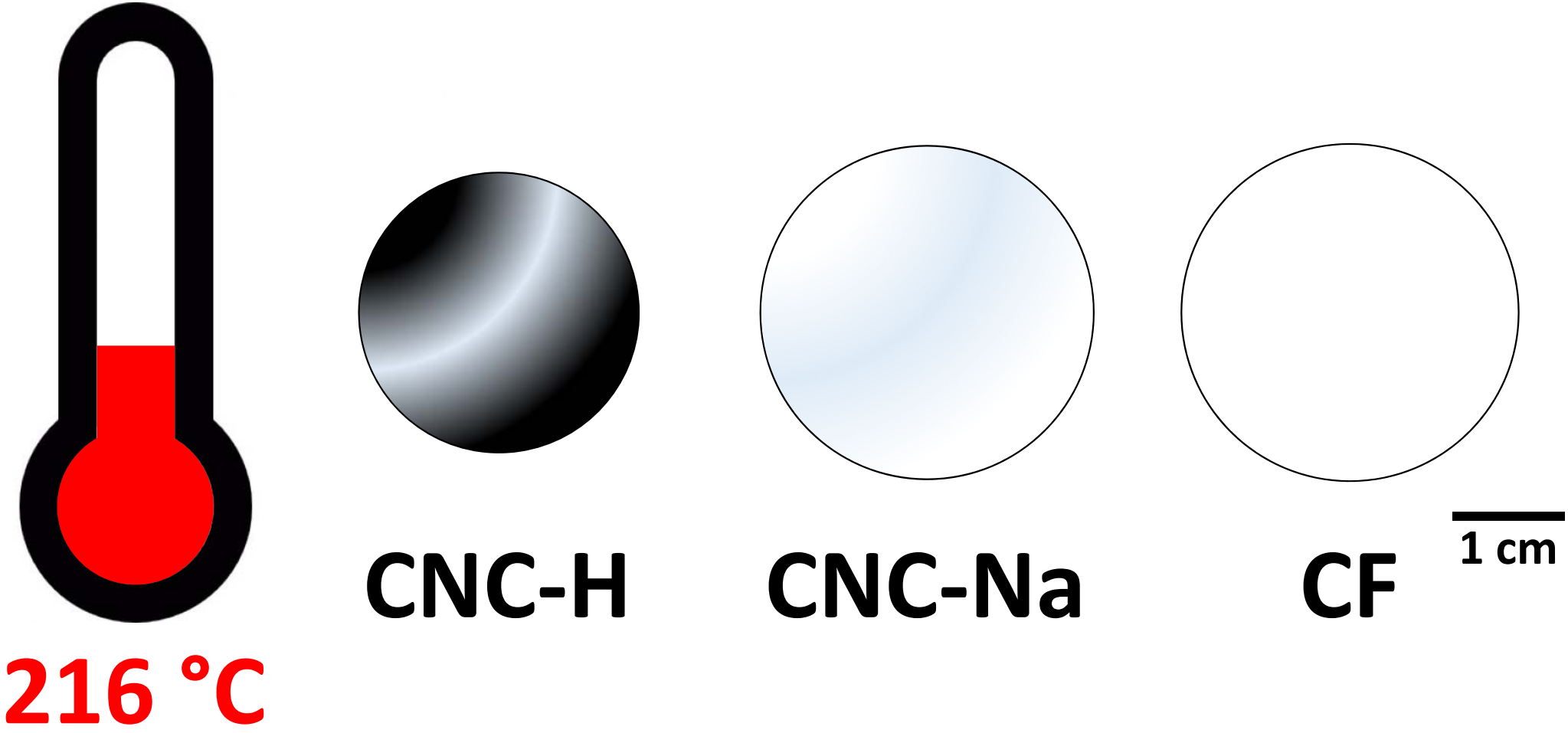

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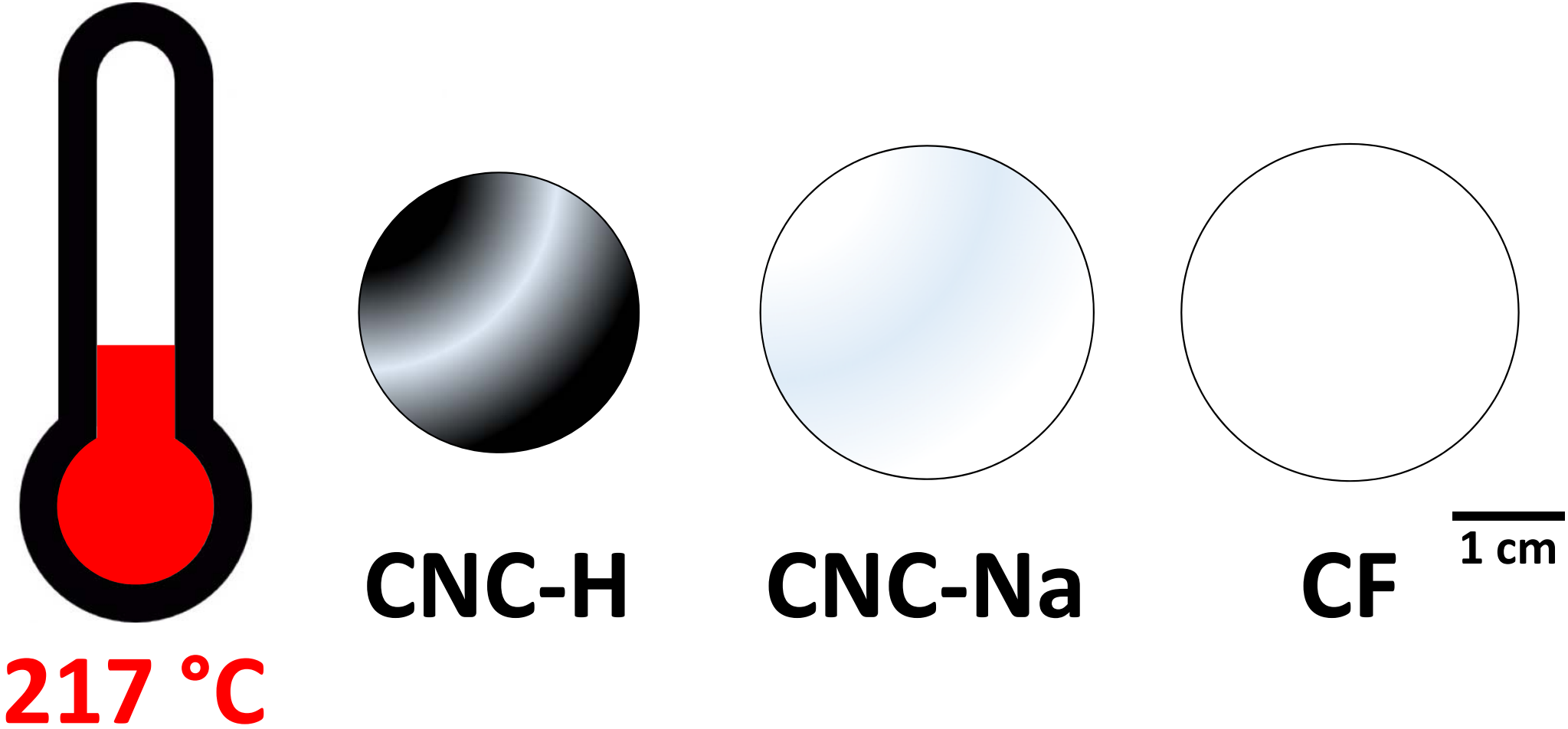

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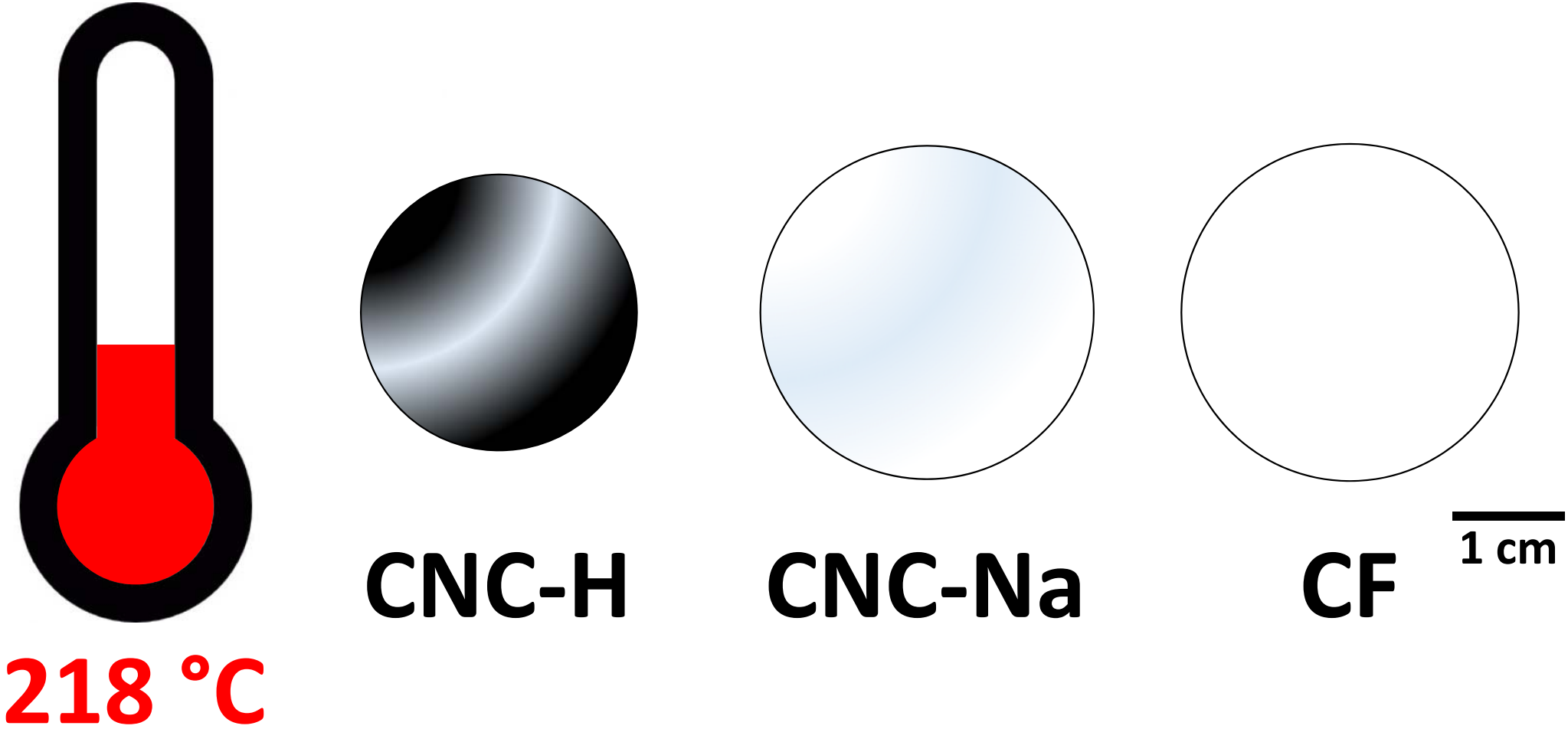

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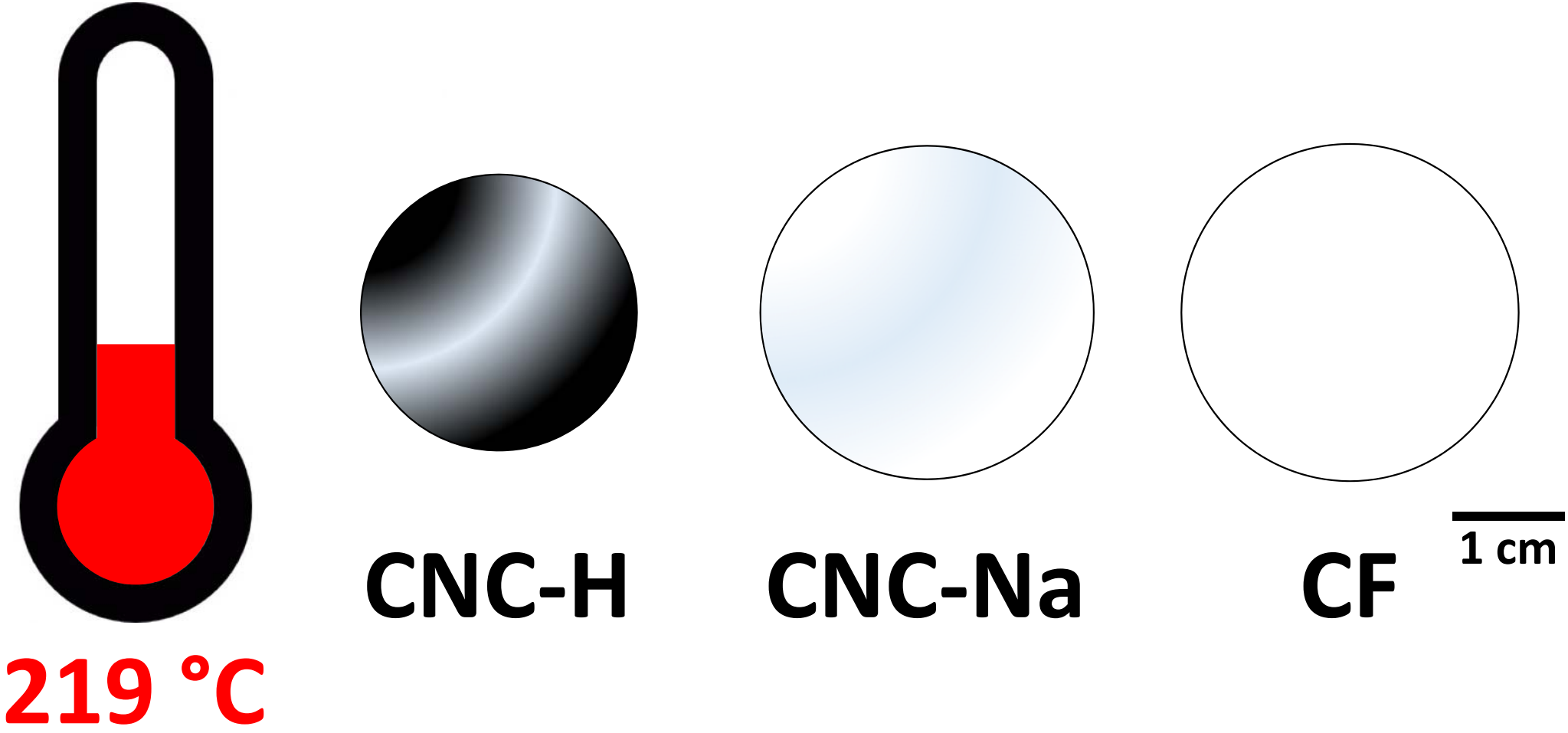

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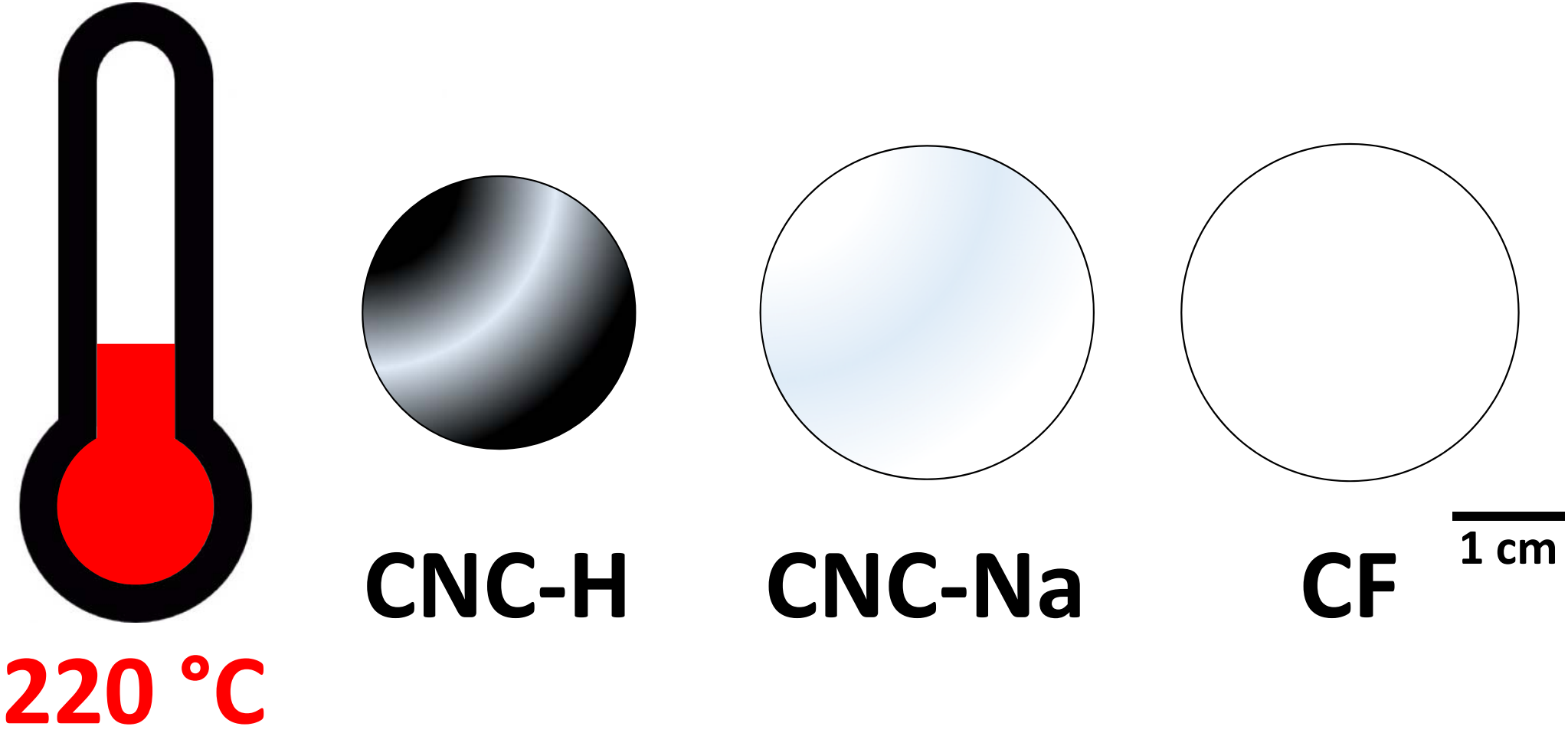

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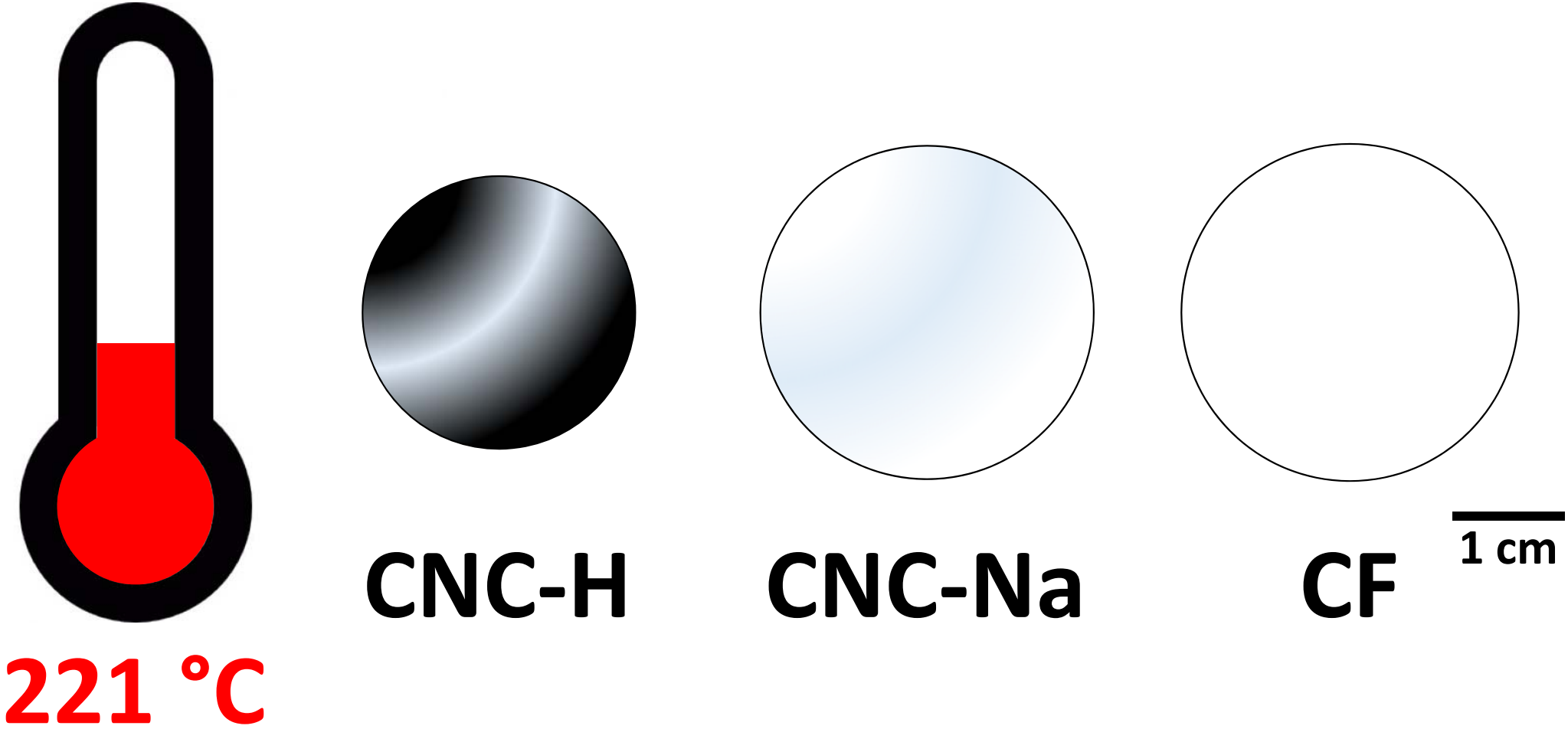

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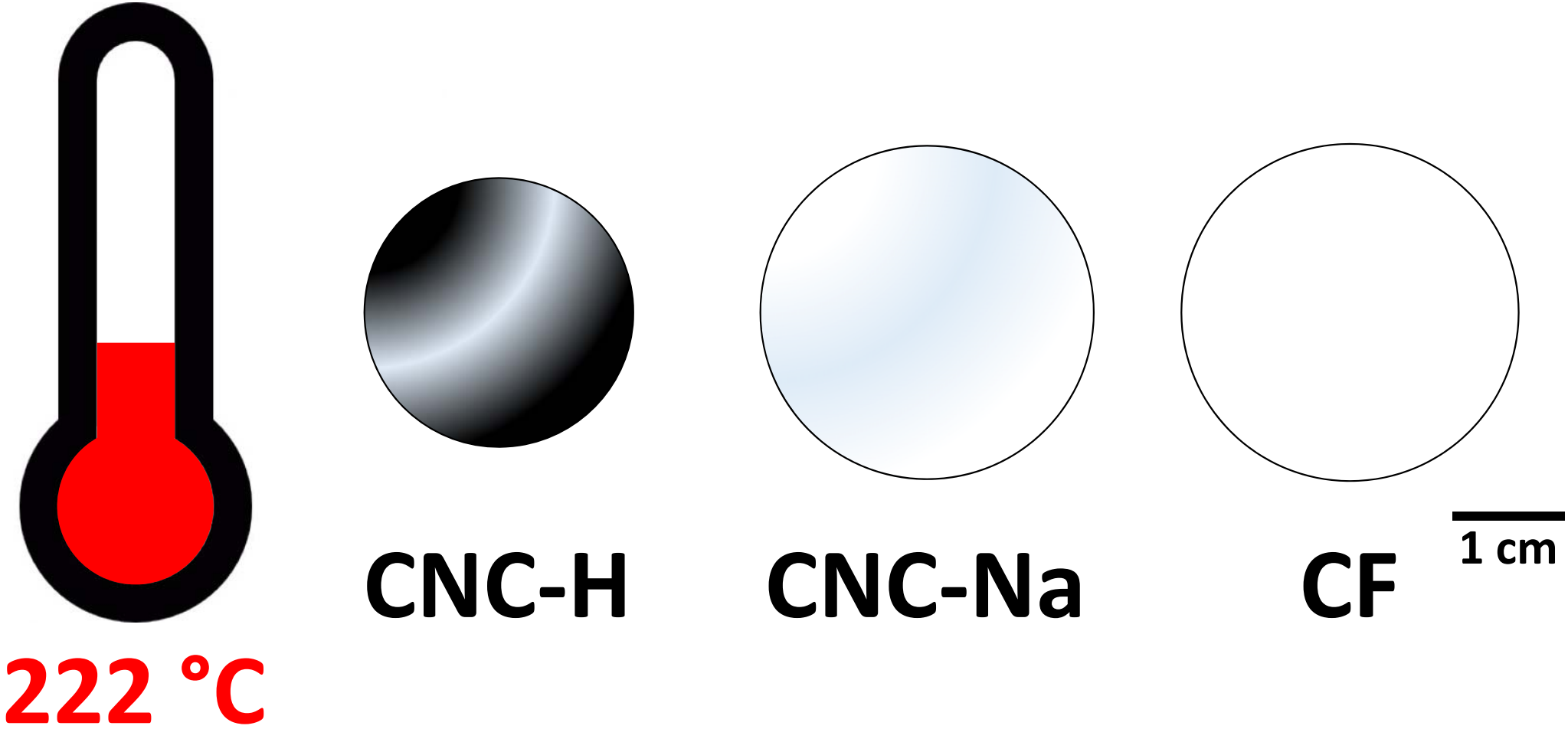

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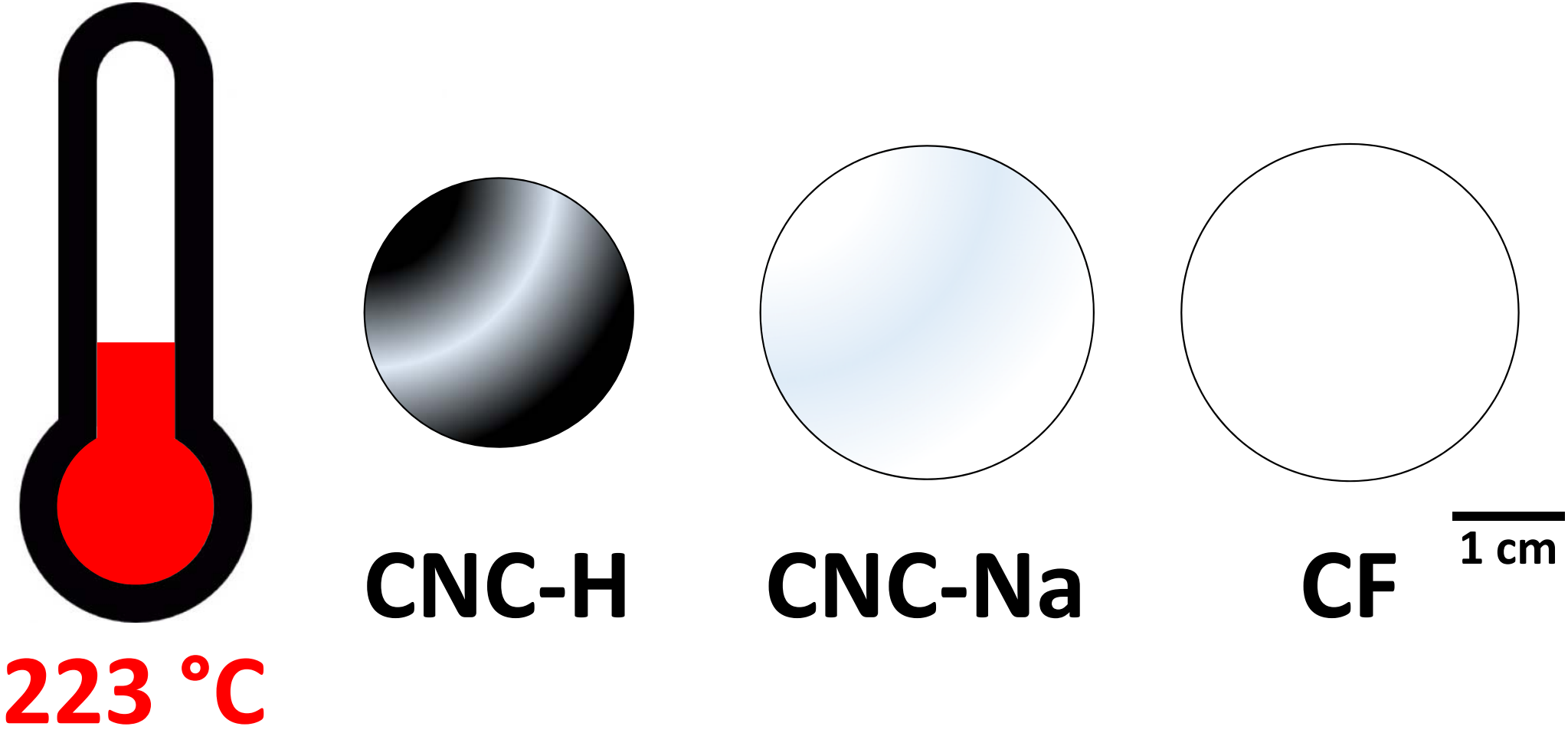

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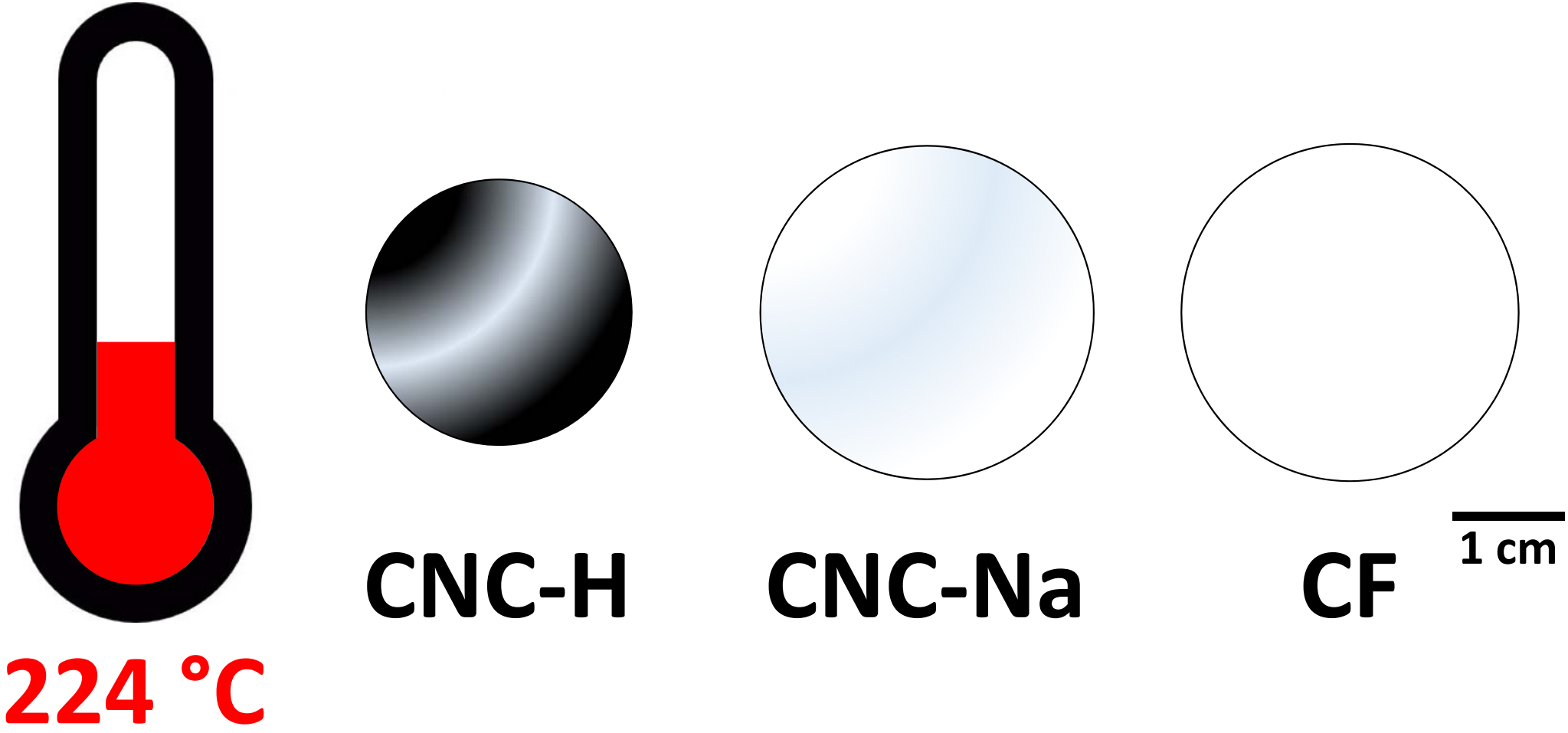

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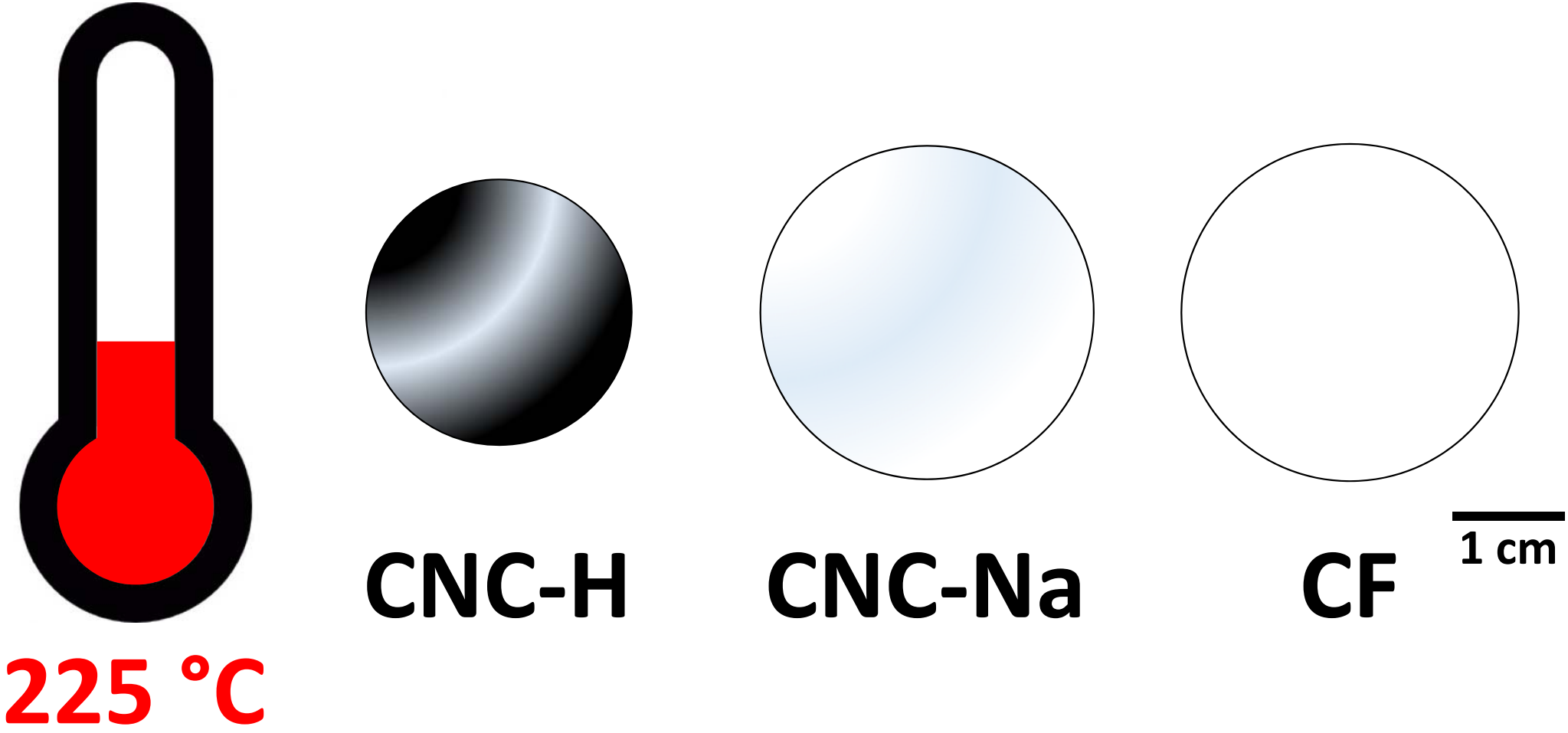

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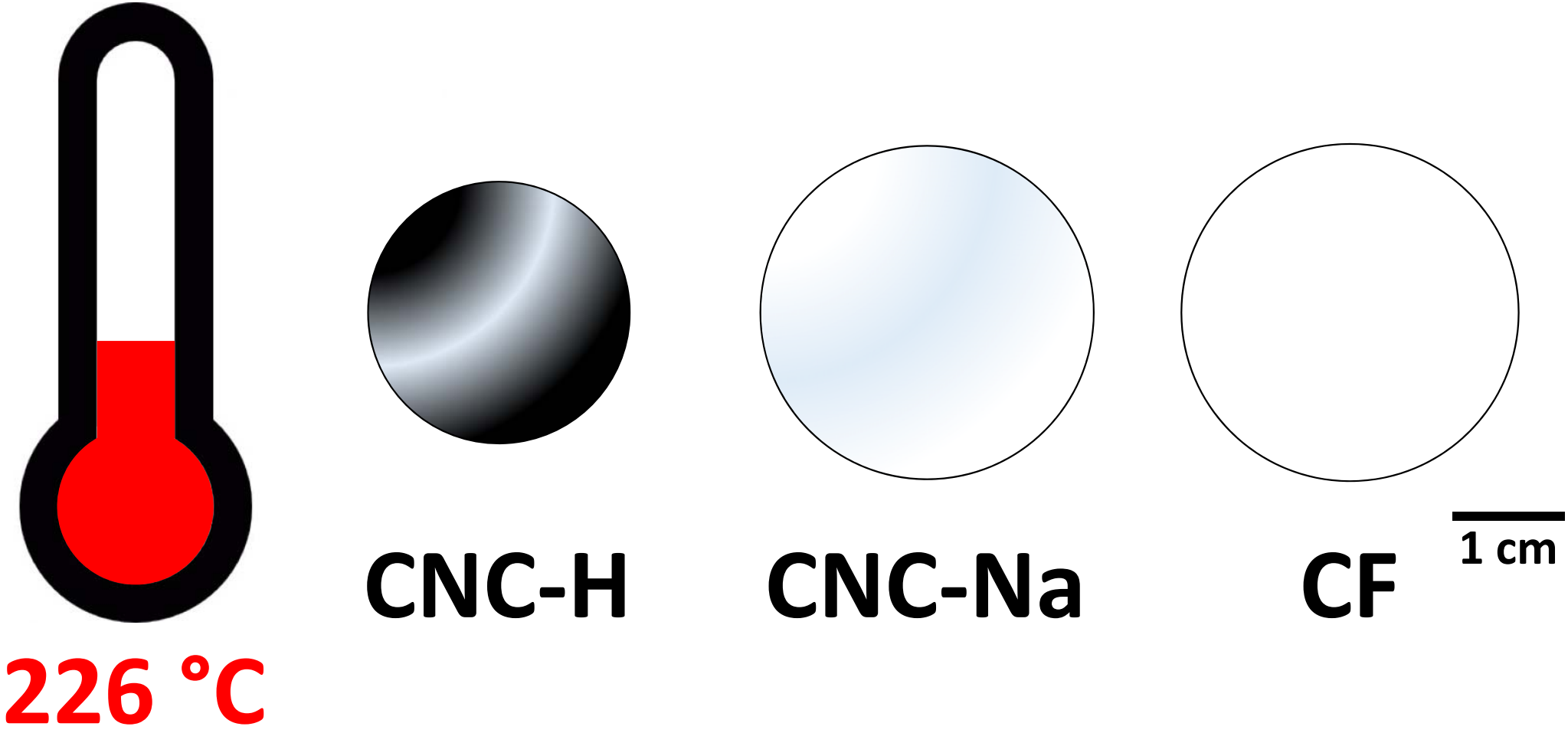

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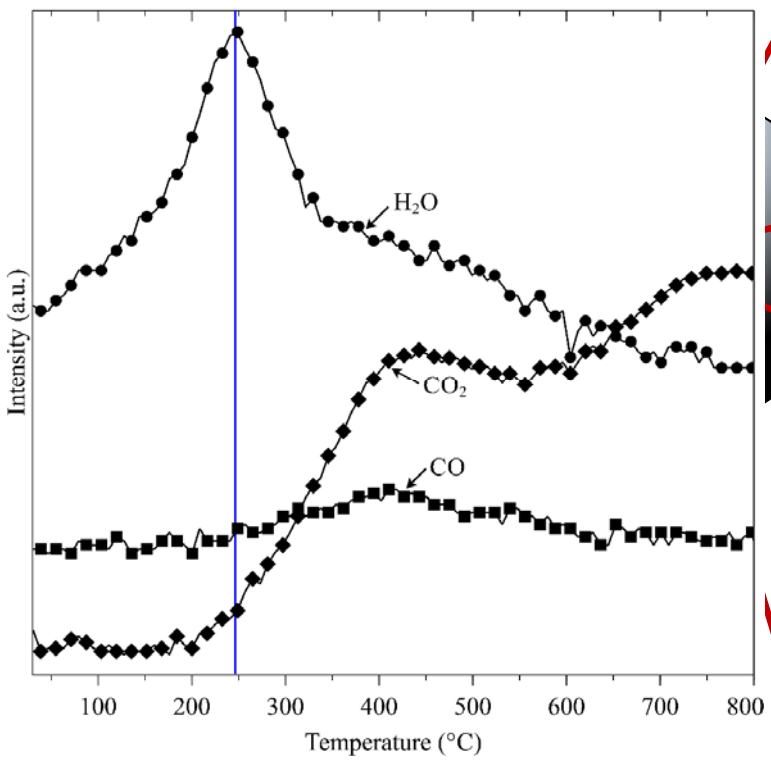

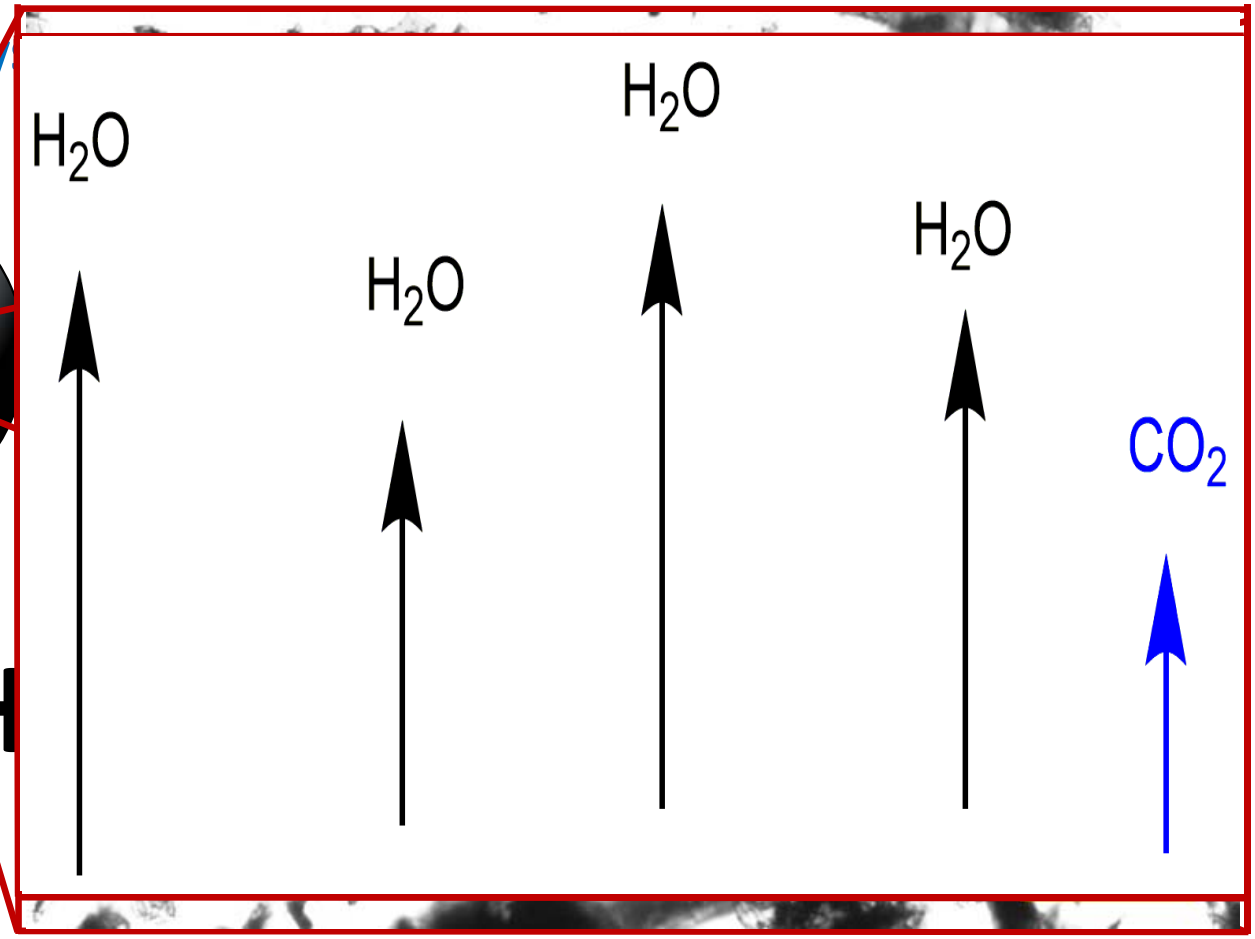

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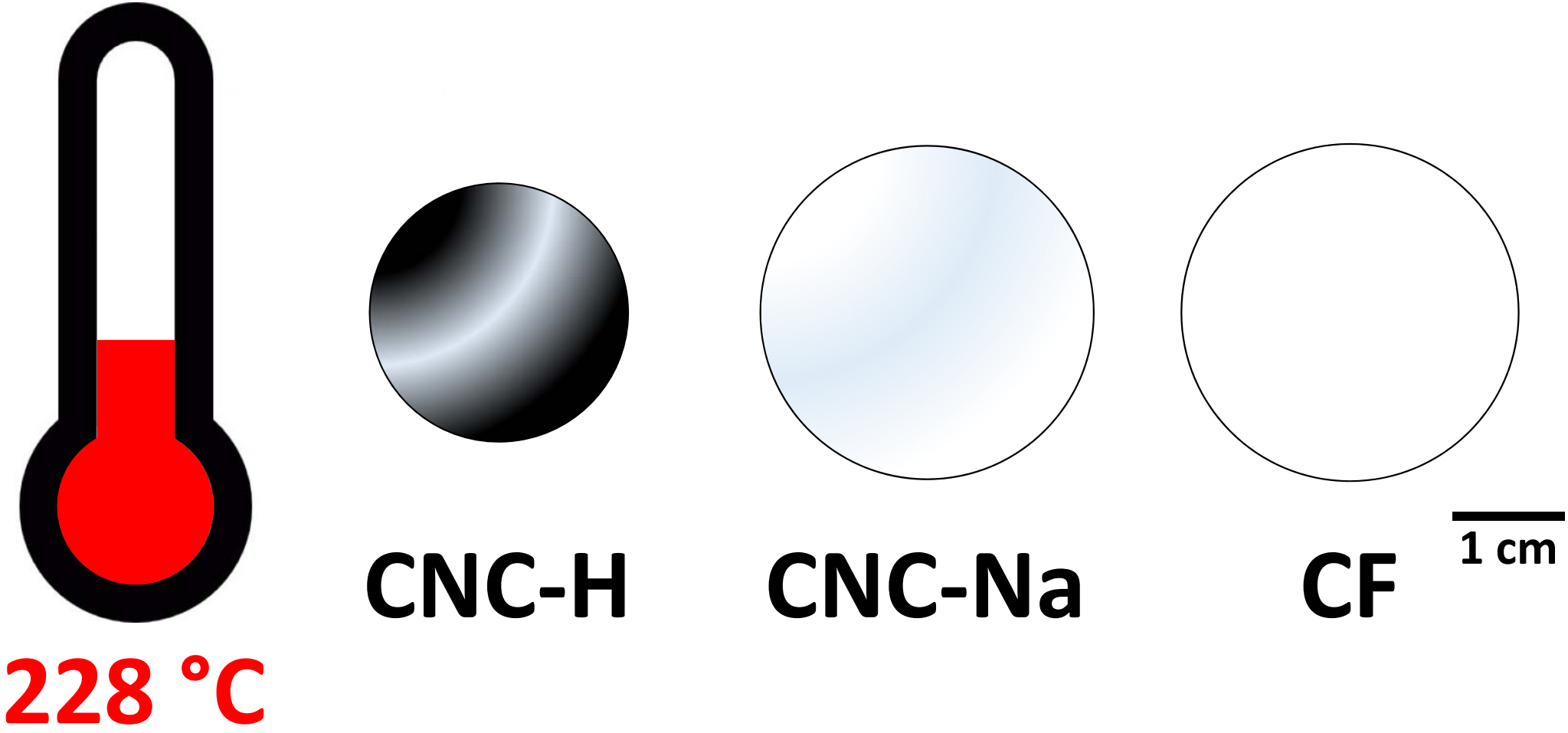

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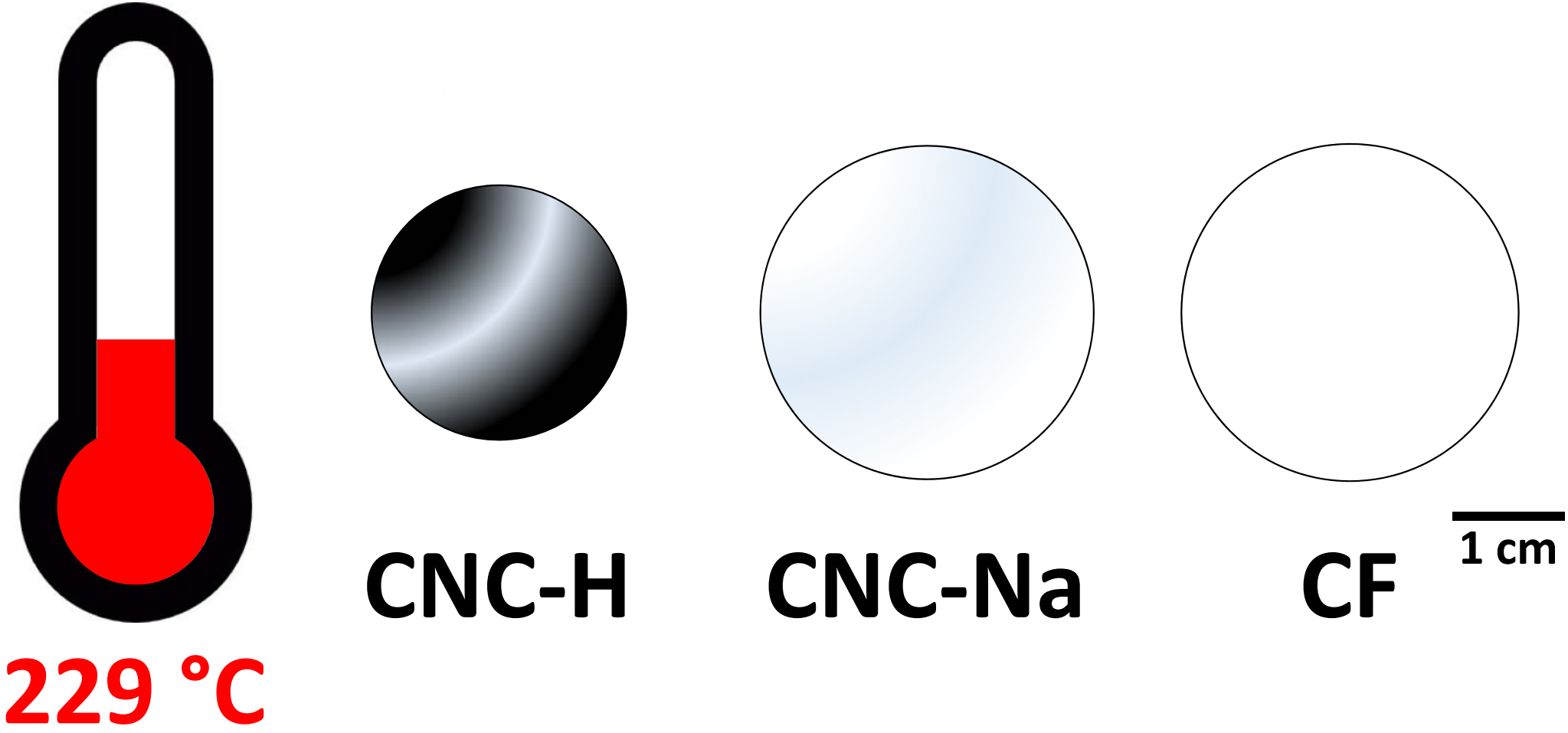

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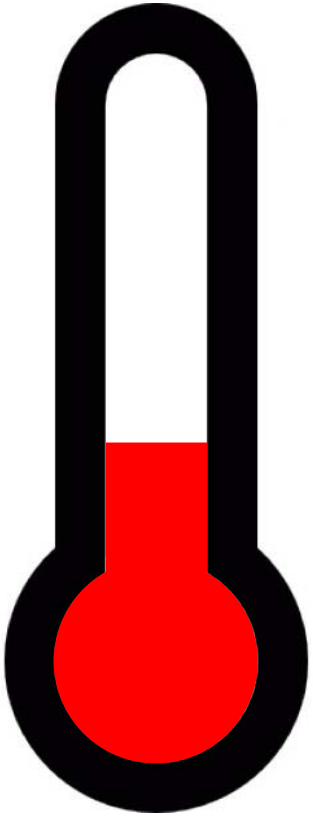
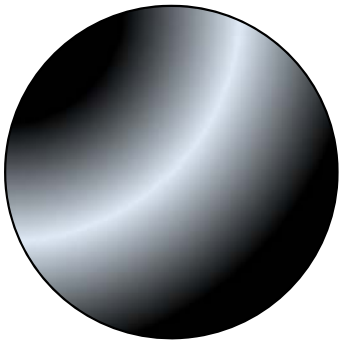
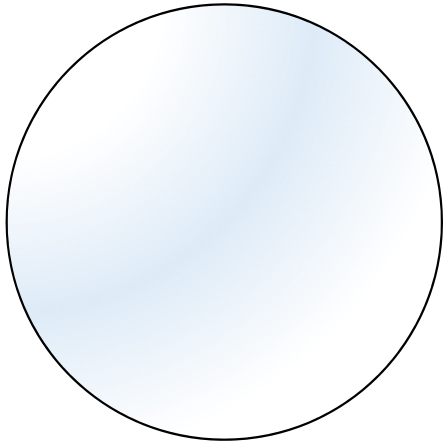


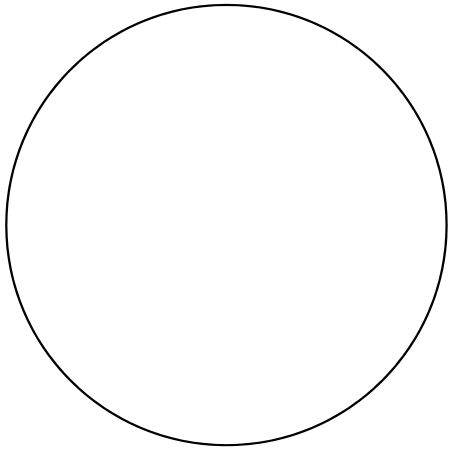
230 °C



CNC-H



CNC-Na

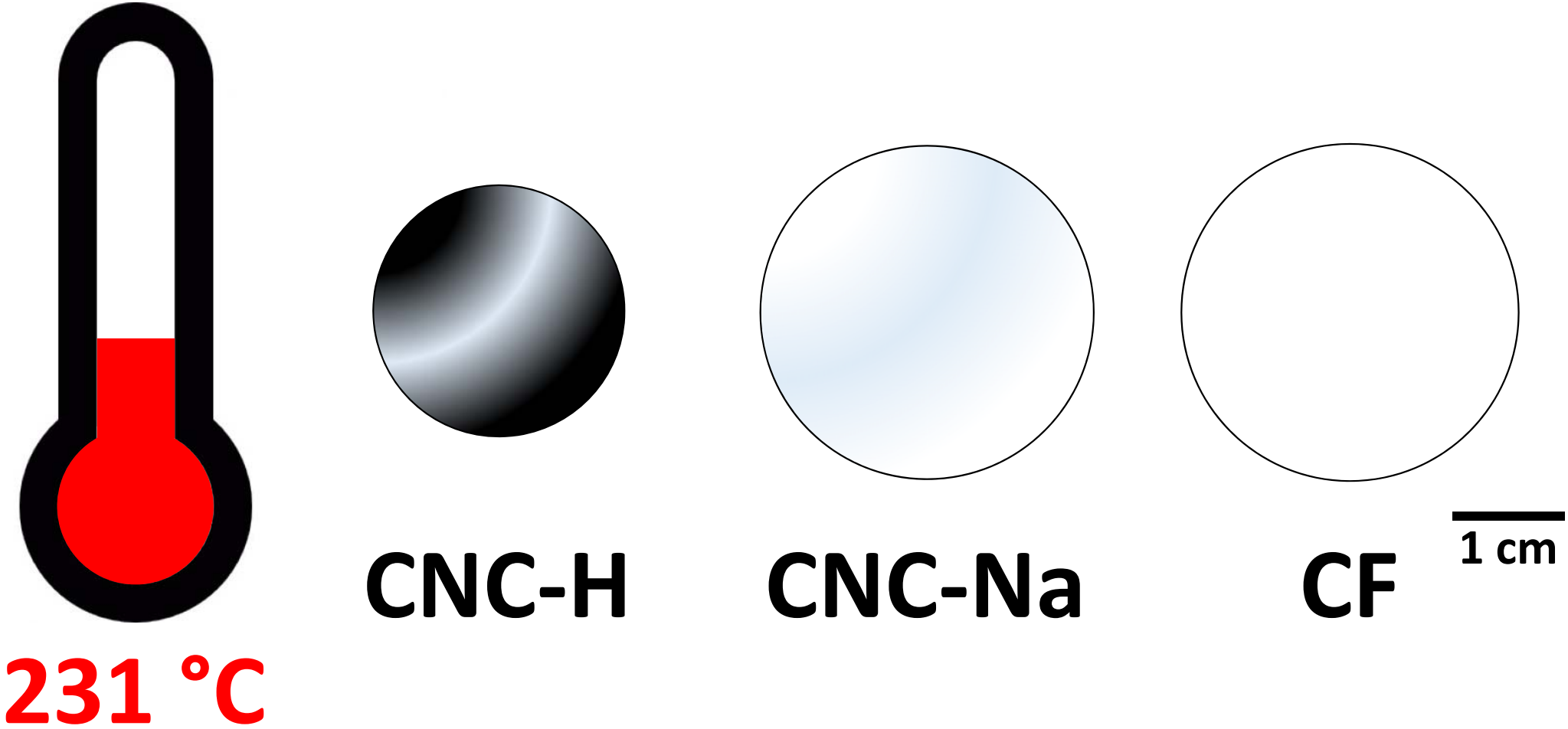


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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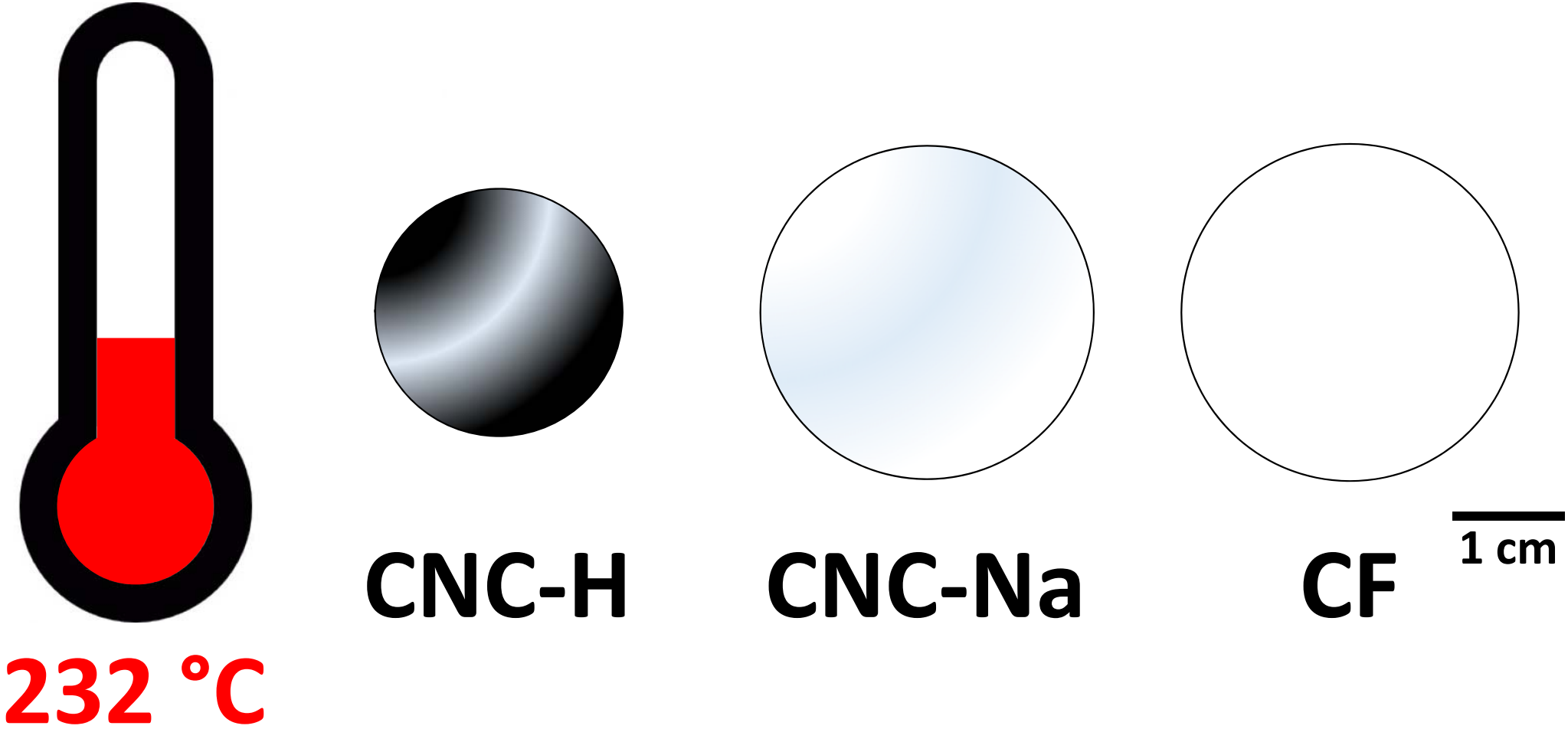

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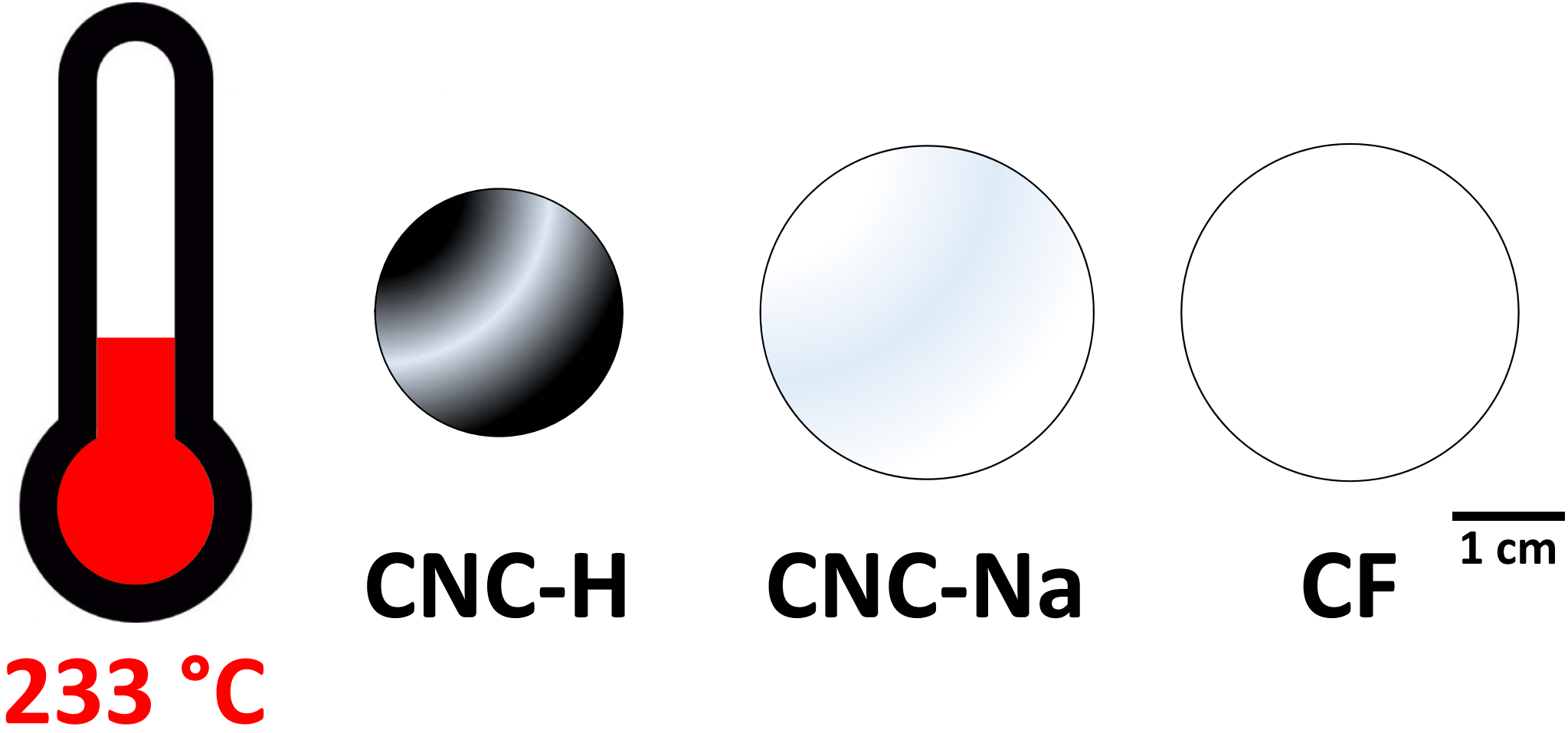

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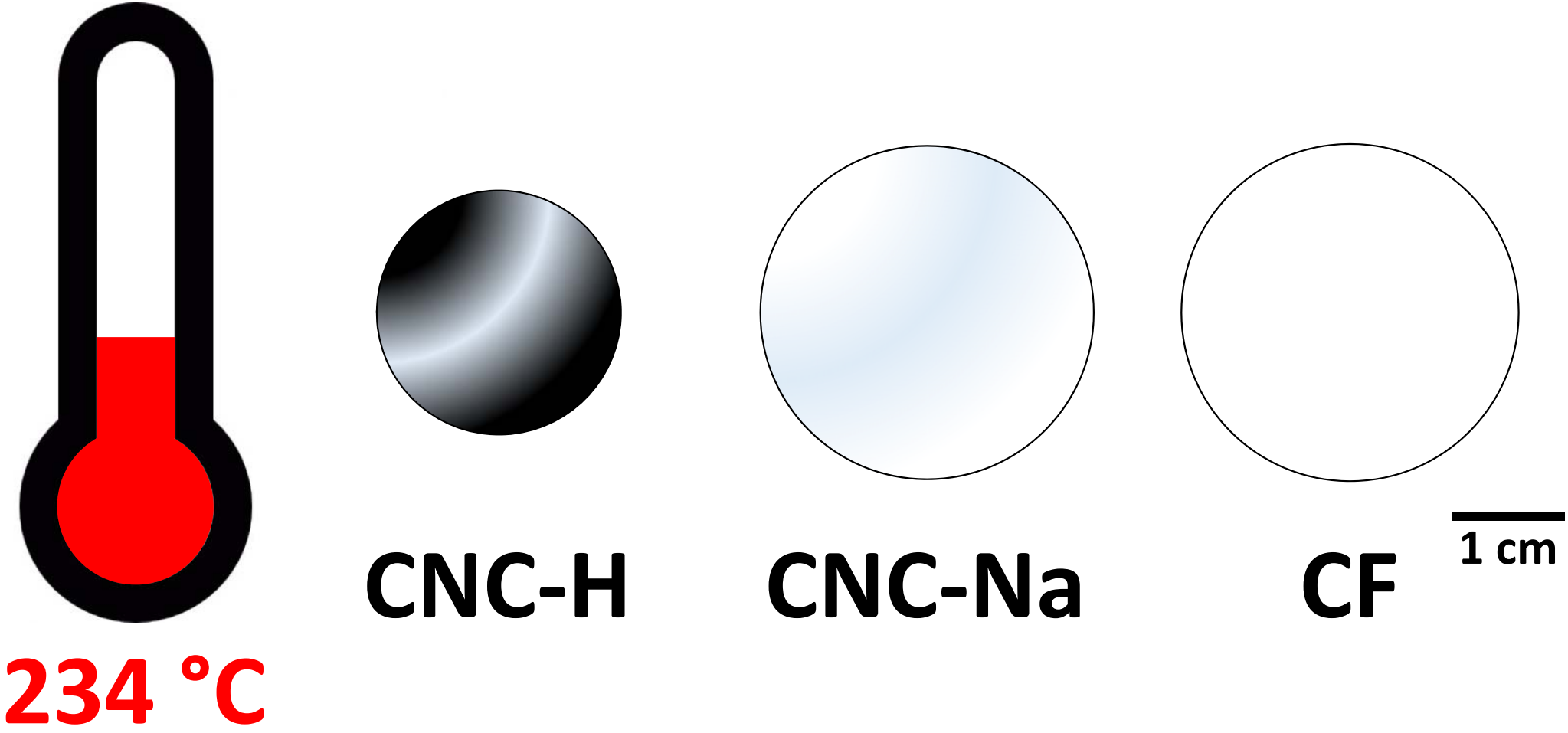

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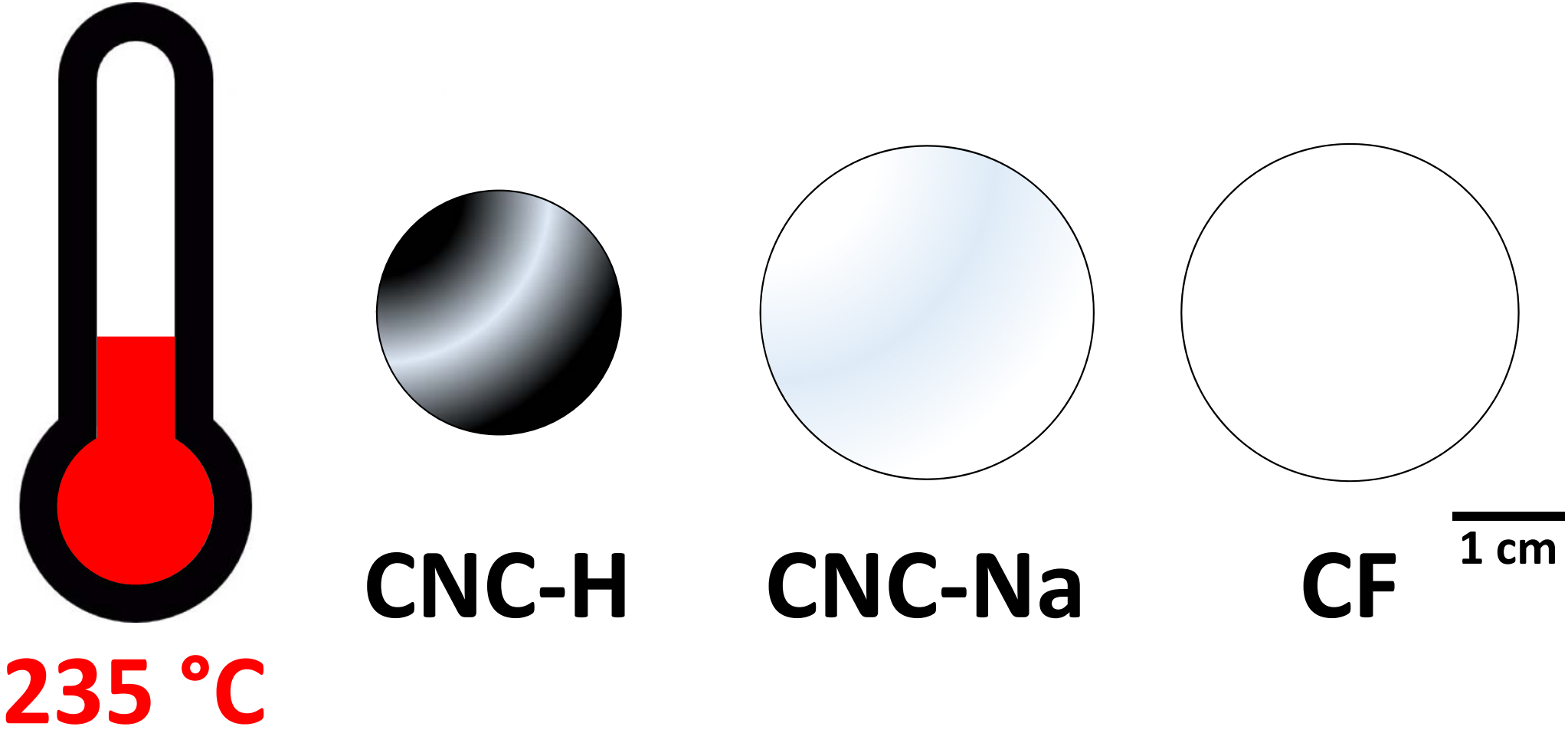

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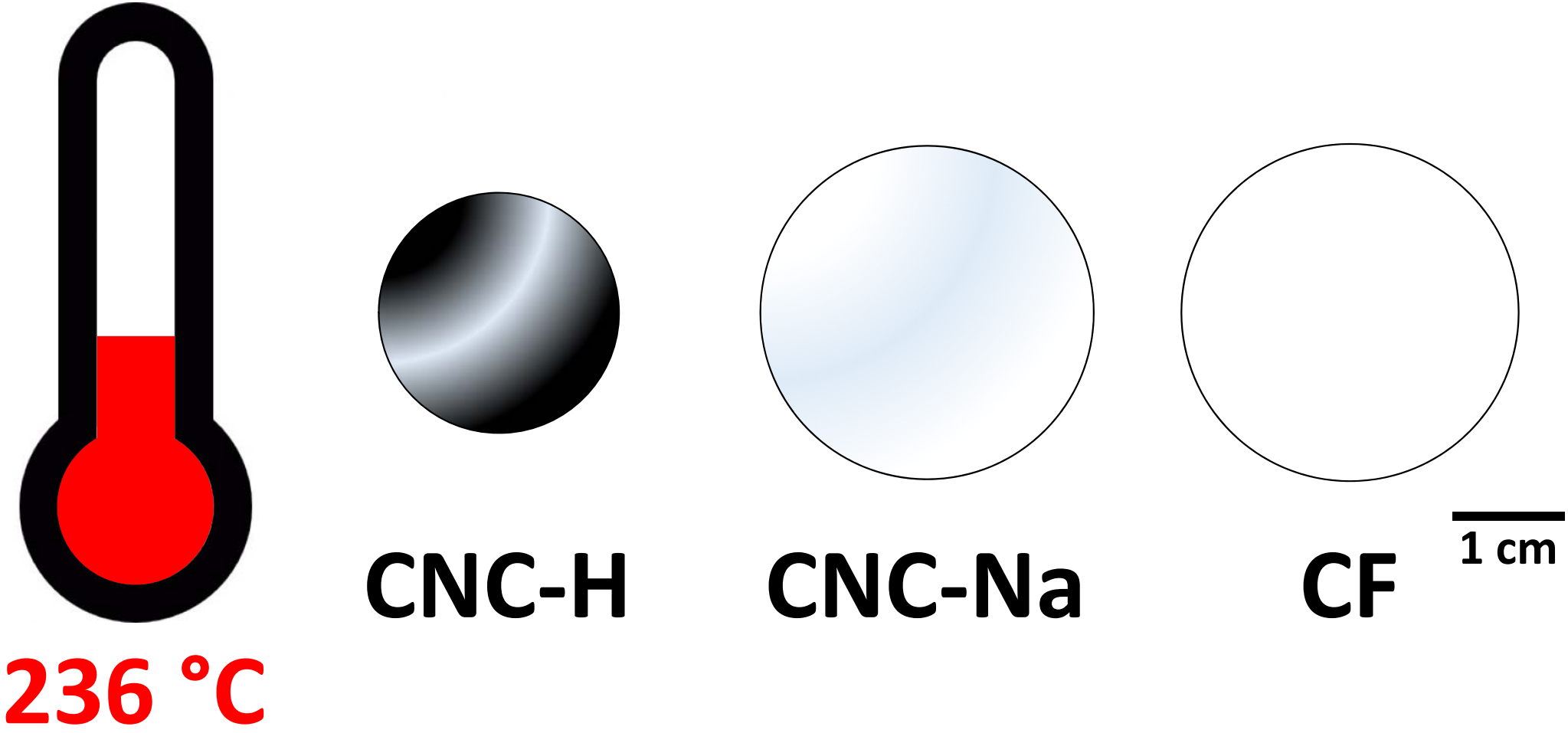

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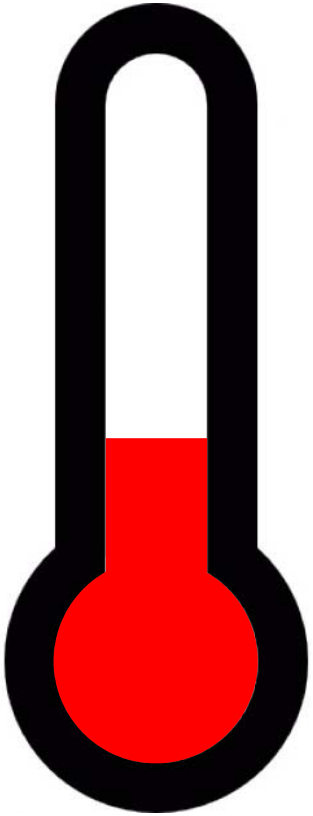
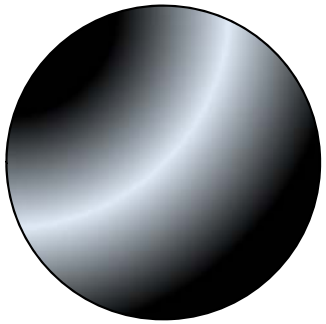
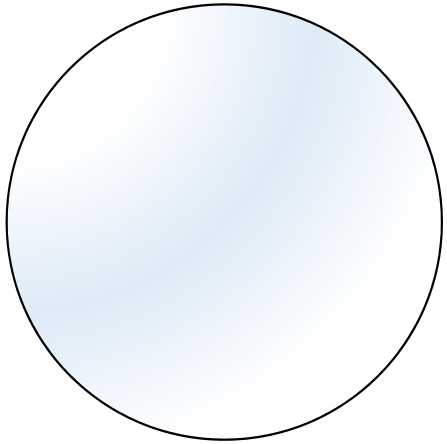


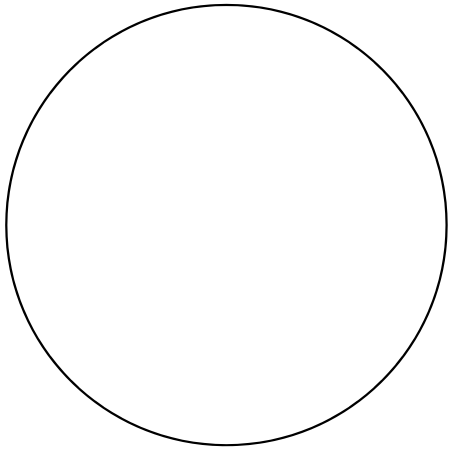
237 °C



CNC-H



CNC-Na

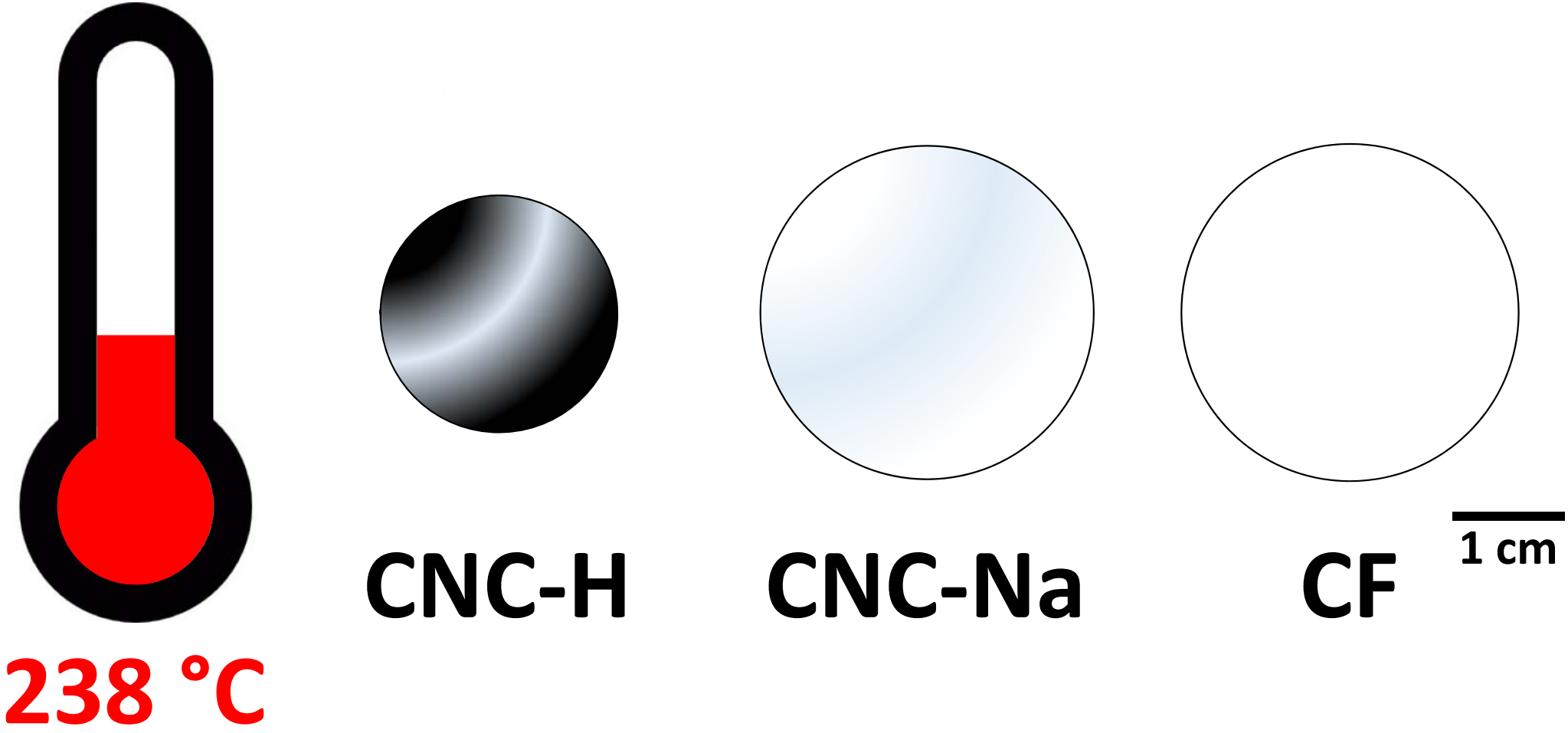


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



Results

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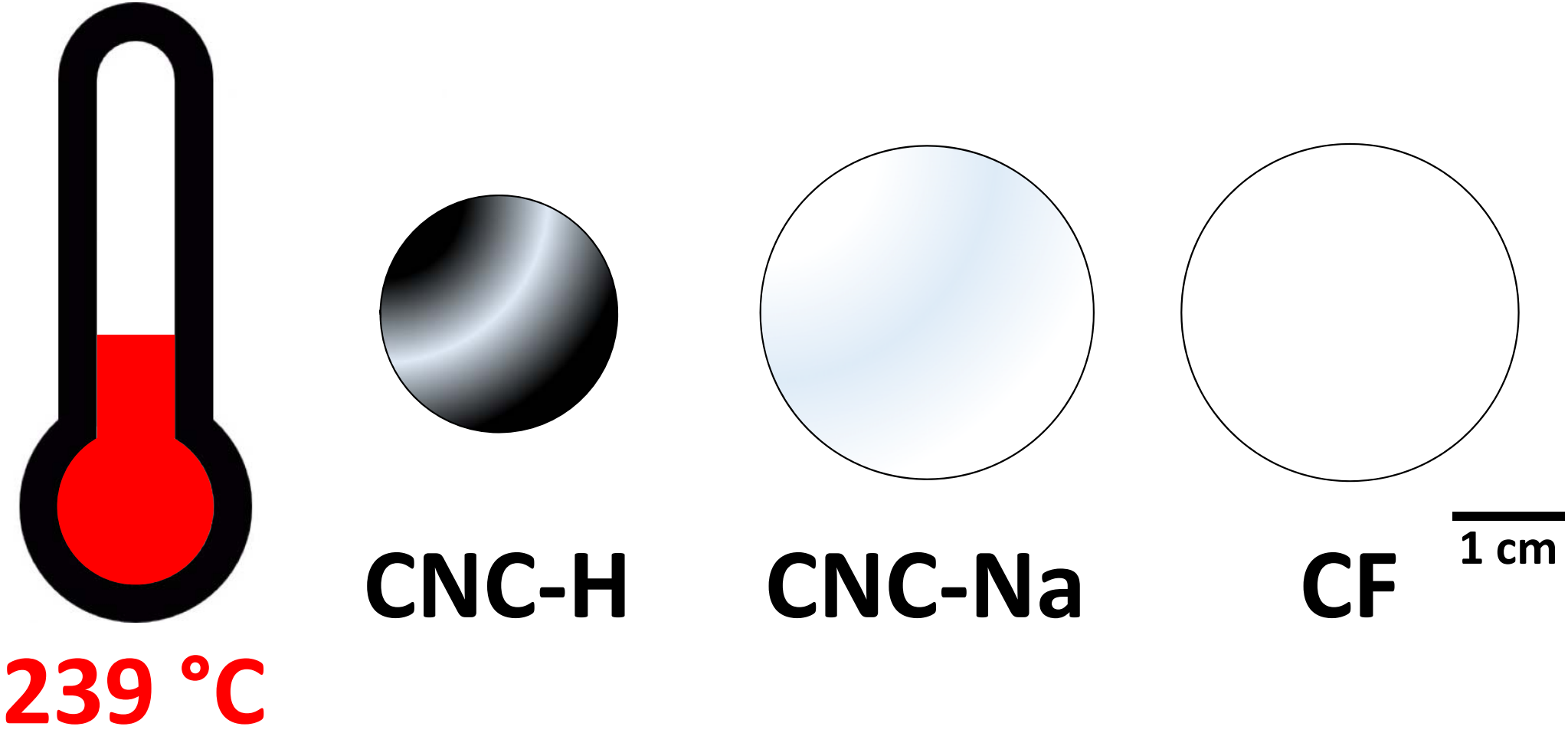

Results

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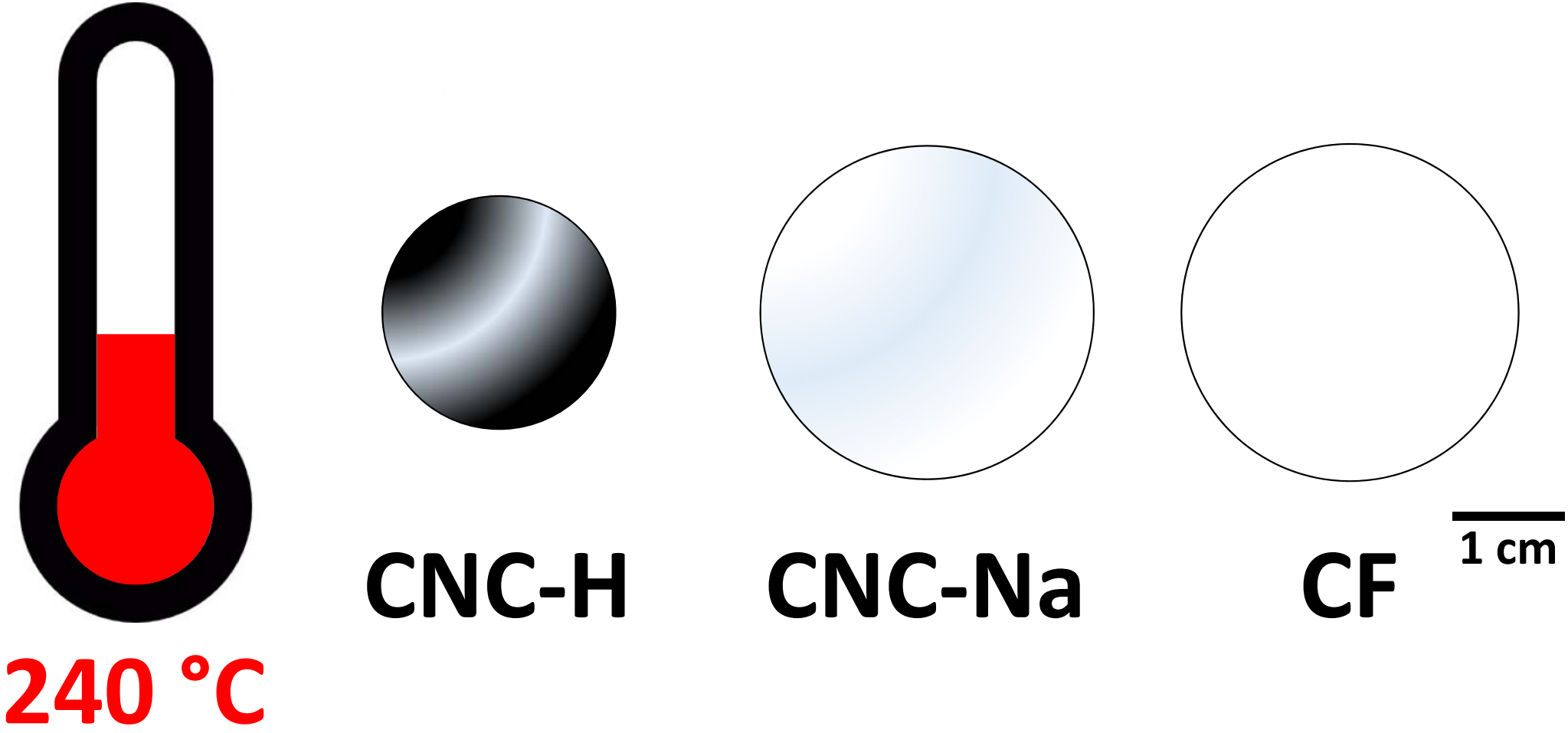

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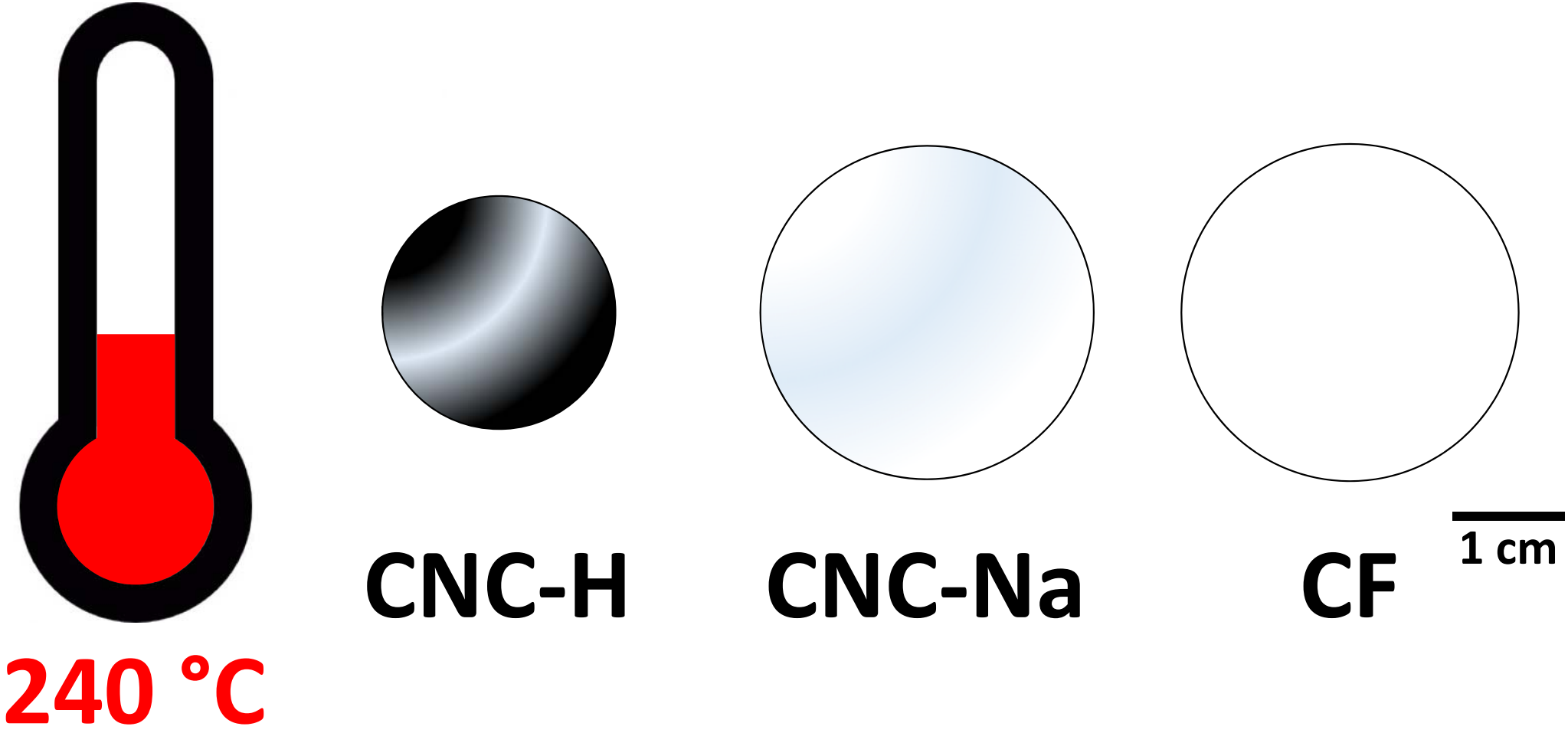

Results

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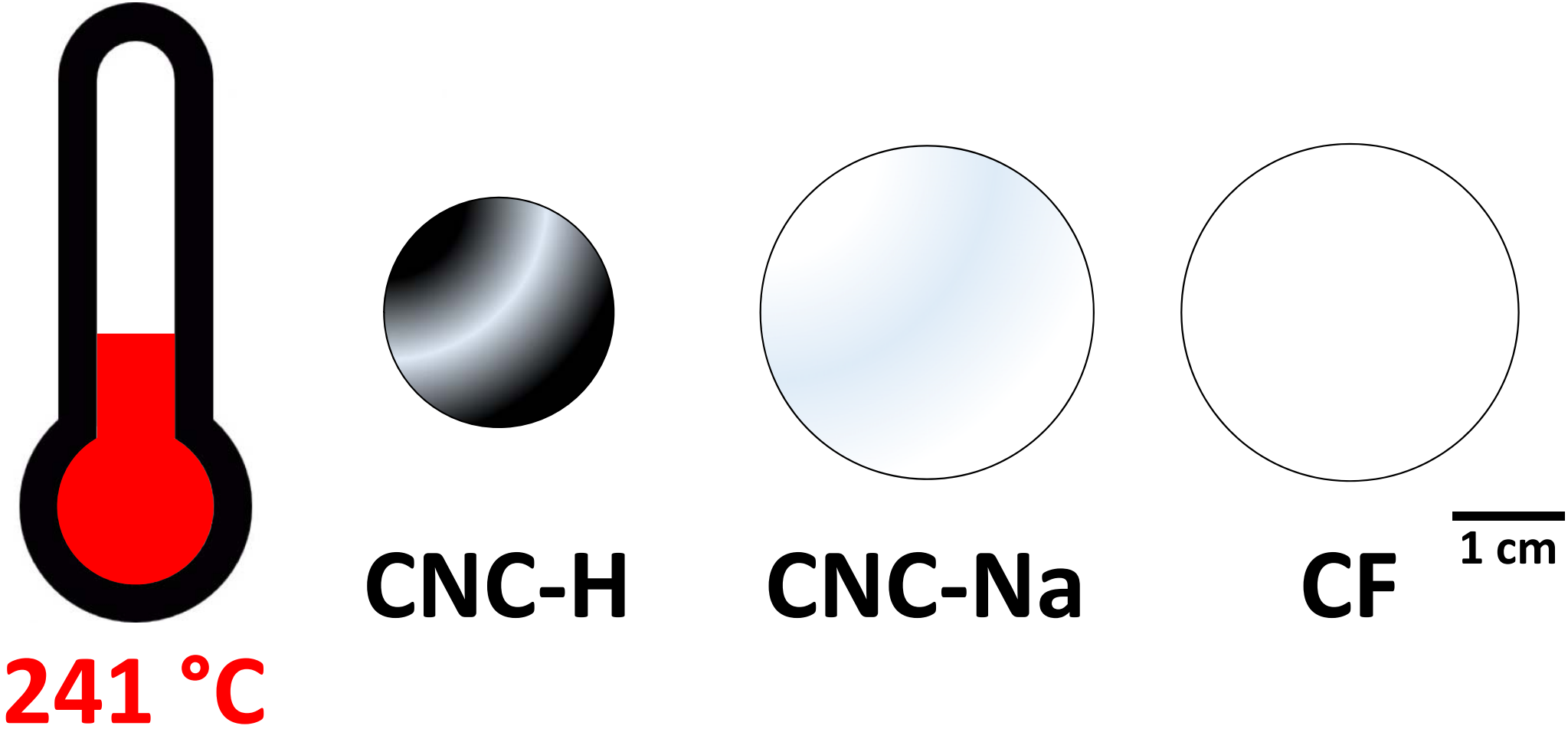

Results

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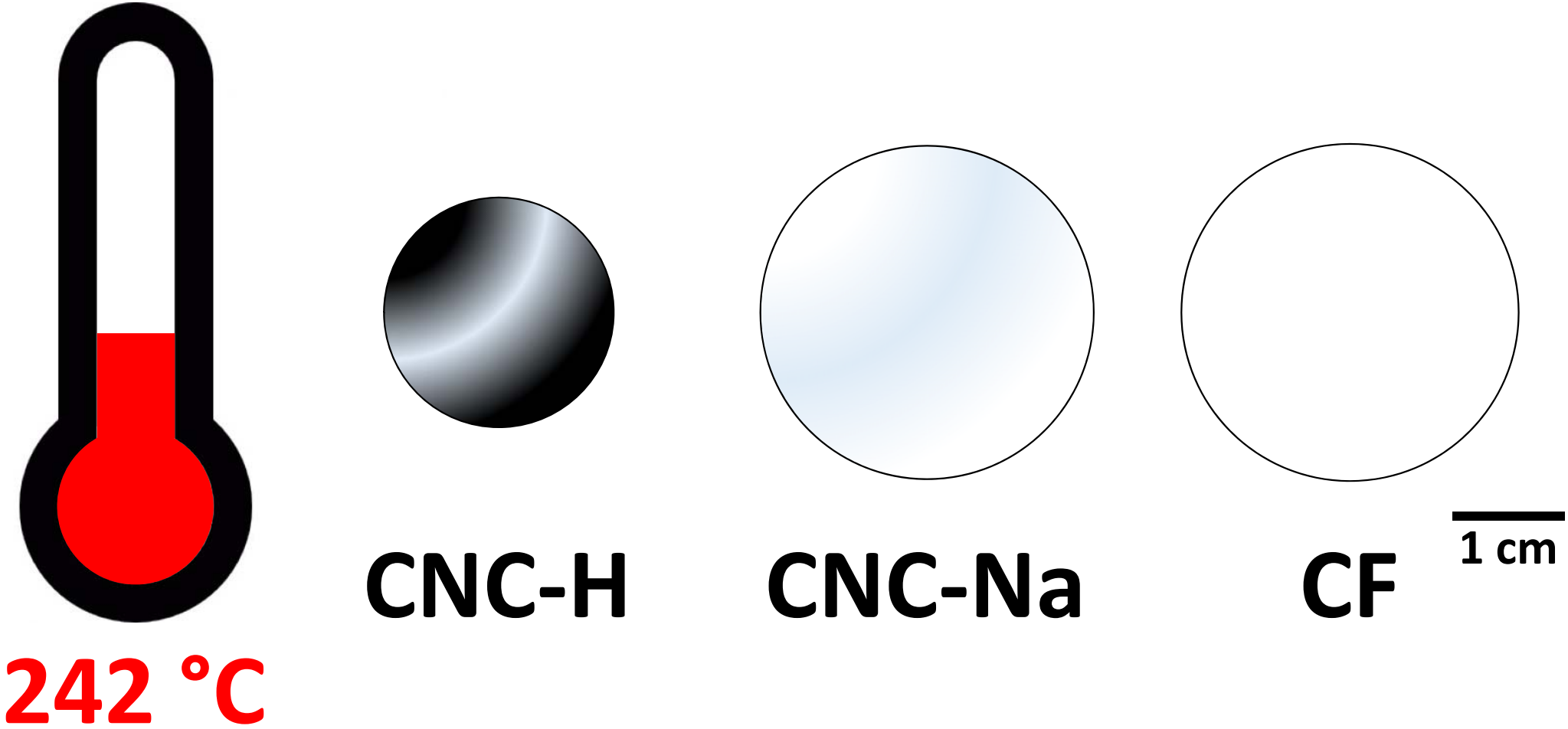

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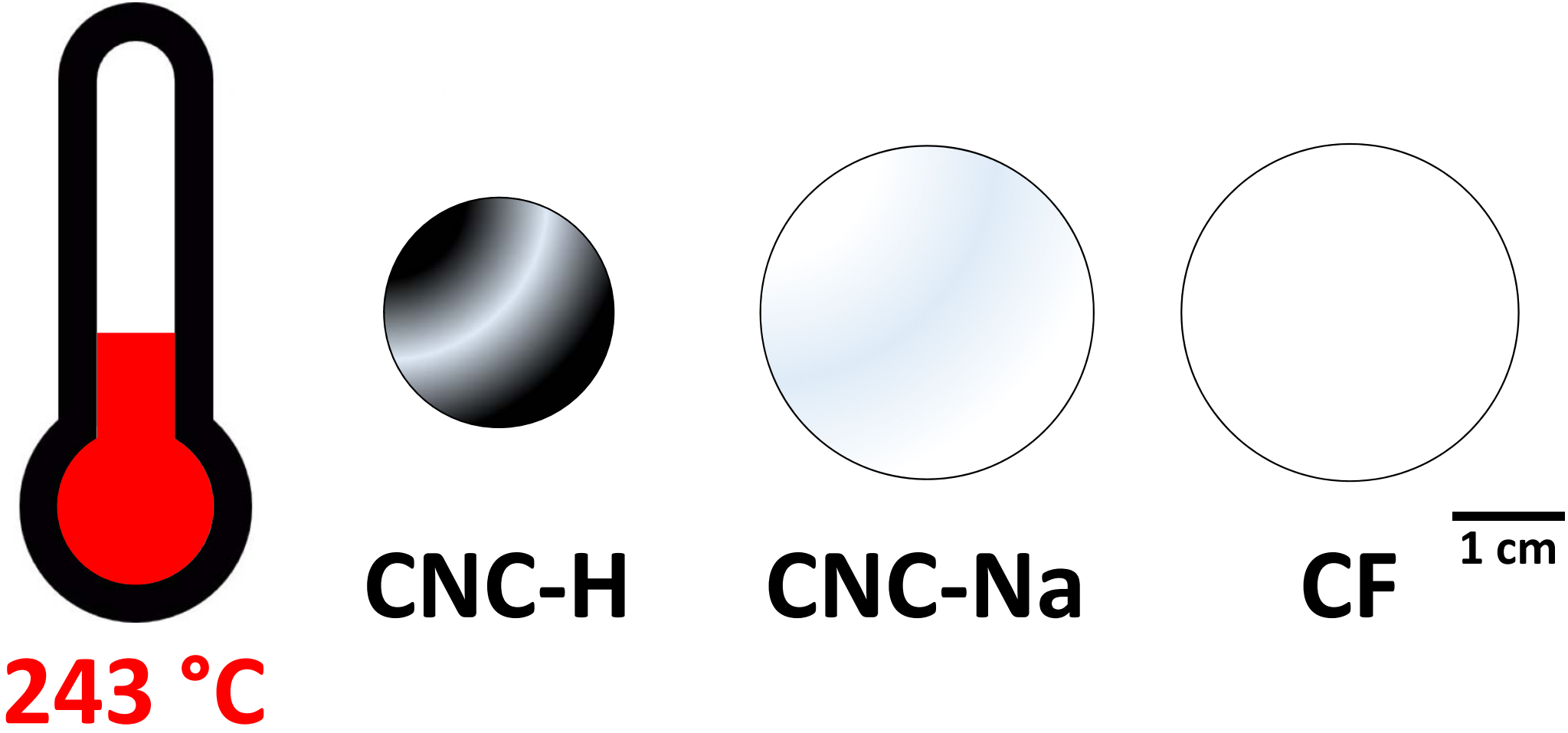

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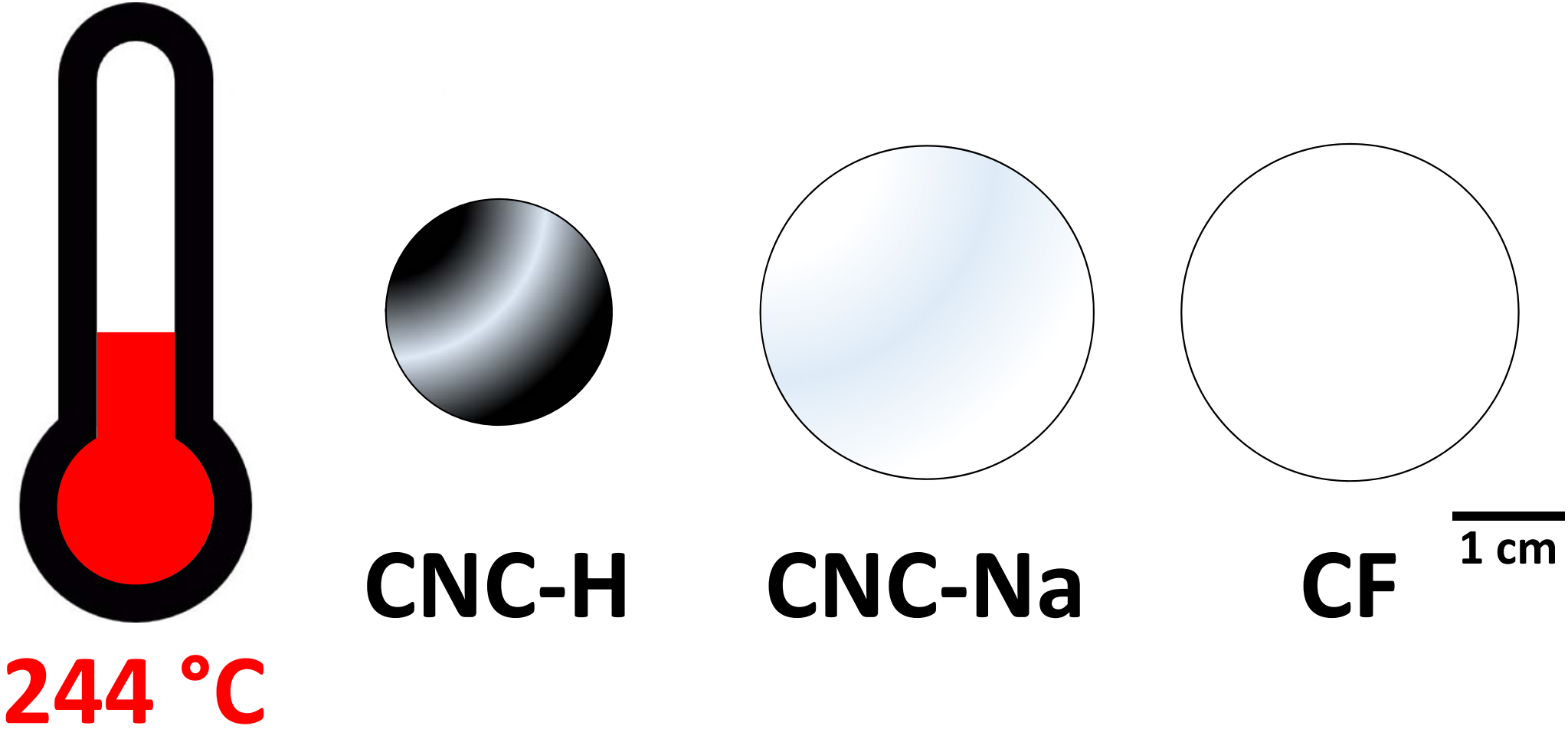

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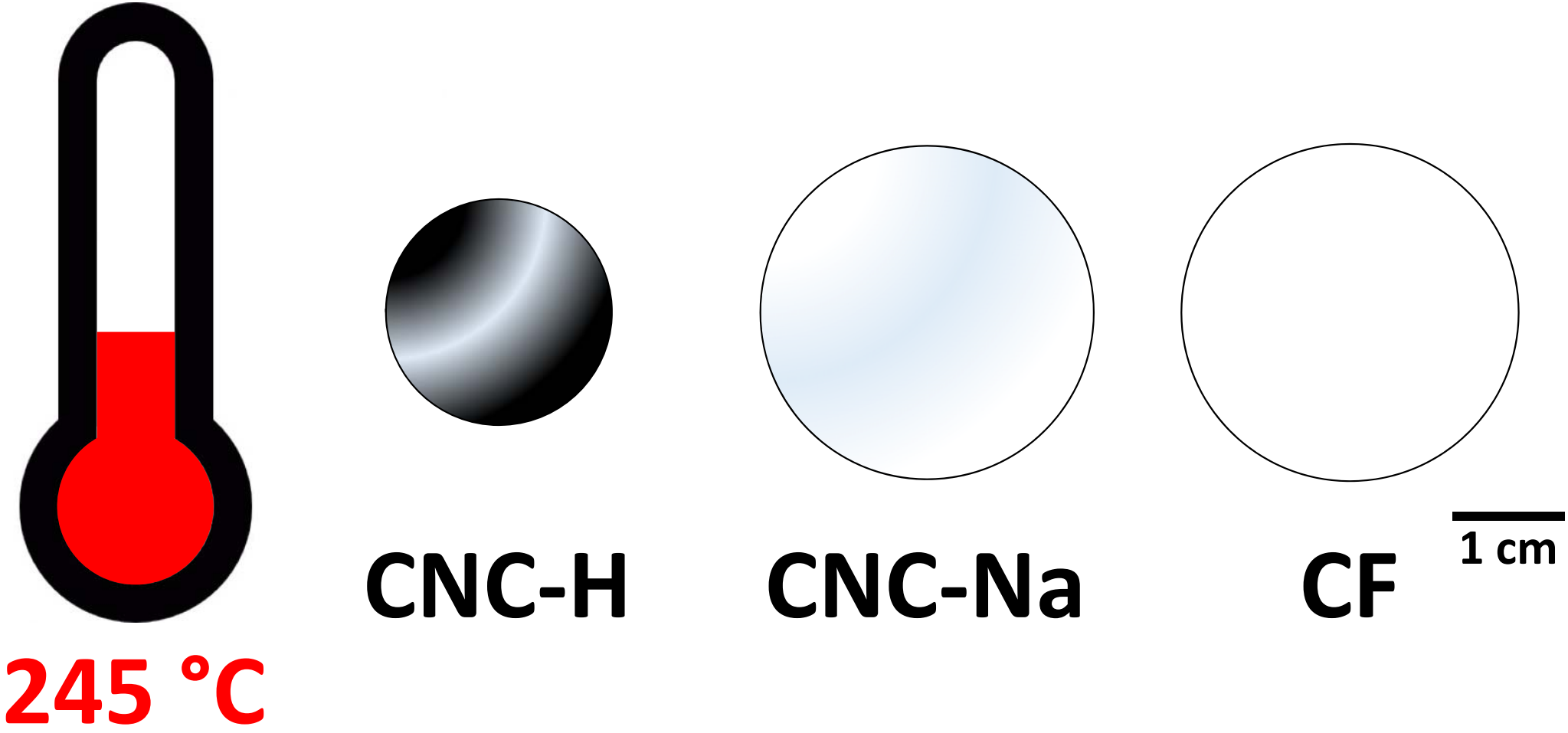

Results

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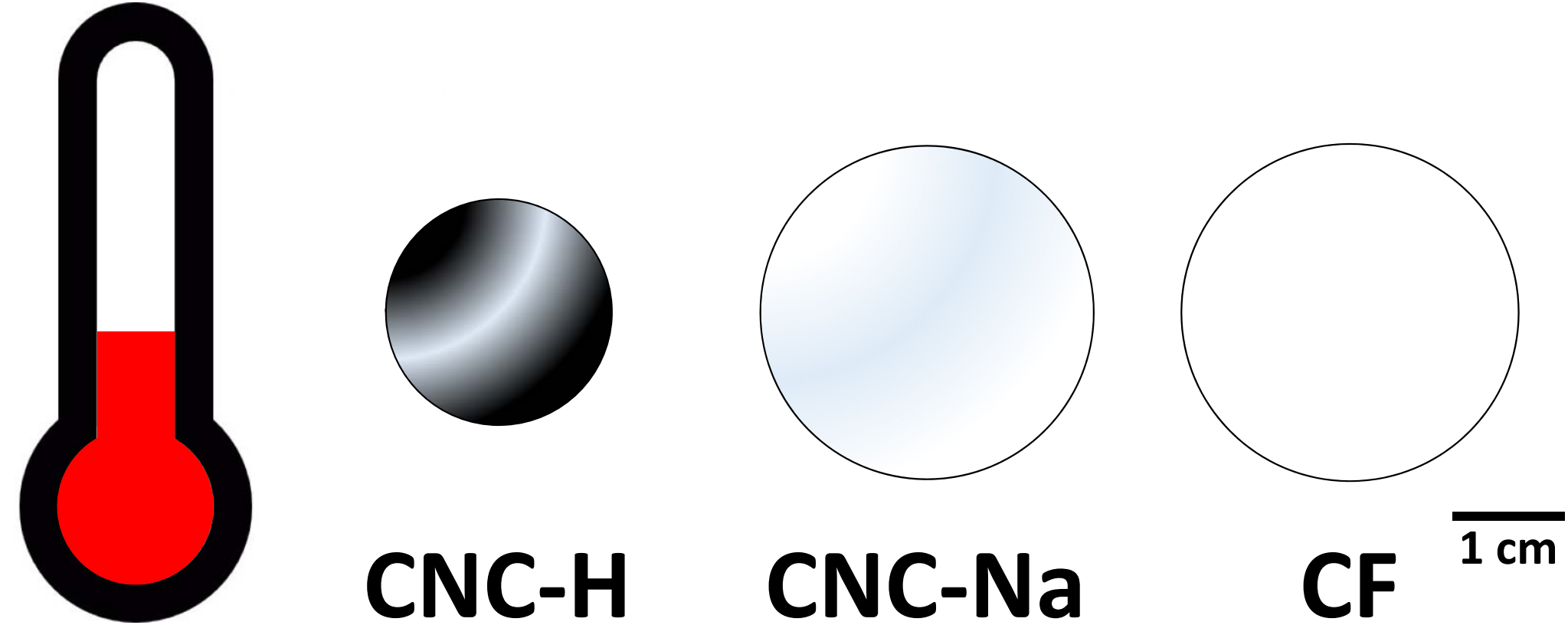
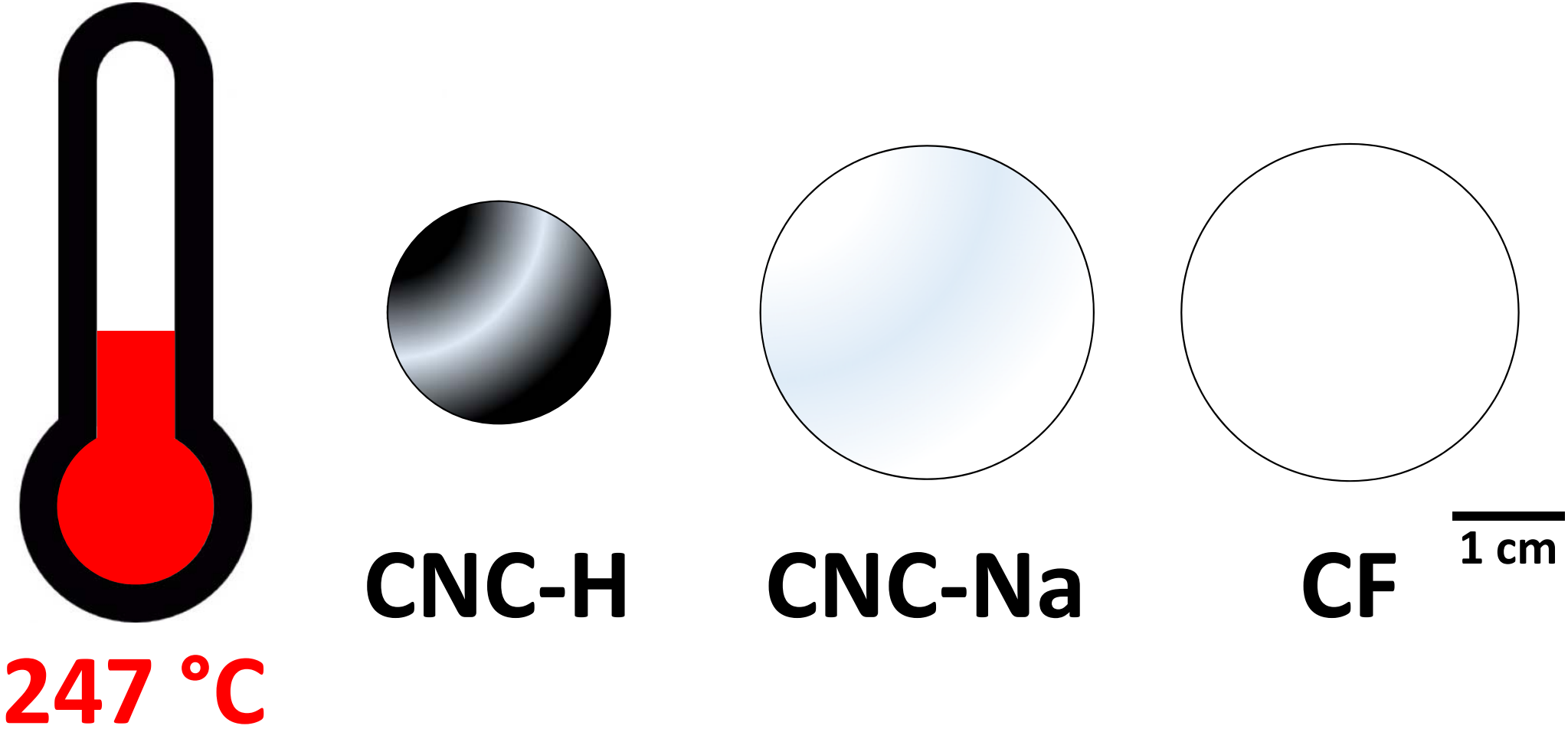


246 °C

Results

THE UNIVERSITY OF BRITISH COLUMBIA



Results

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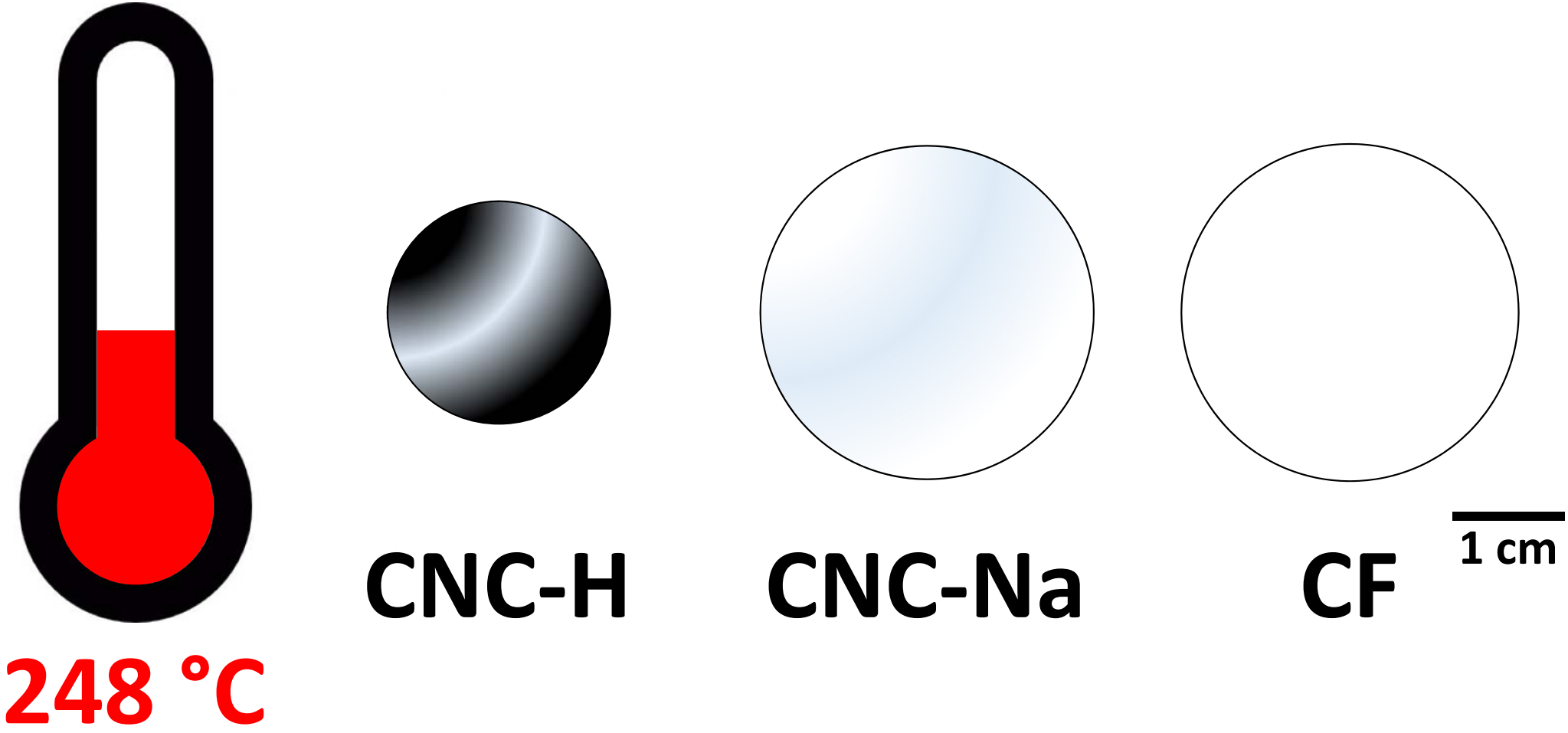

Results

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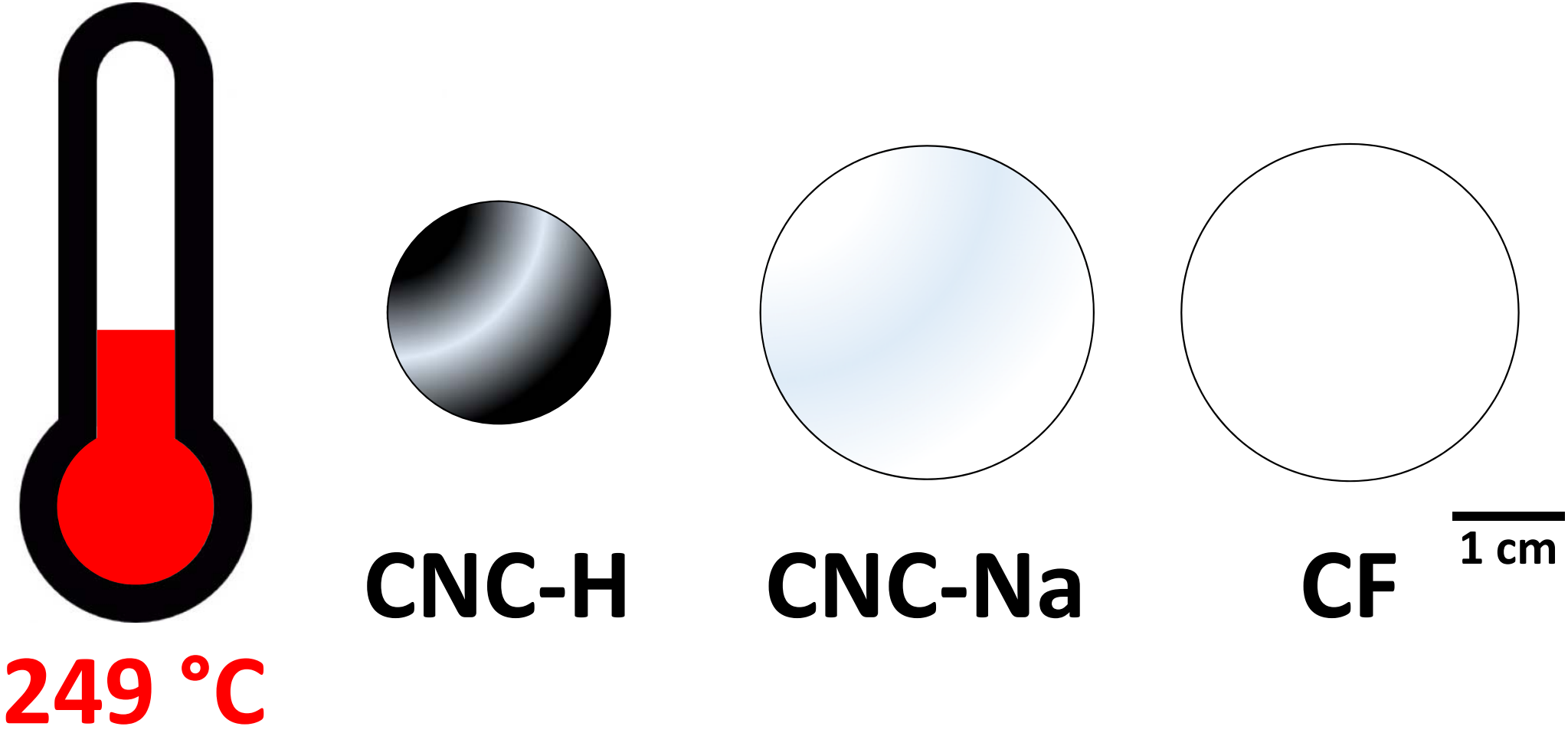

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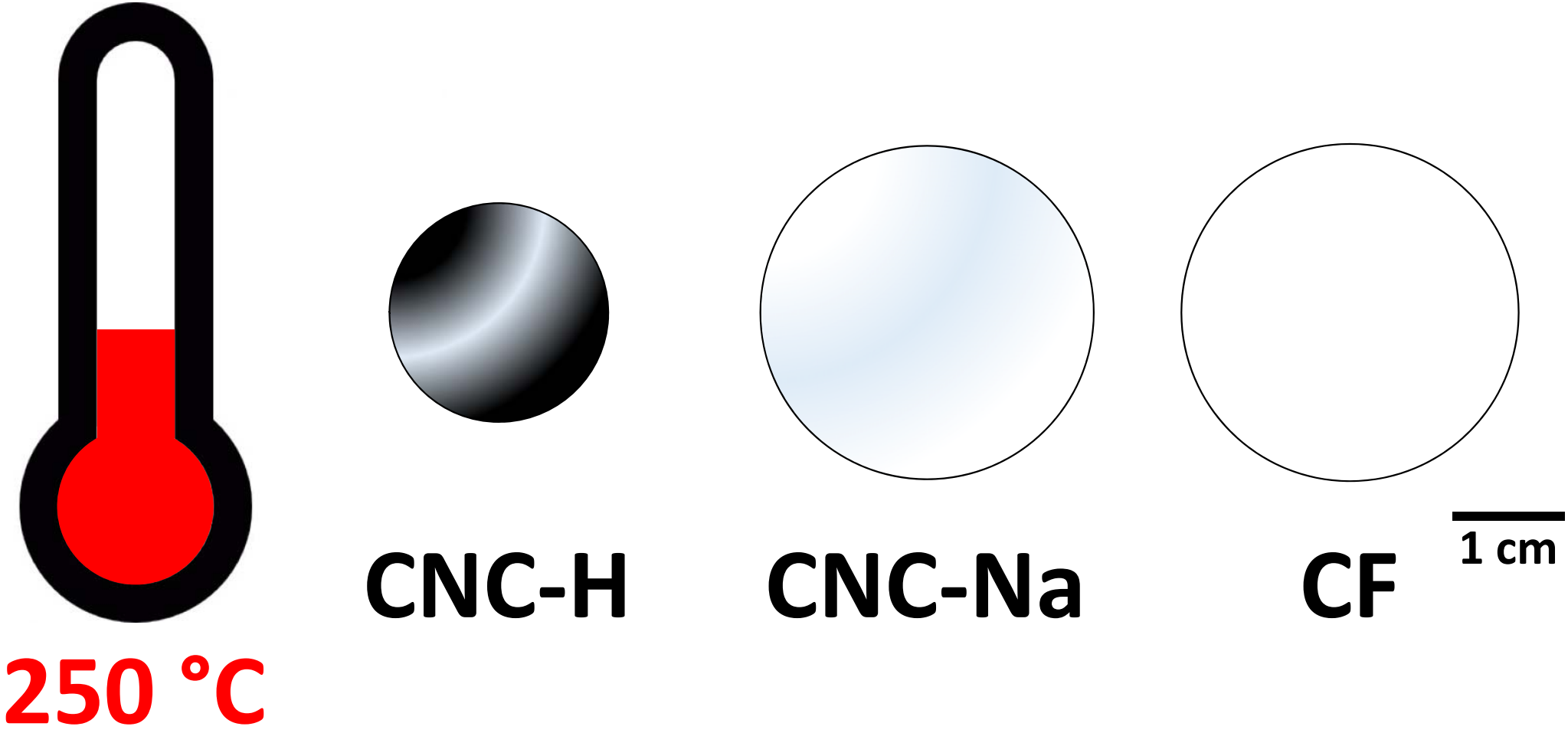

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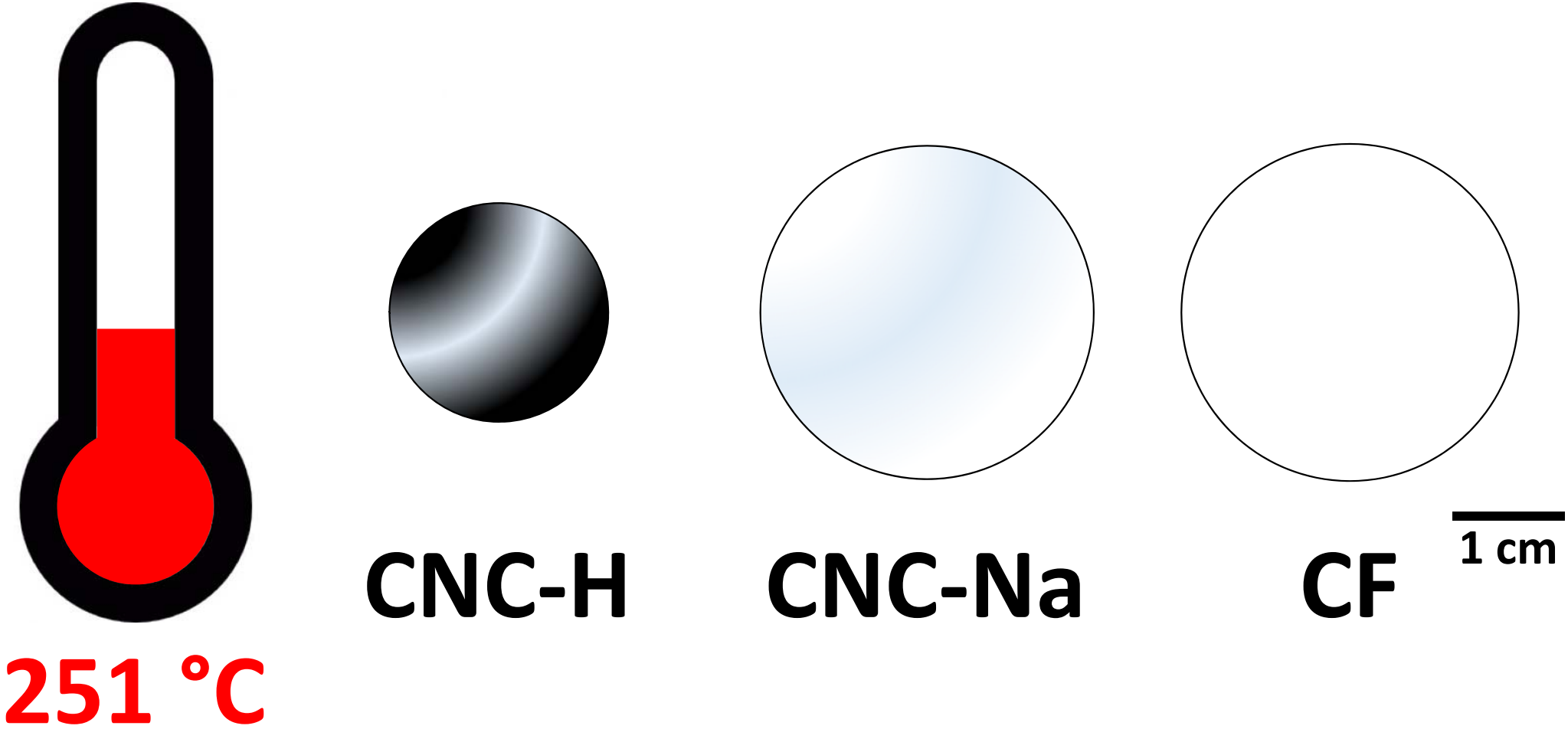

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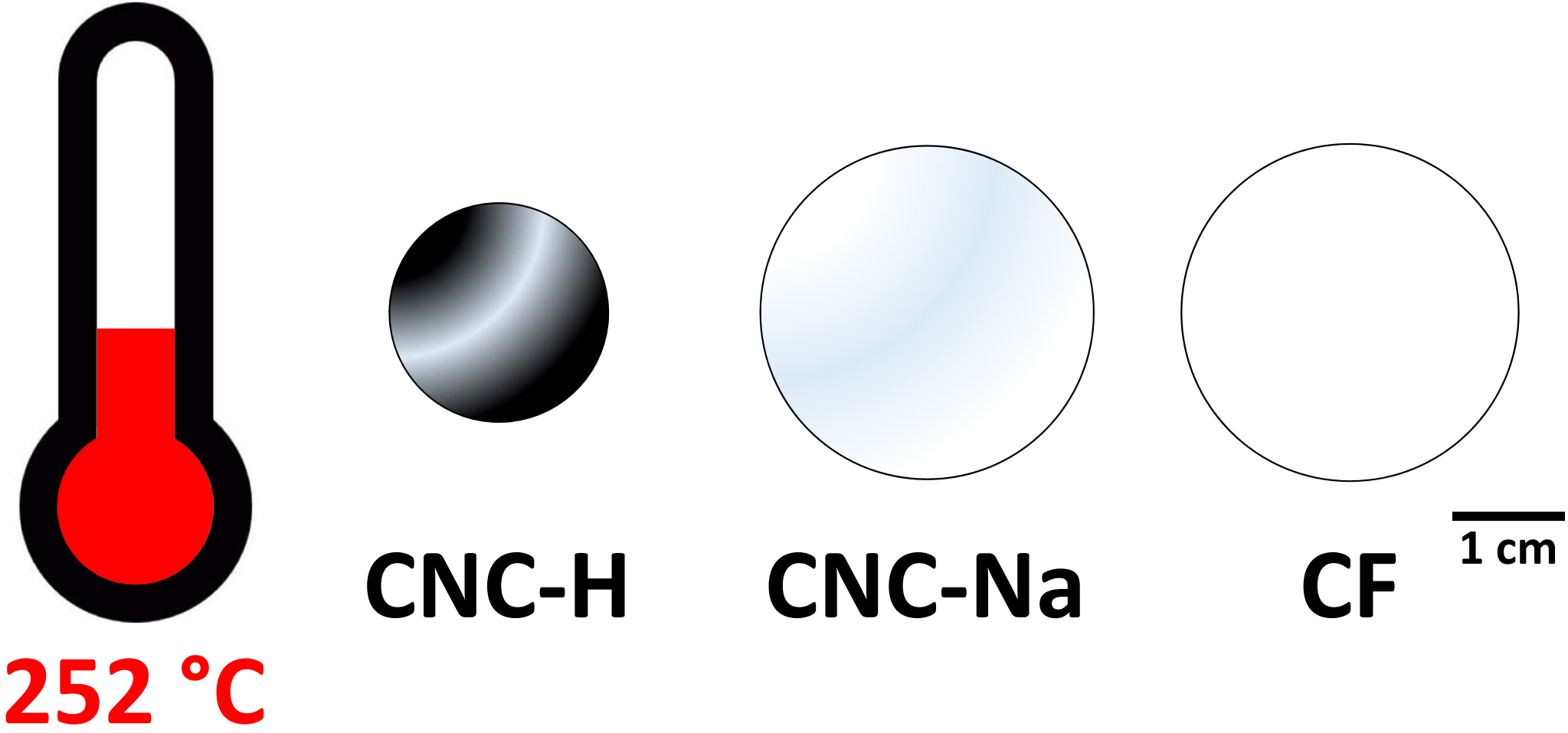

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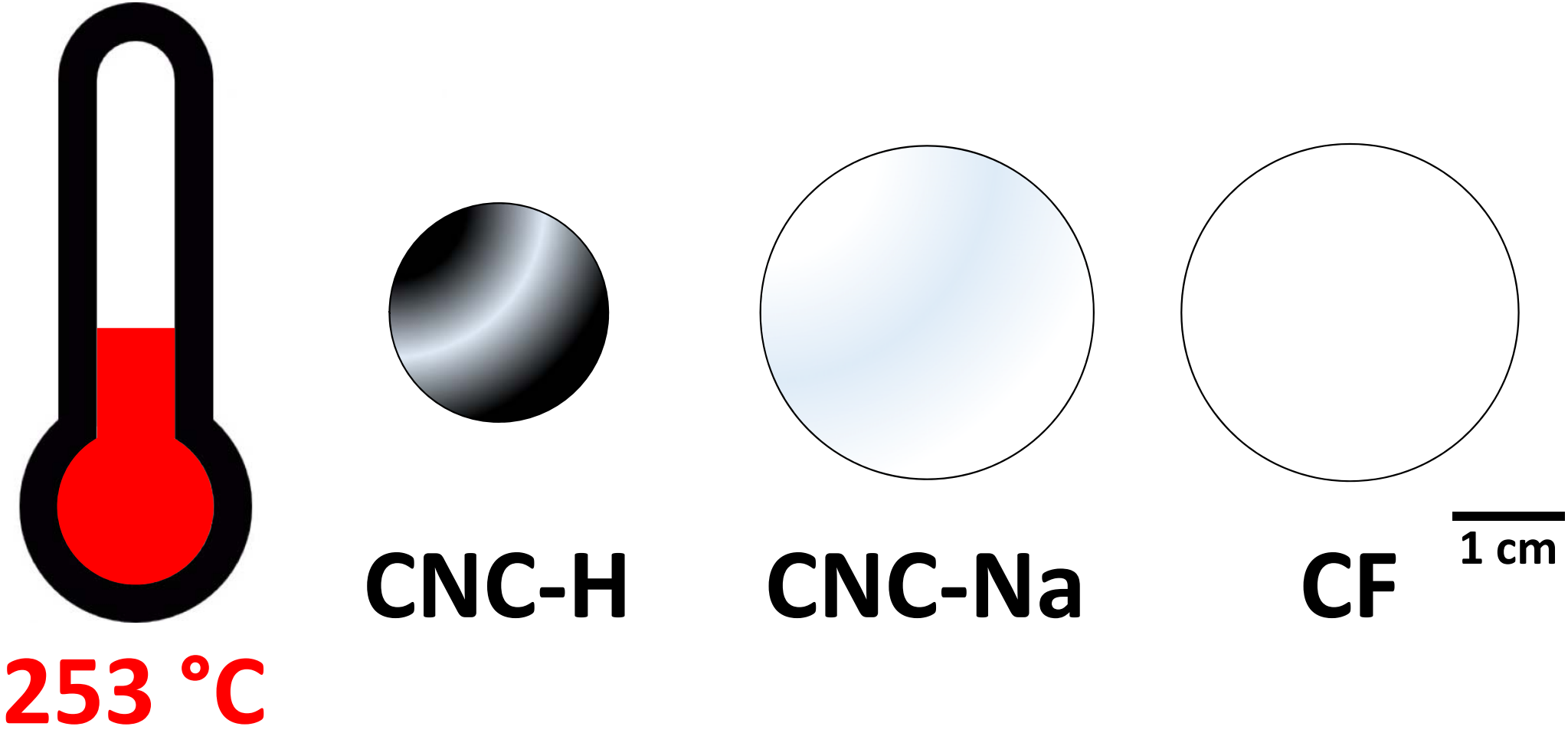

Results

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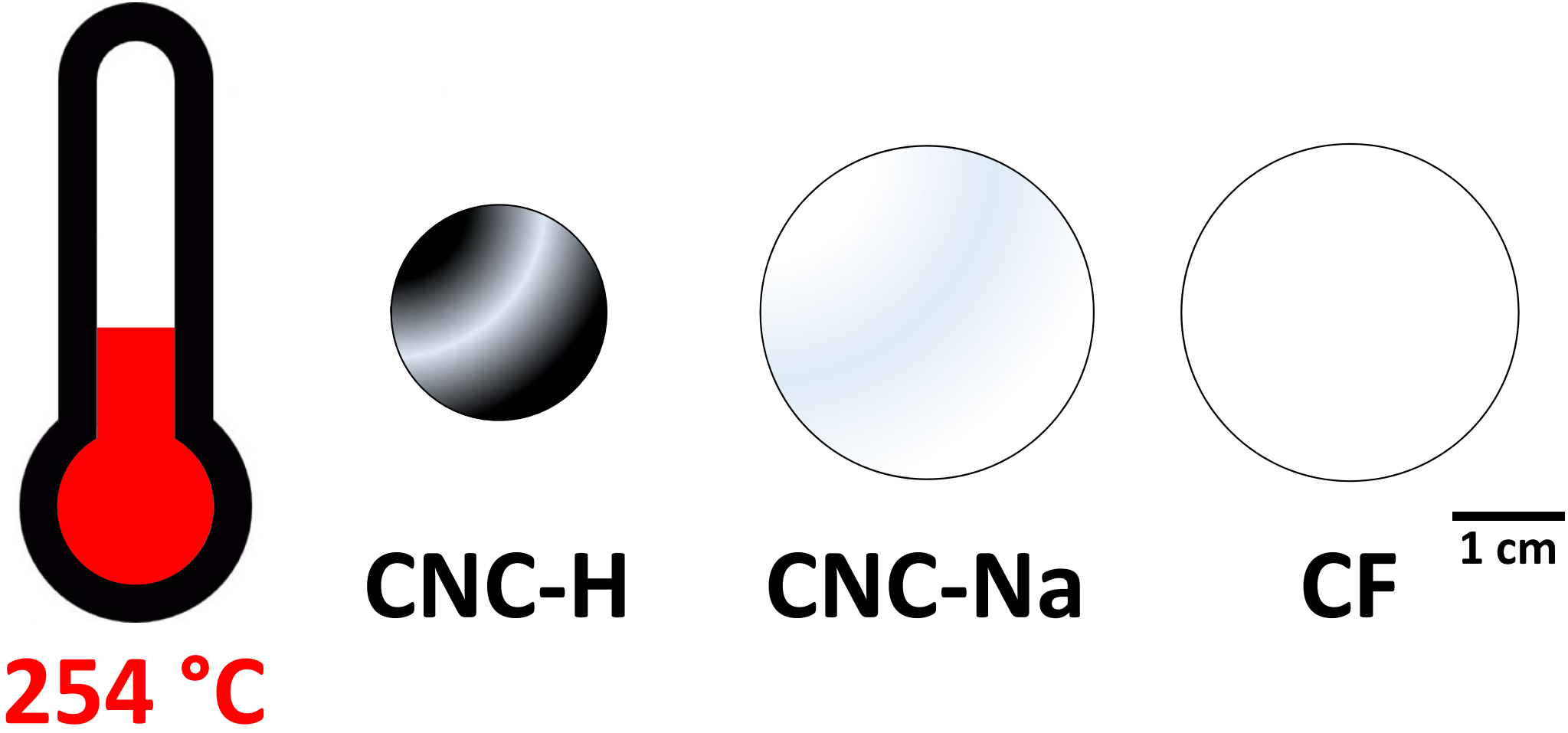

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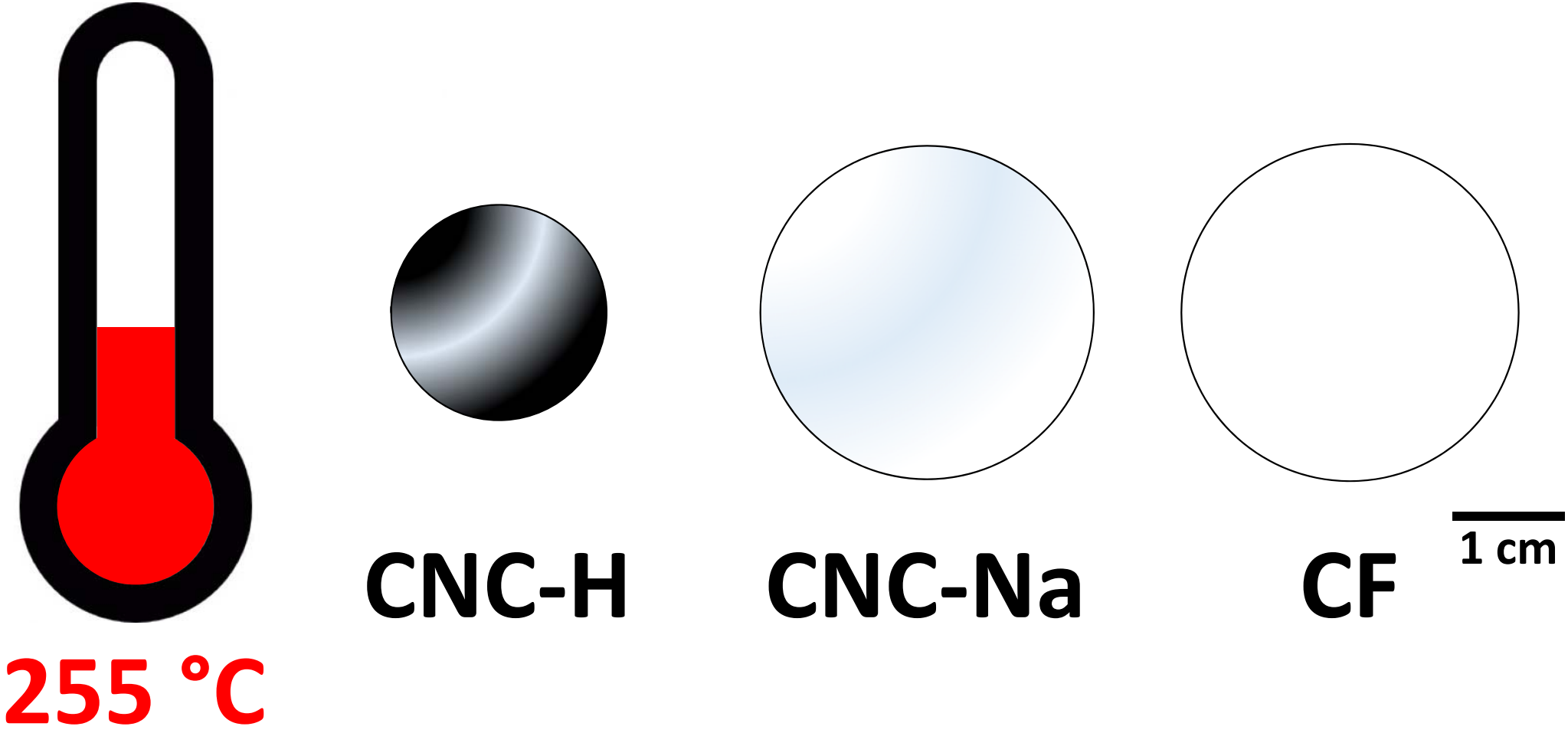

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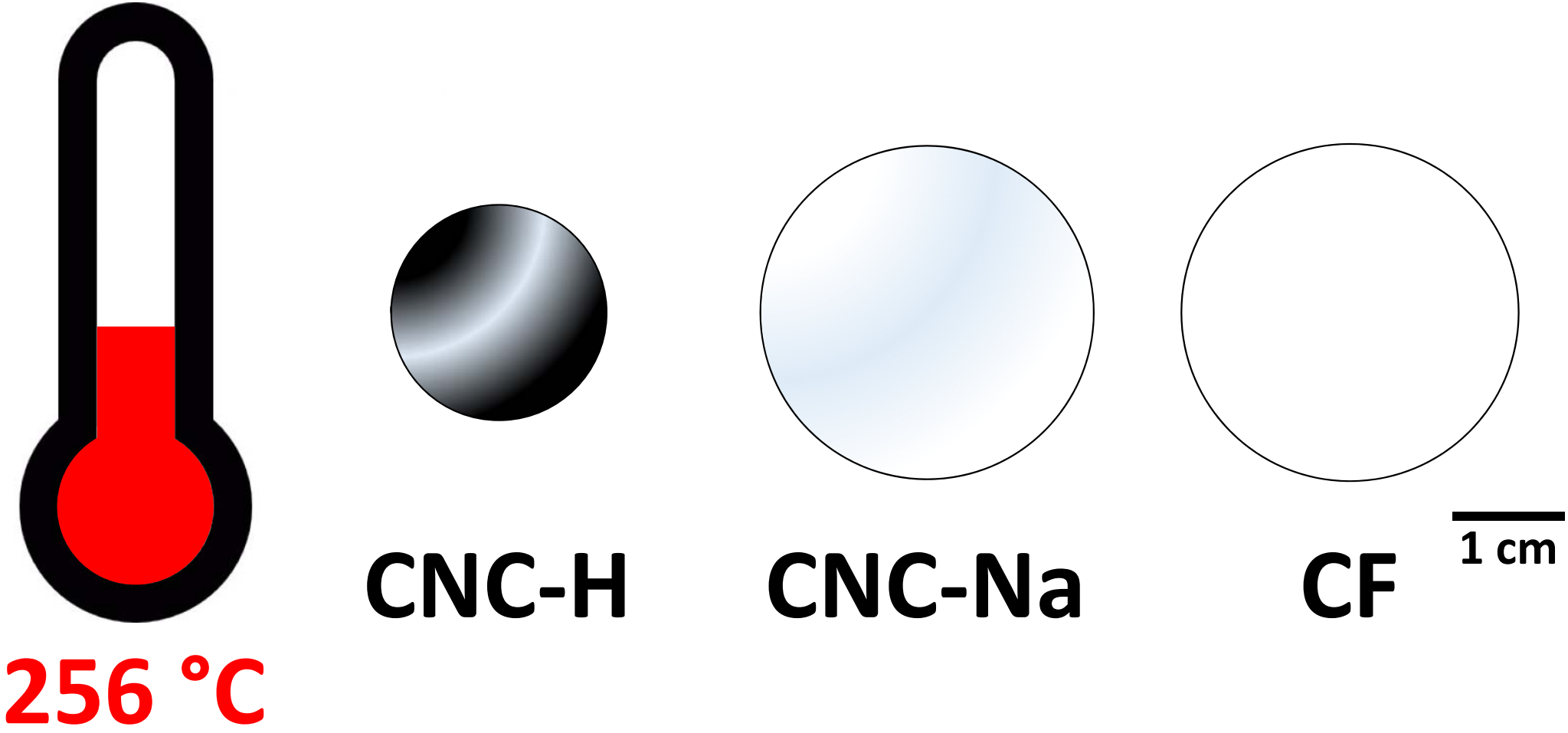

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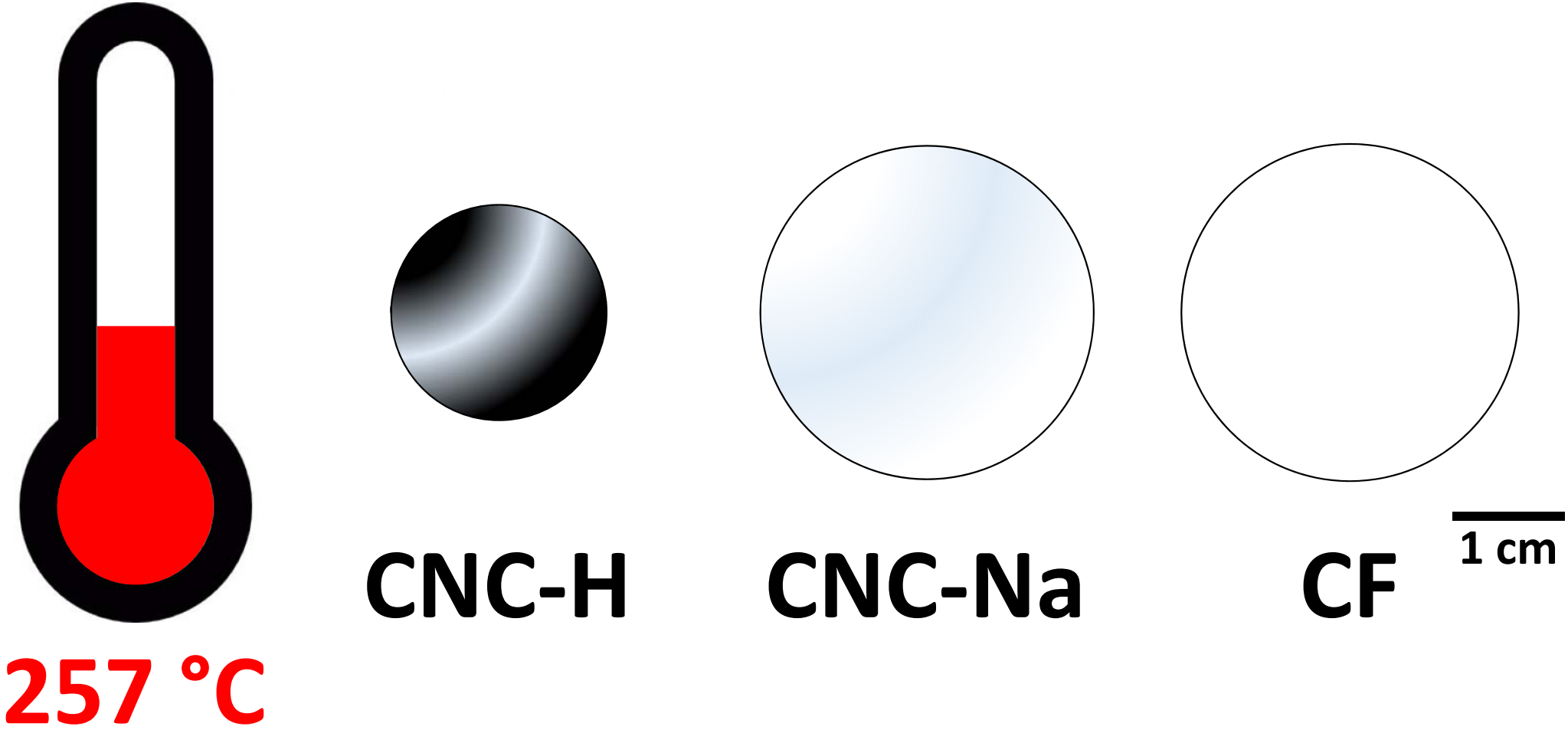

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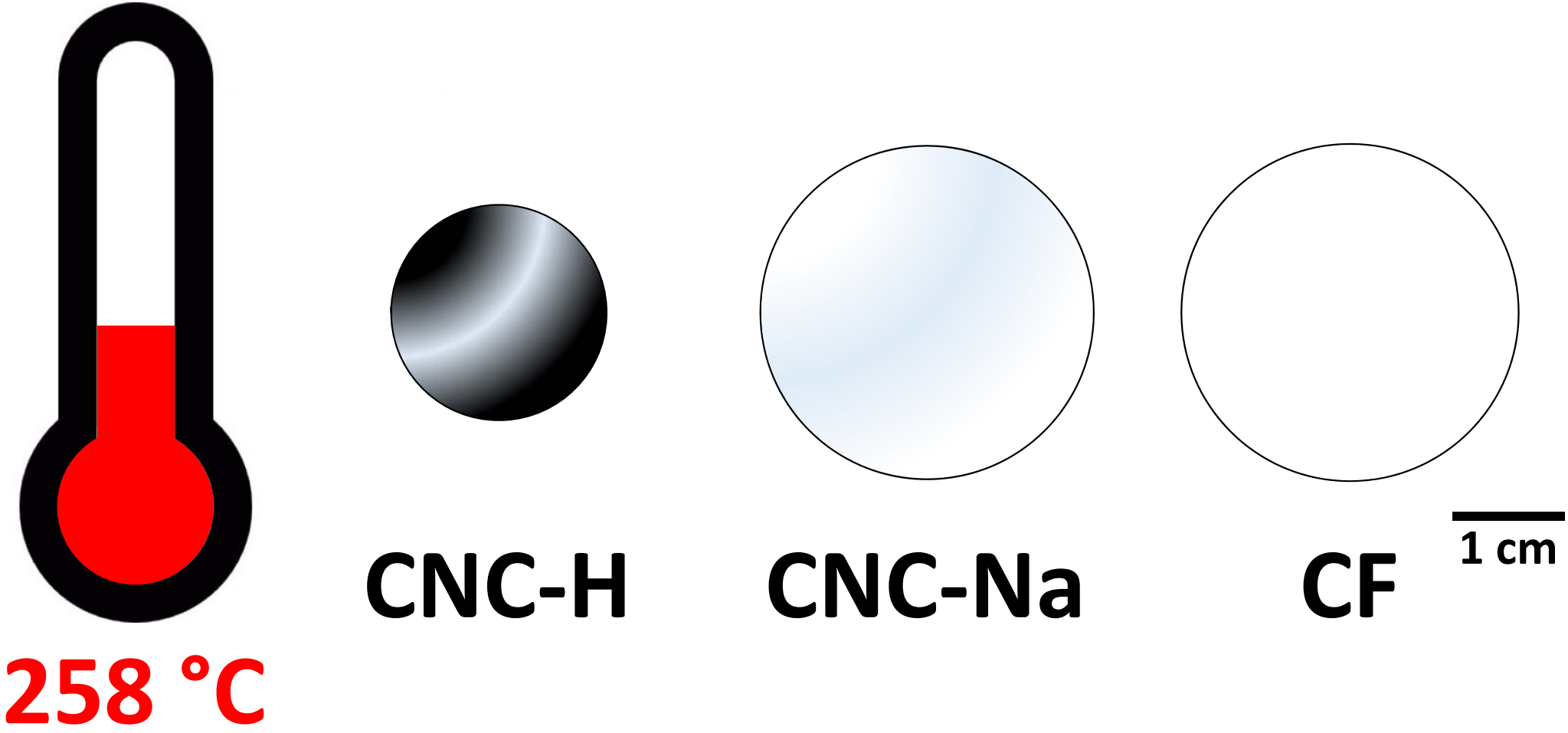

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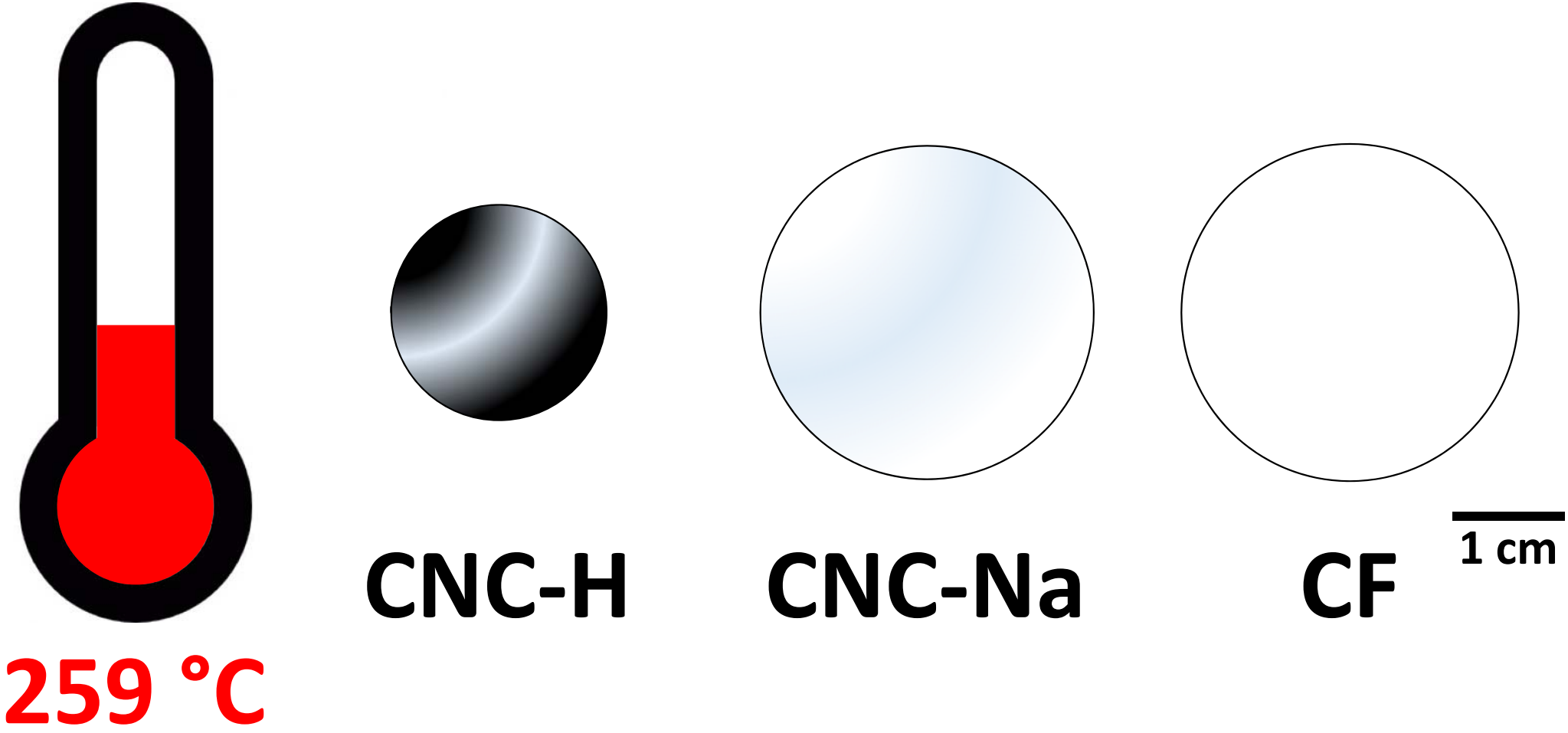

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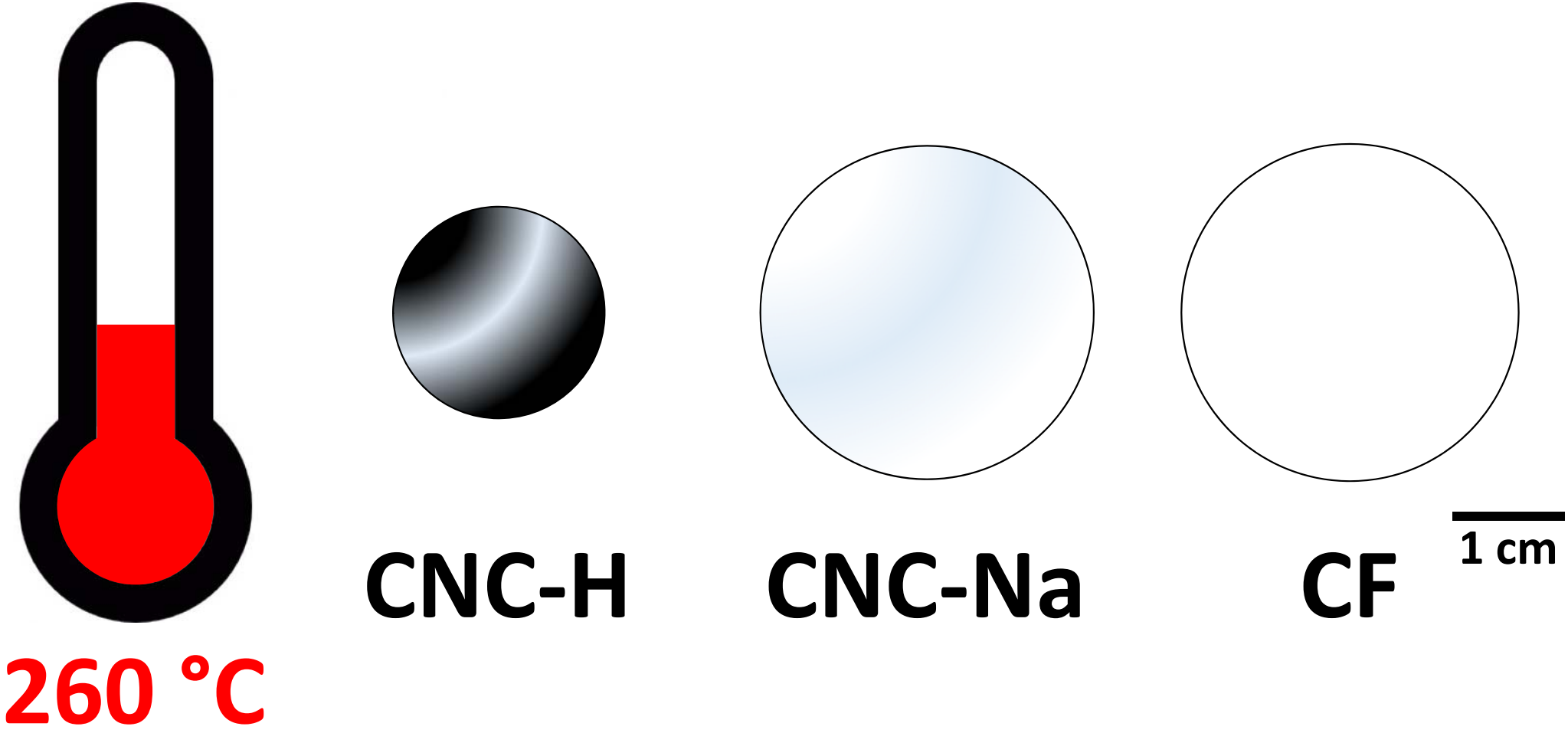

Results

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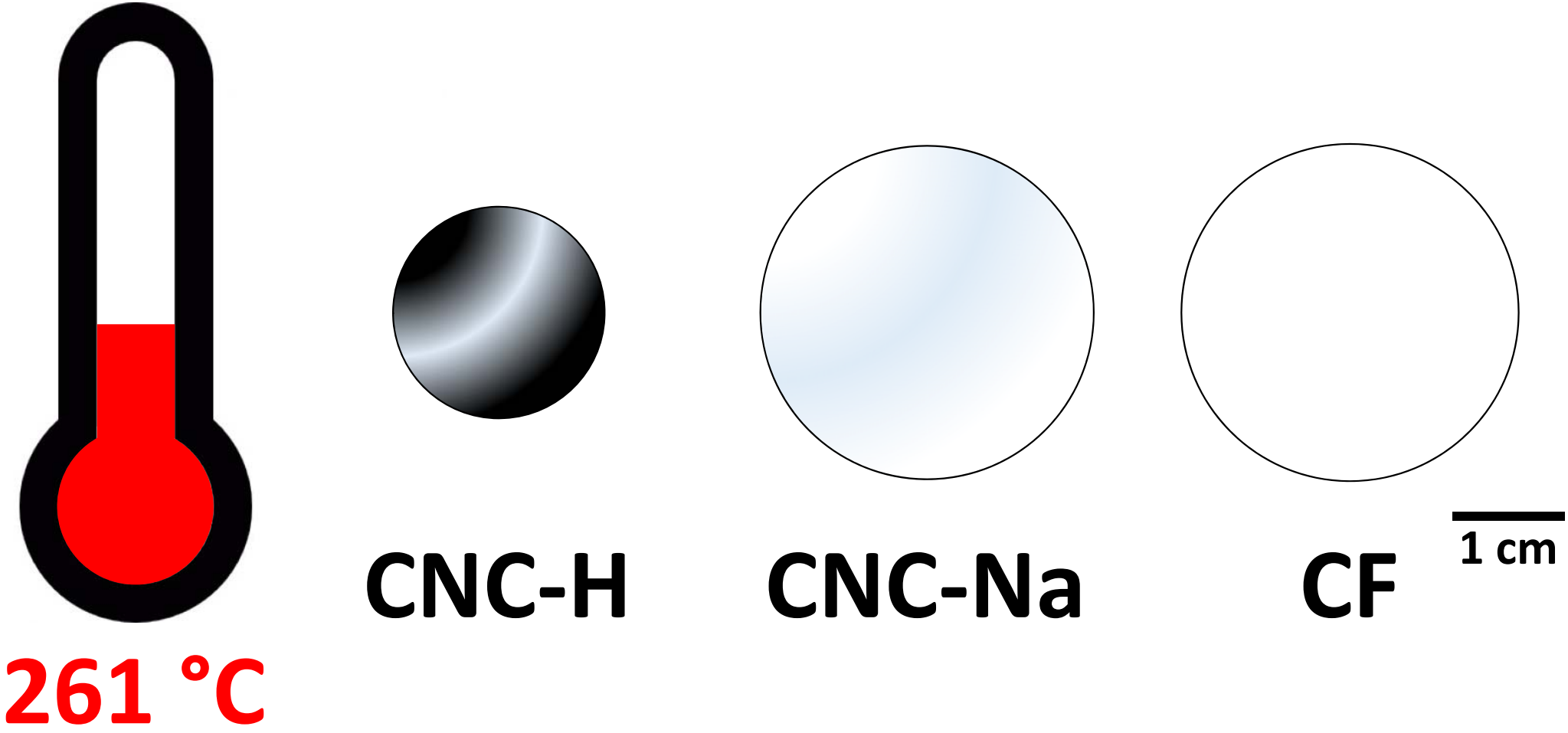

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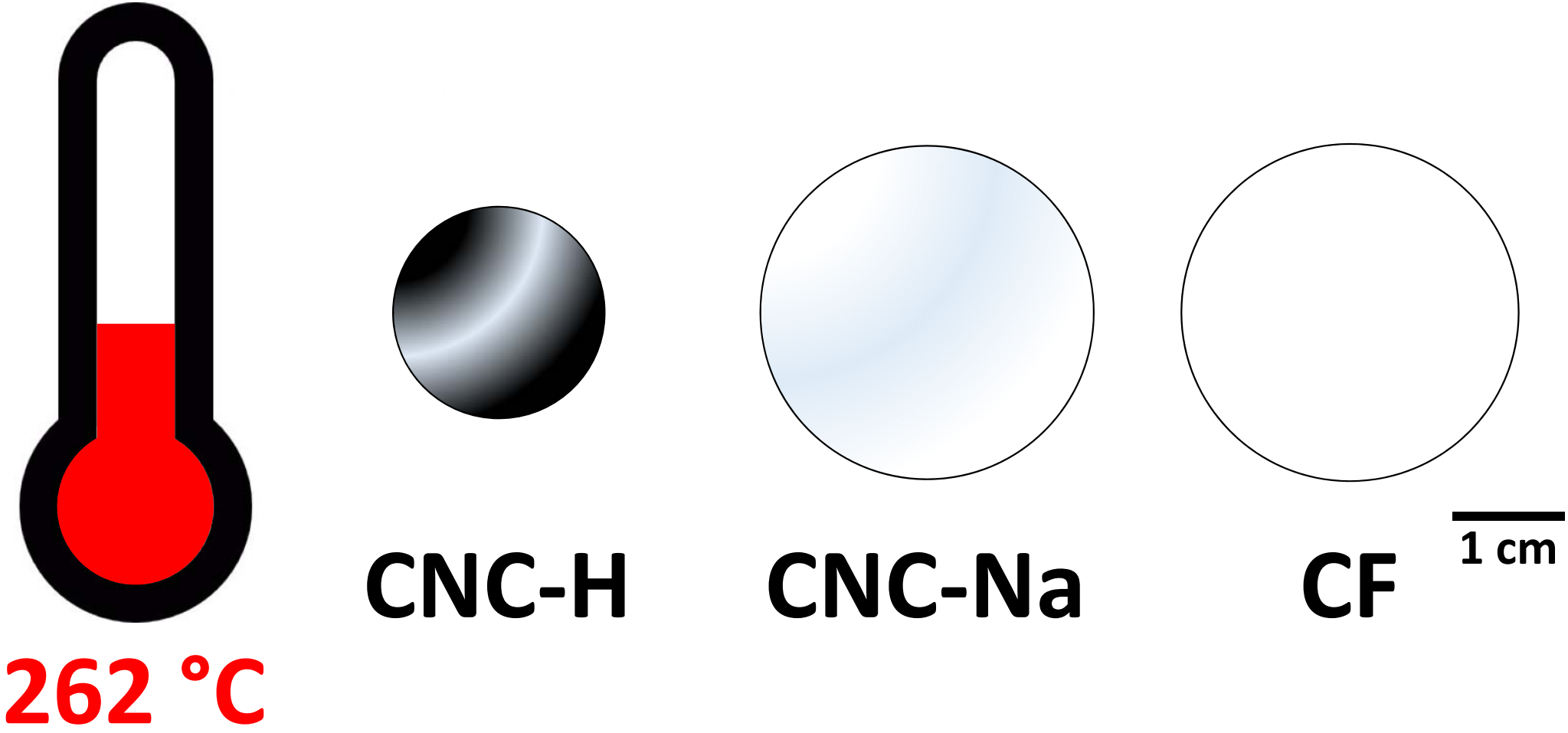

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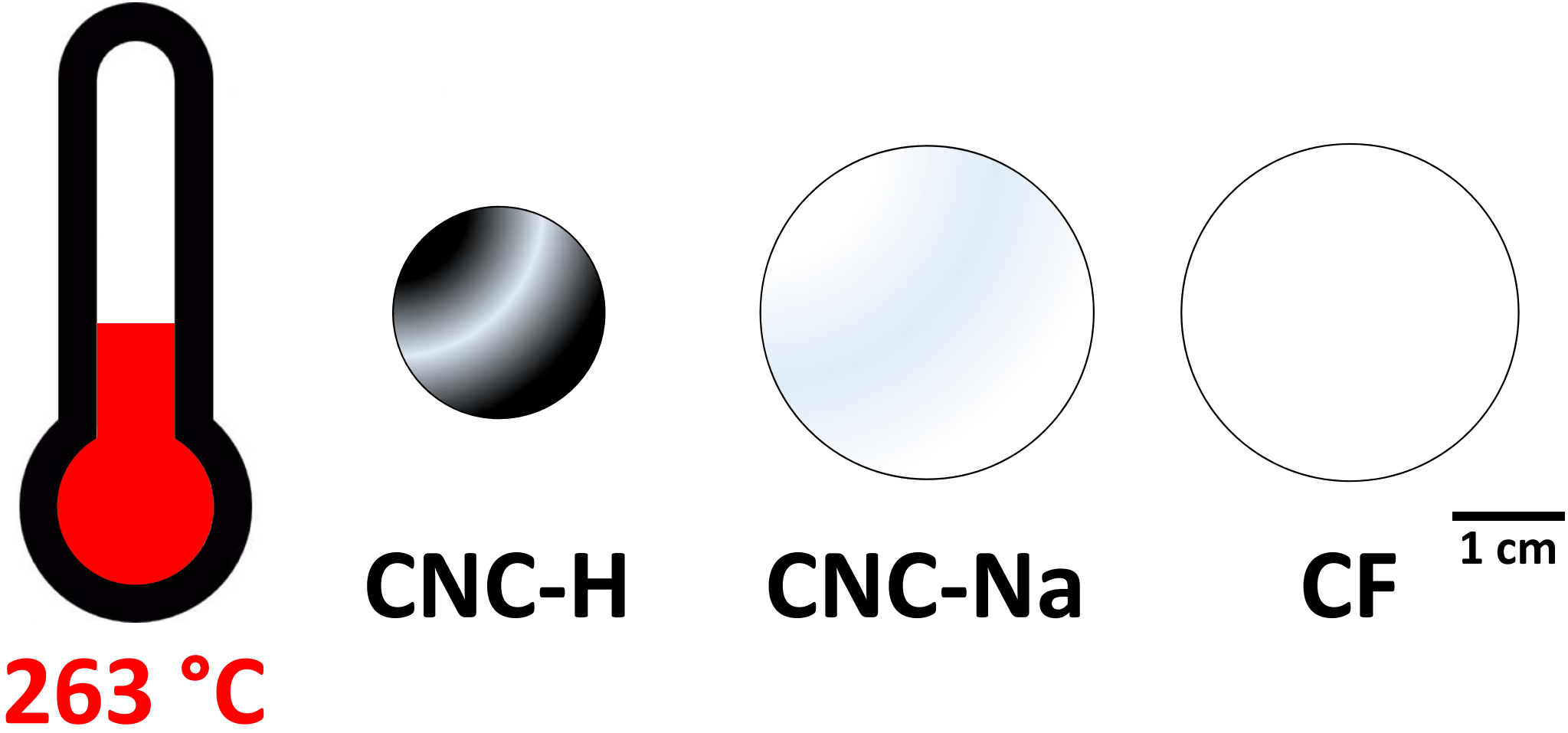

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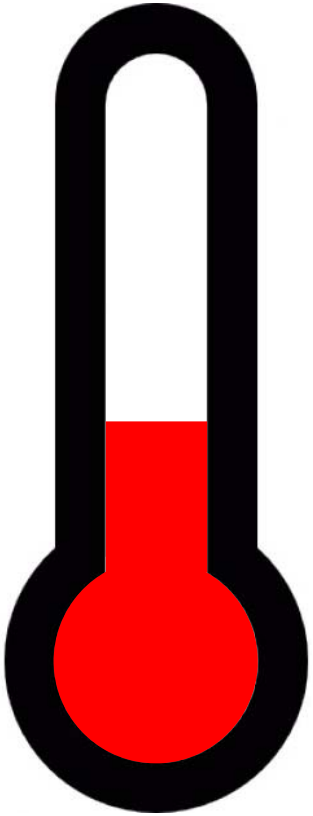
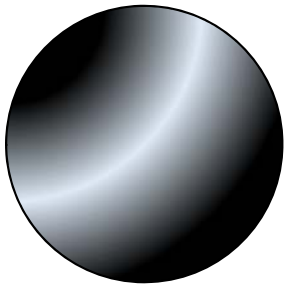
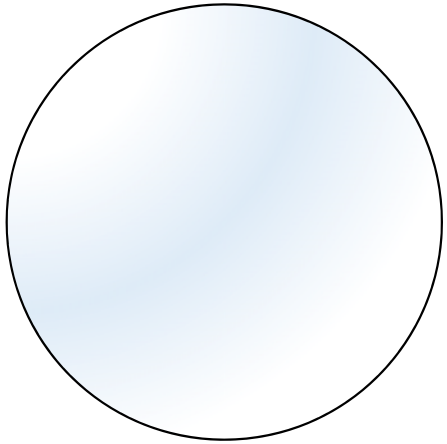


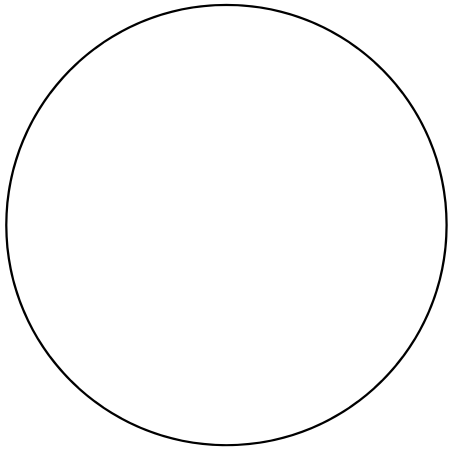
264 °C



CNC-H



CNC-Na

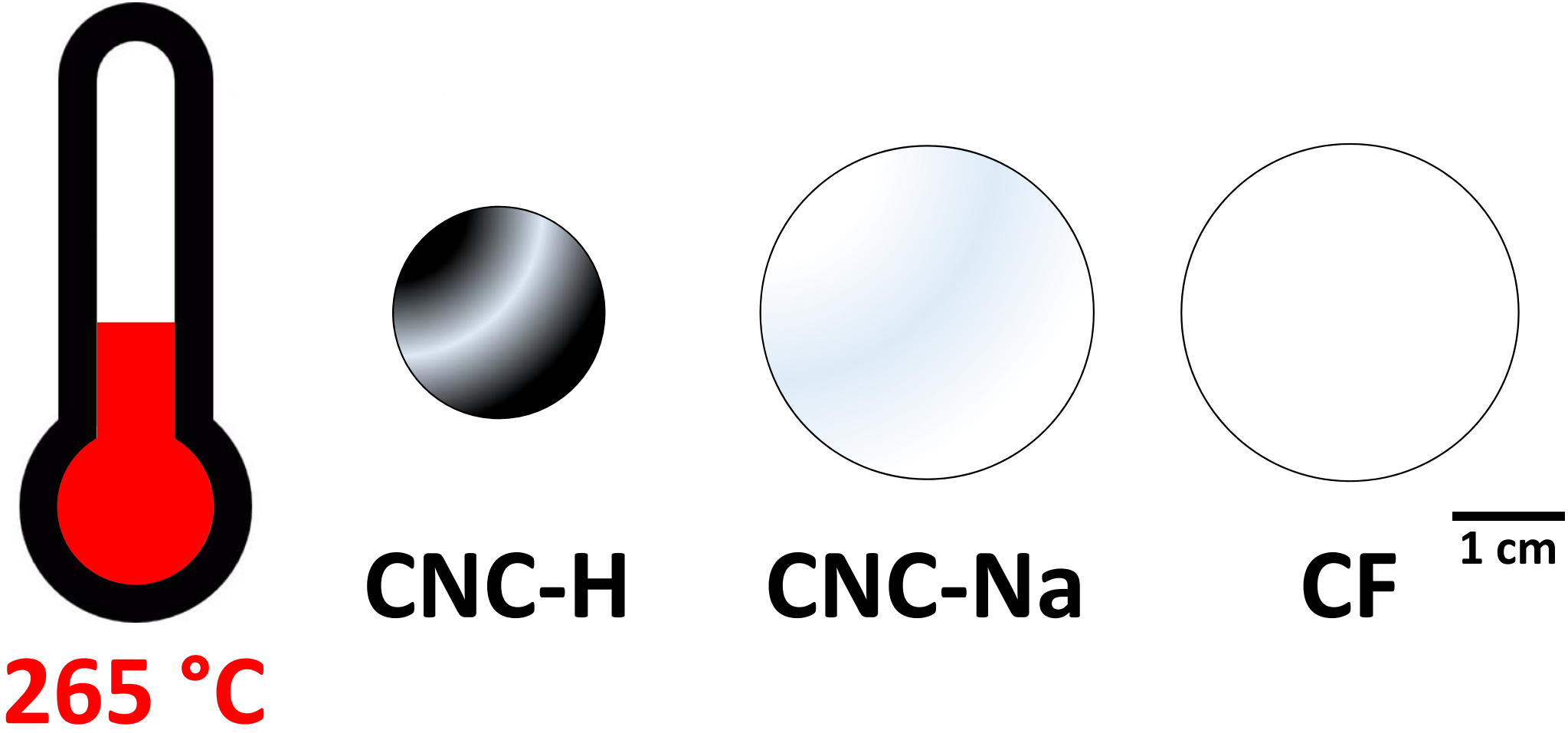


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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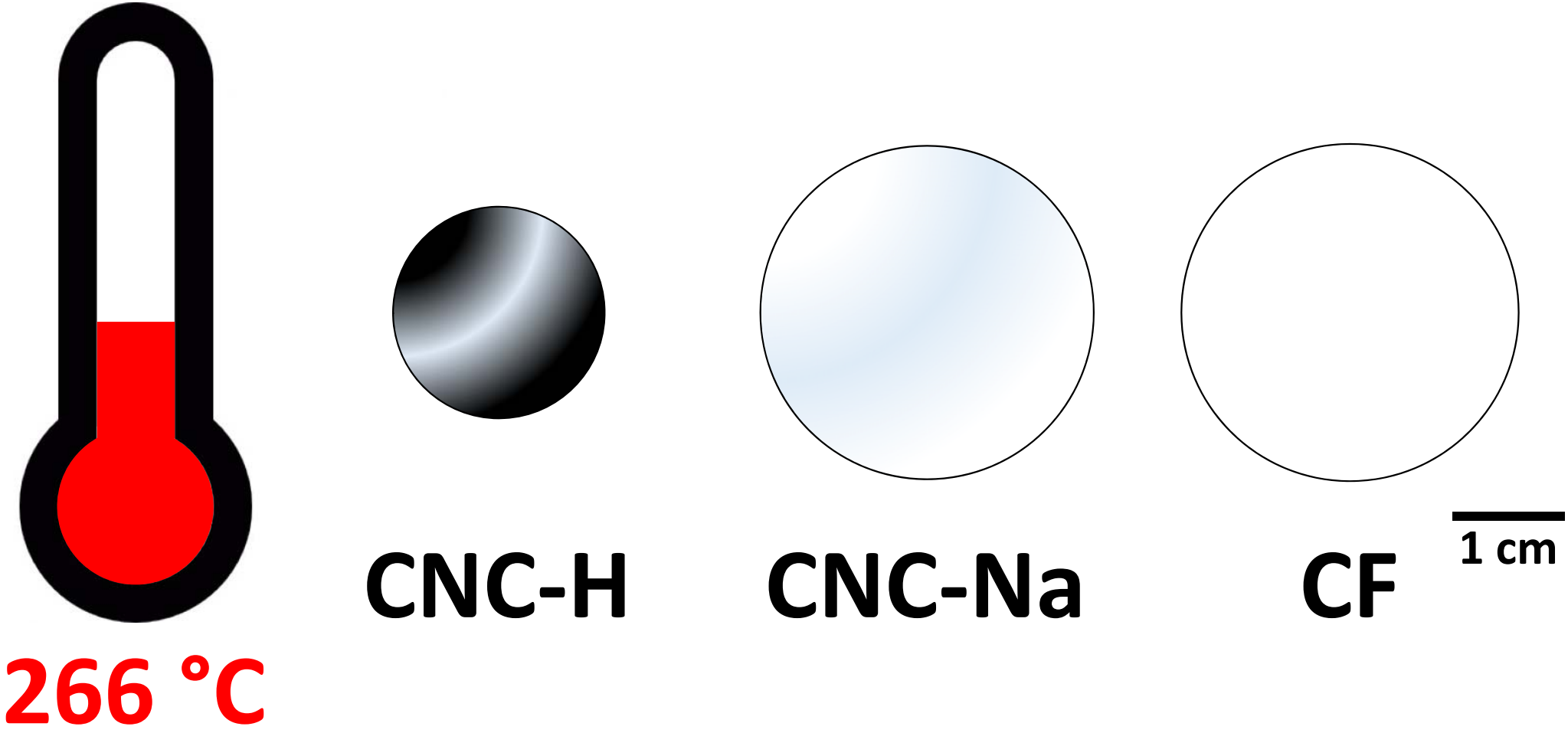

Results

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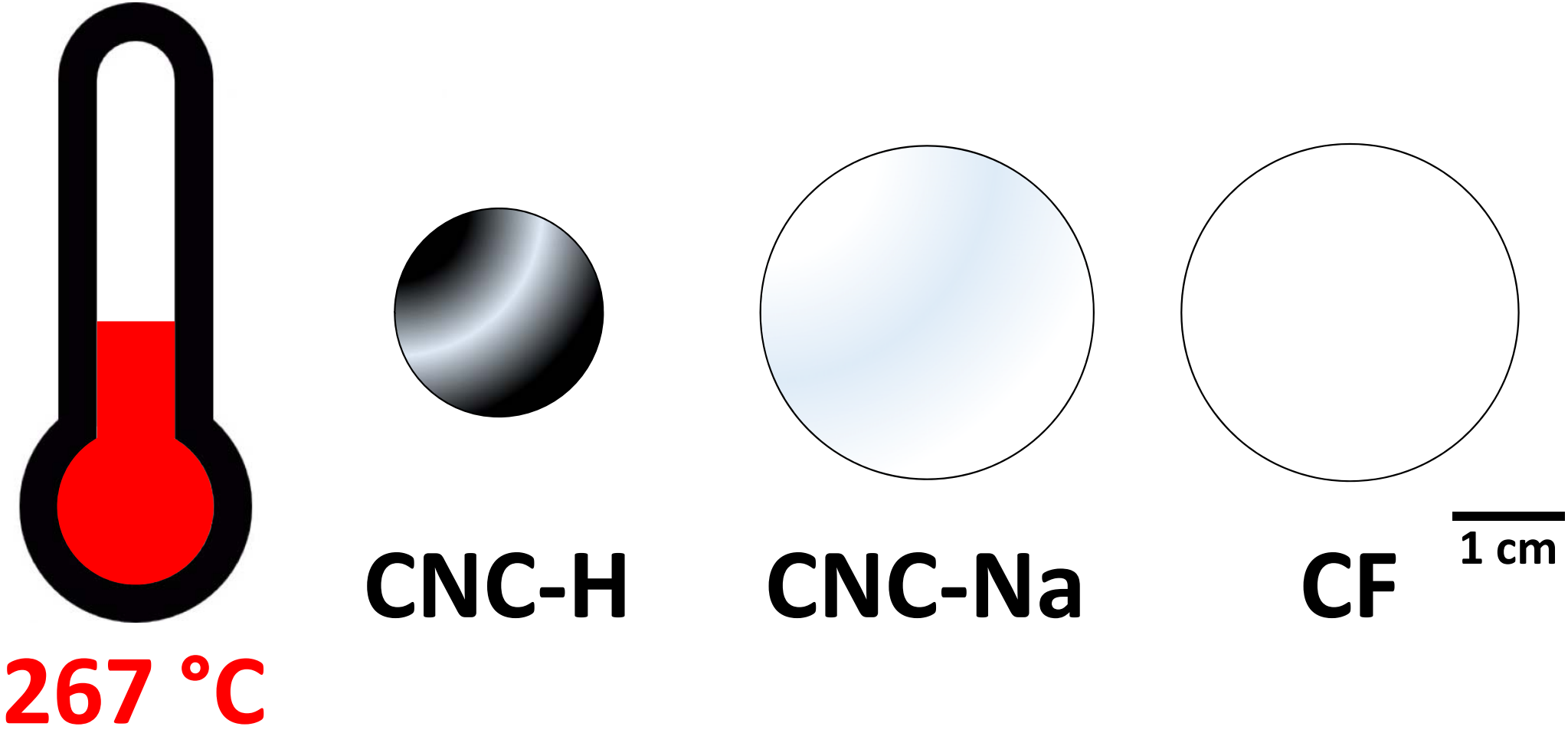

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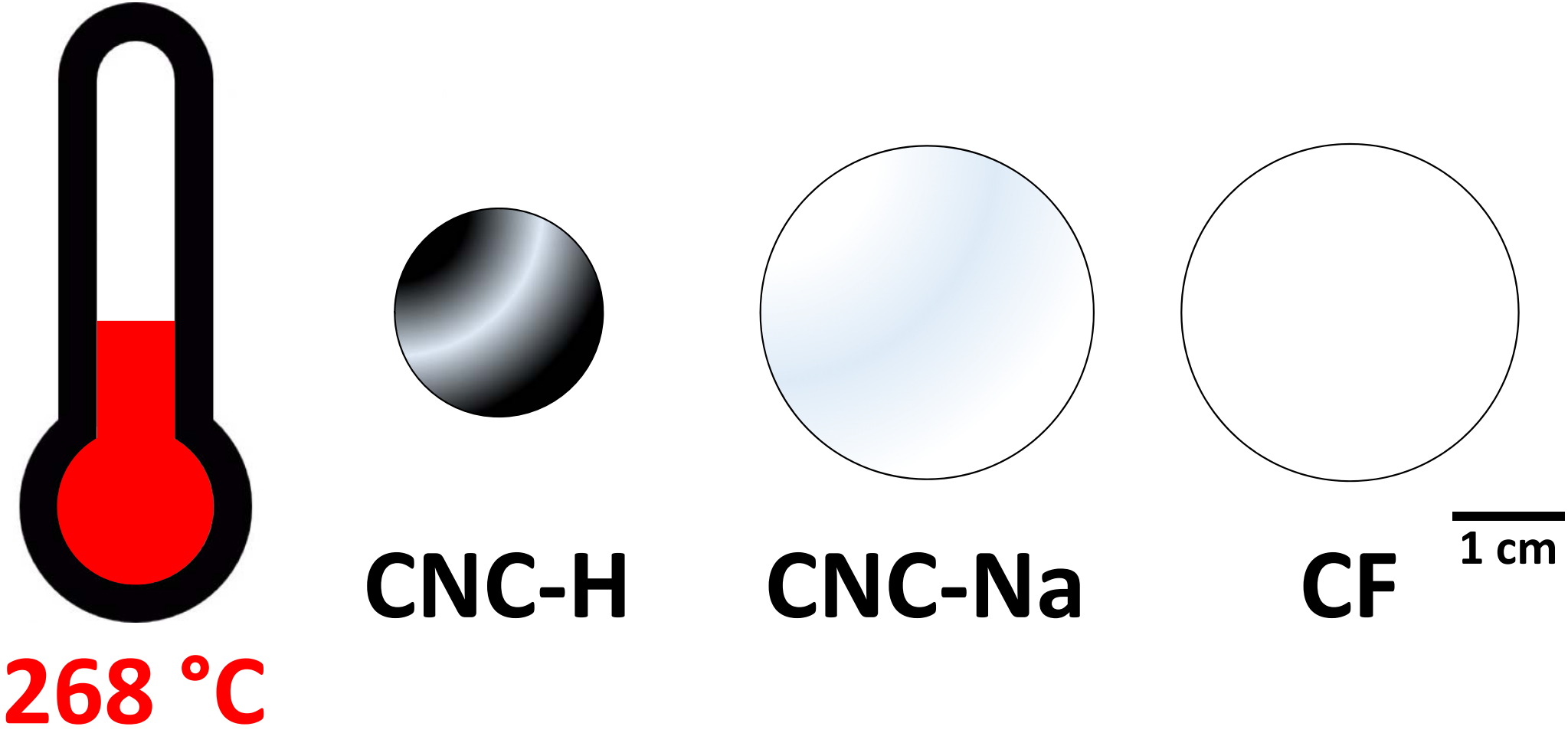

Results

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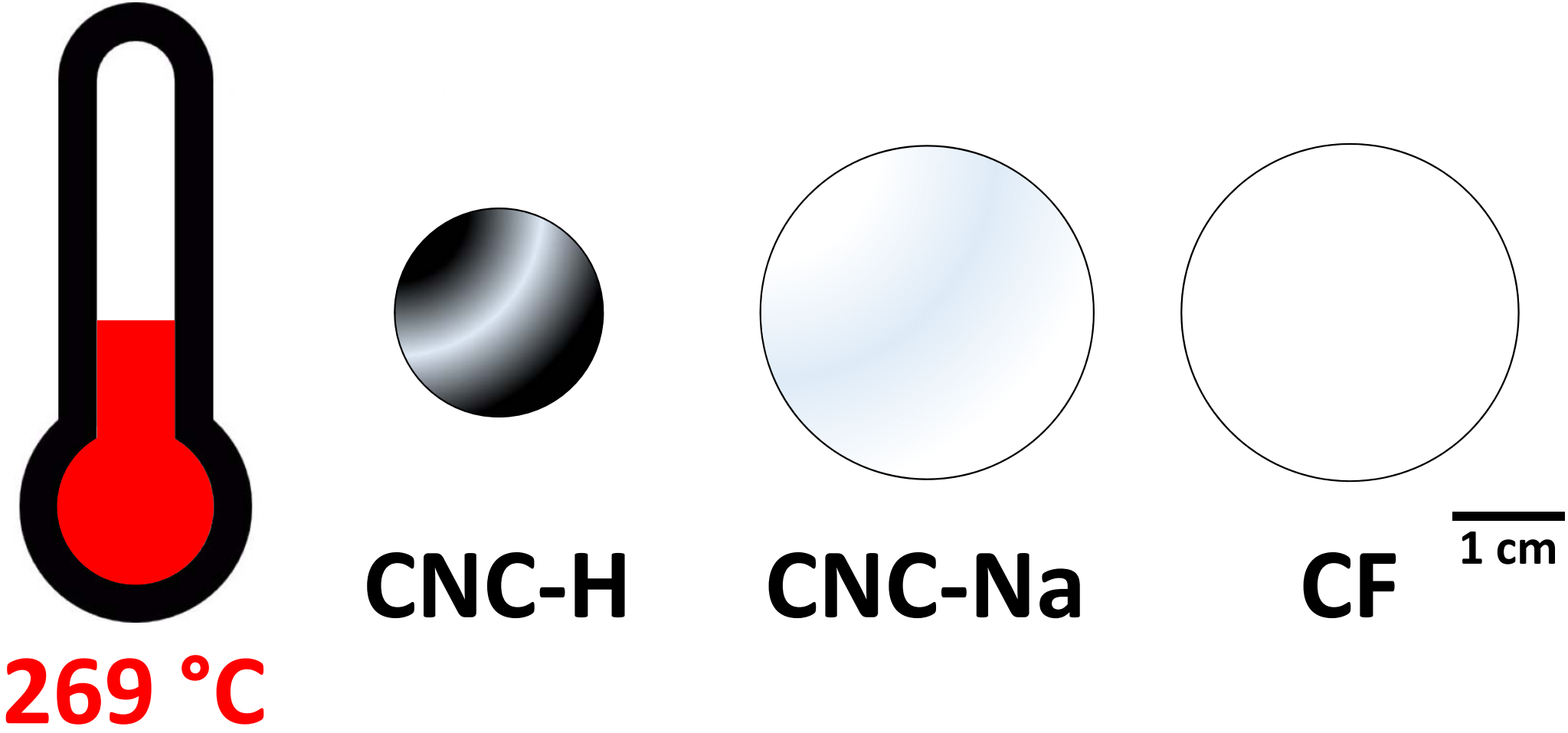

Results

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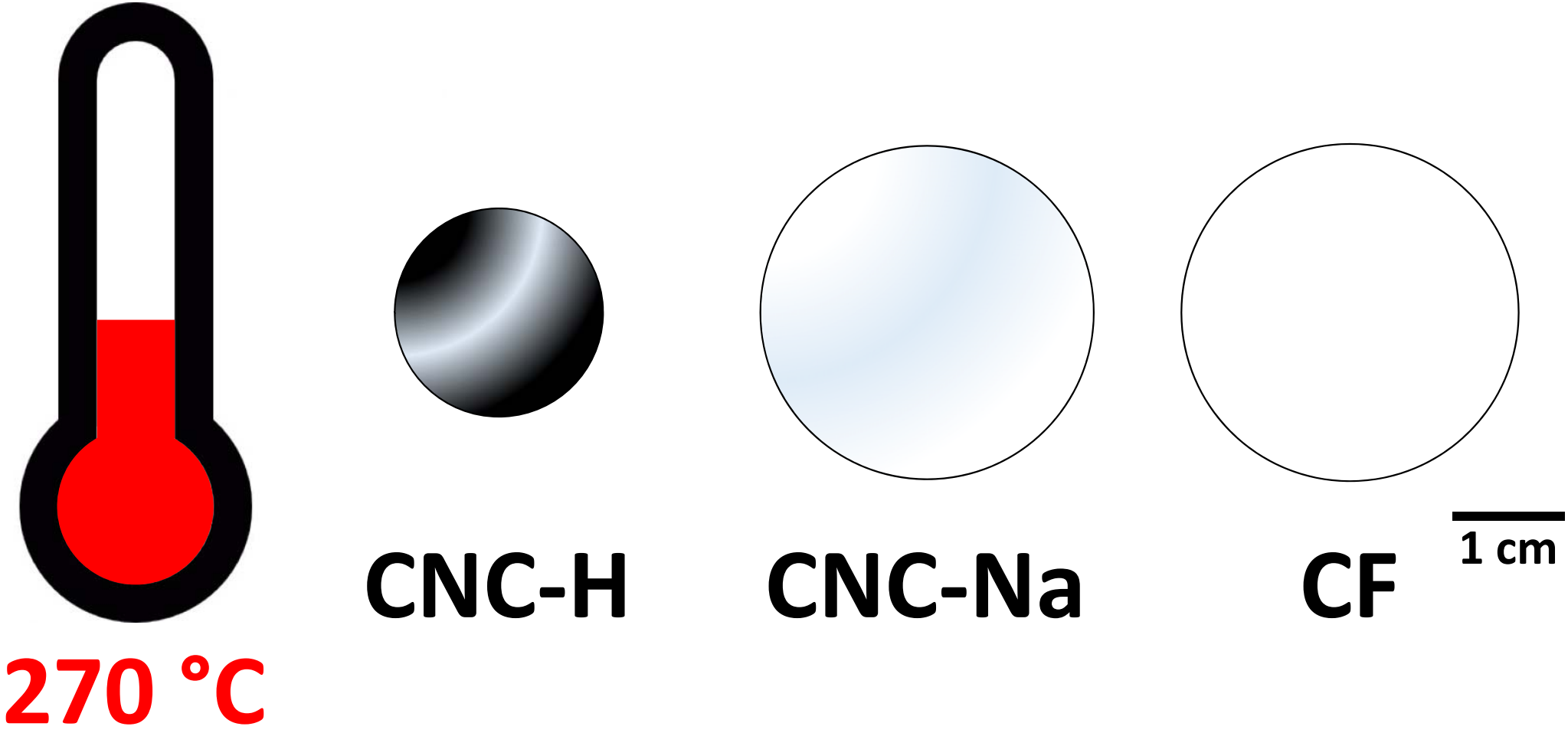

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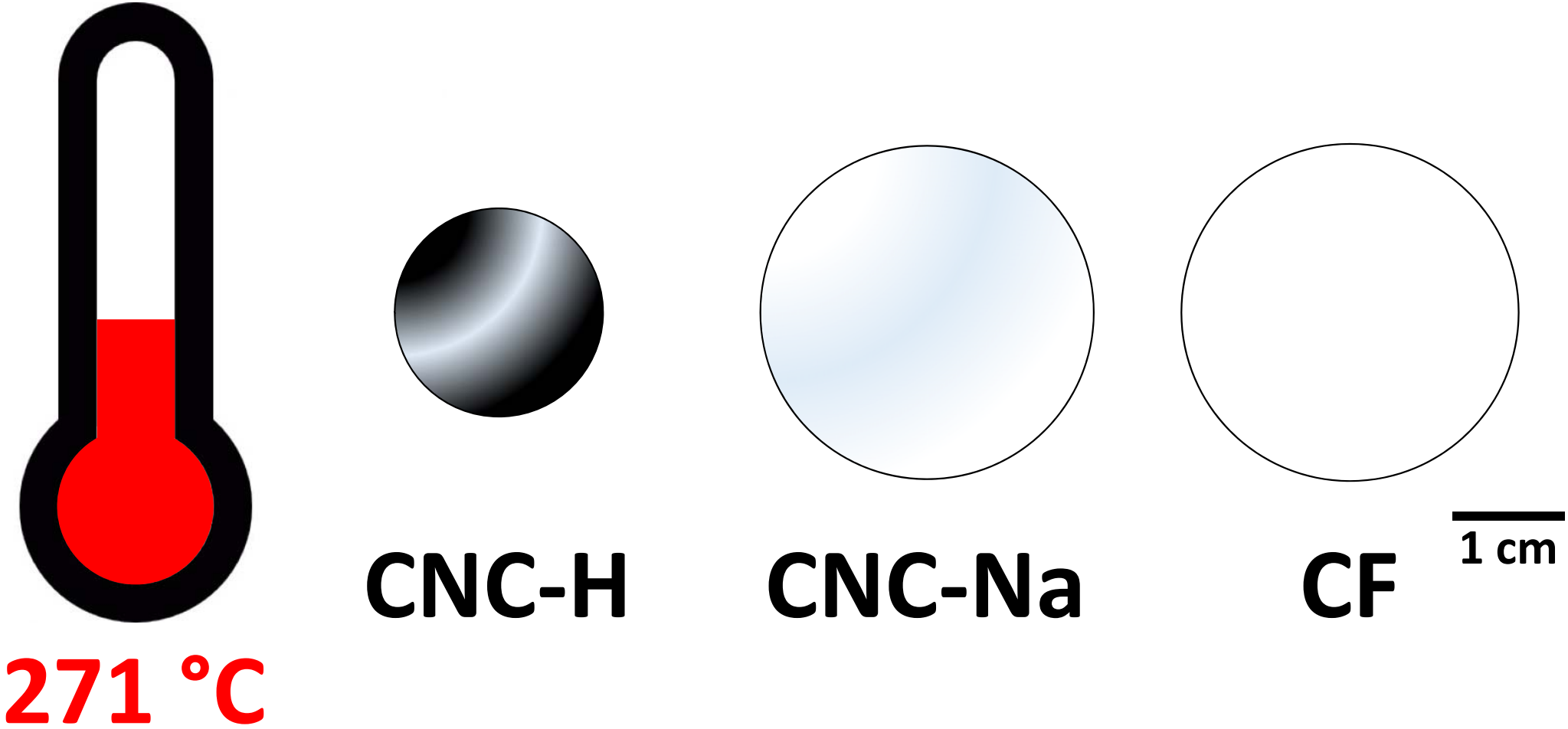

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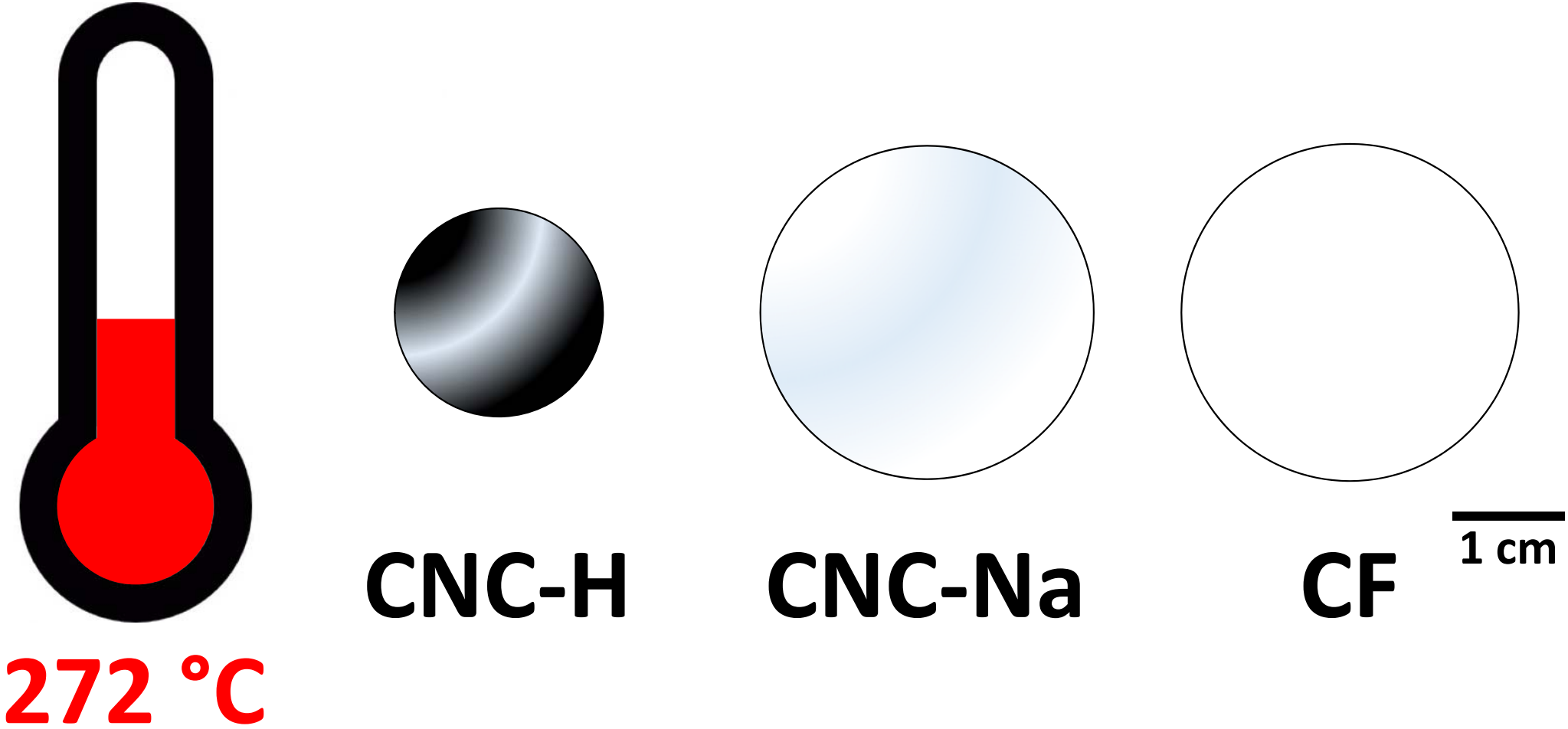

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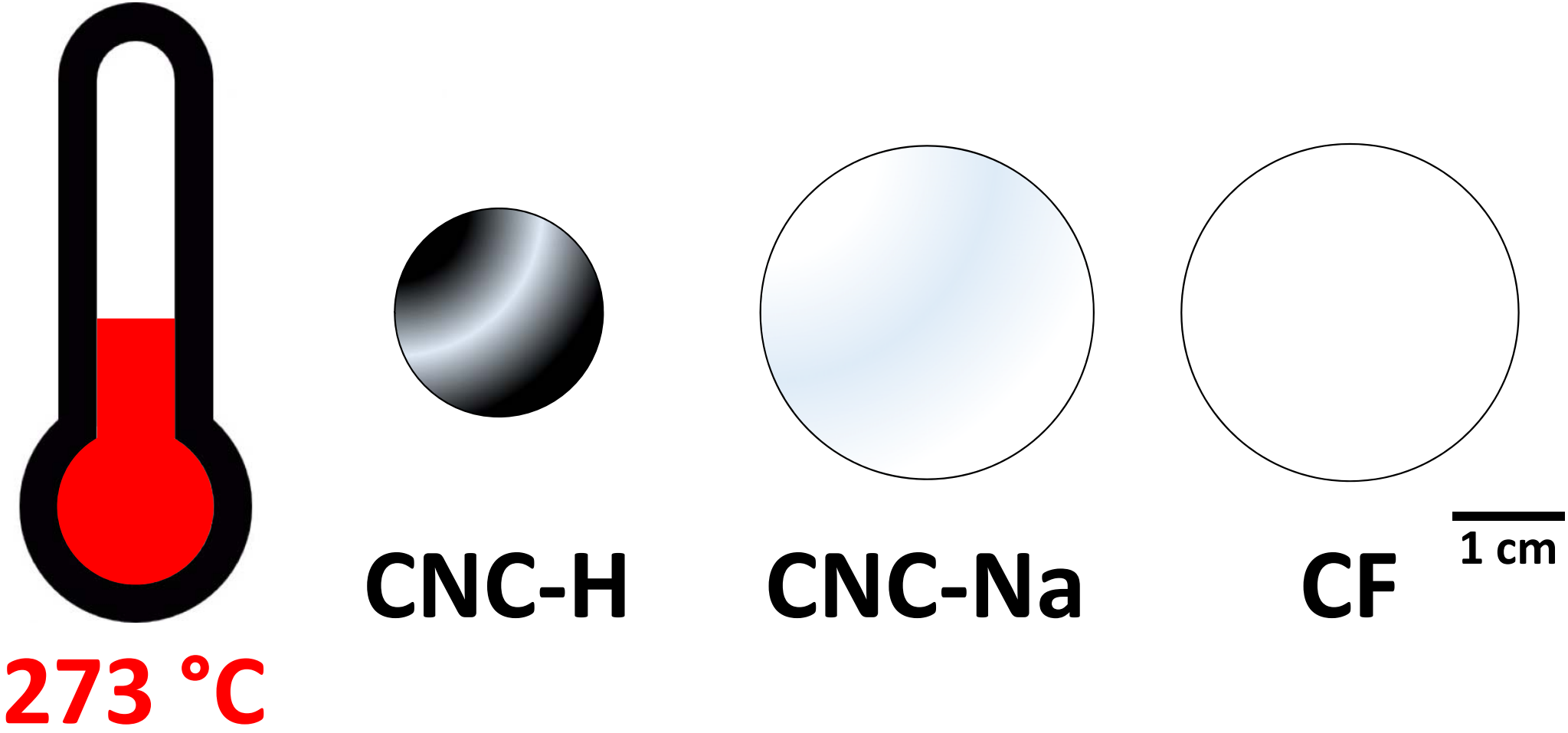

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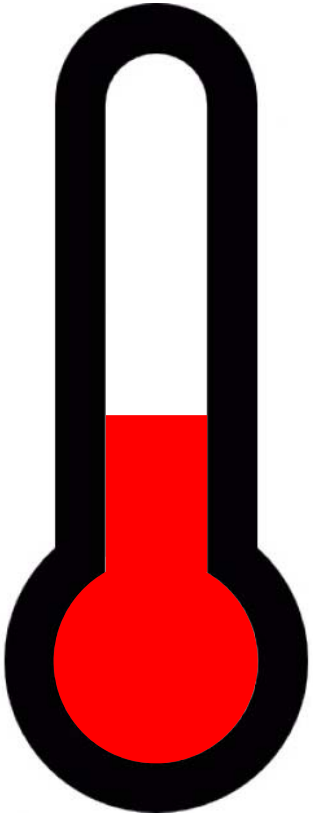
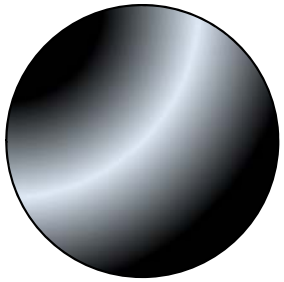
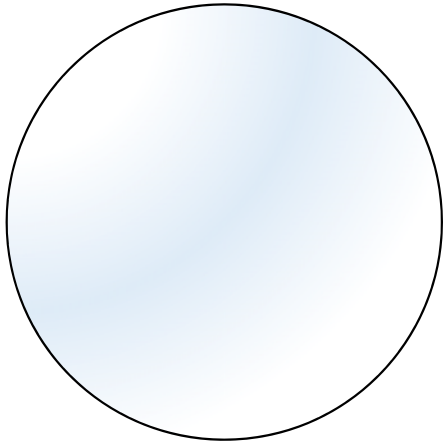


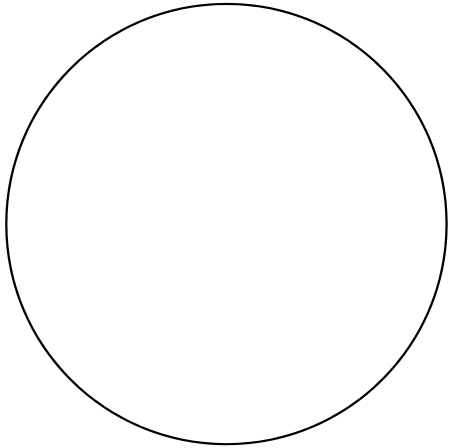
274 °C



CNC-H



CNC-Na

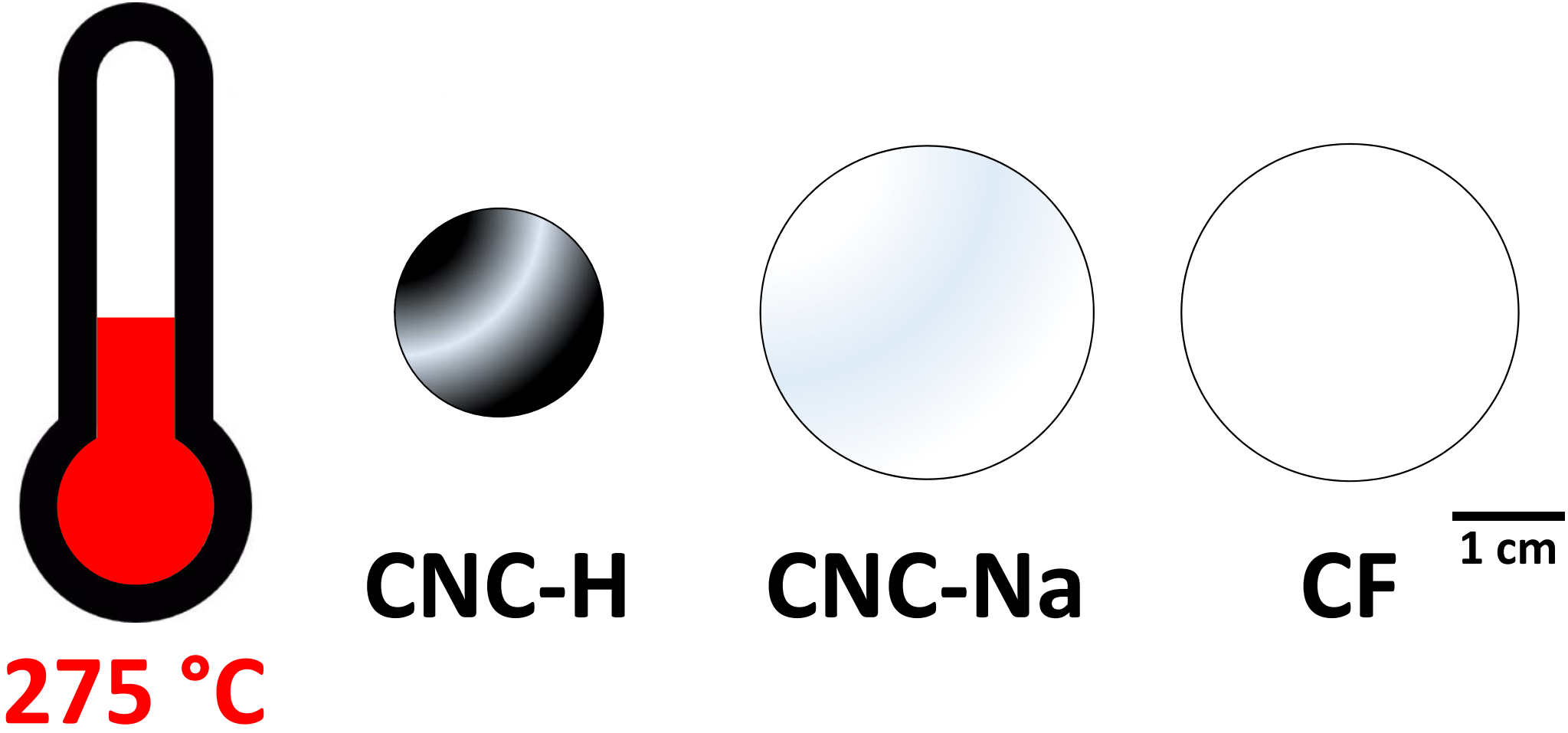


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



Results

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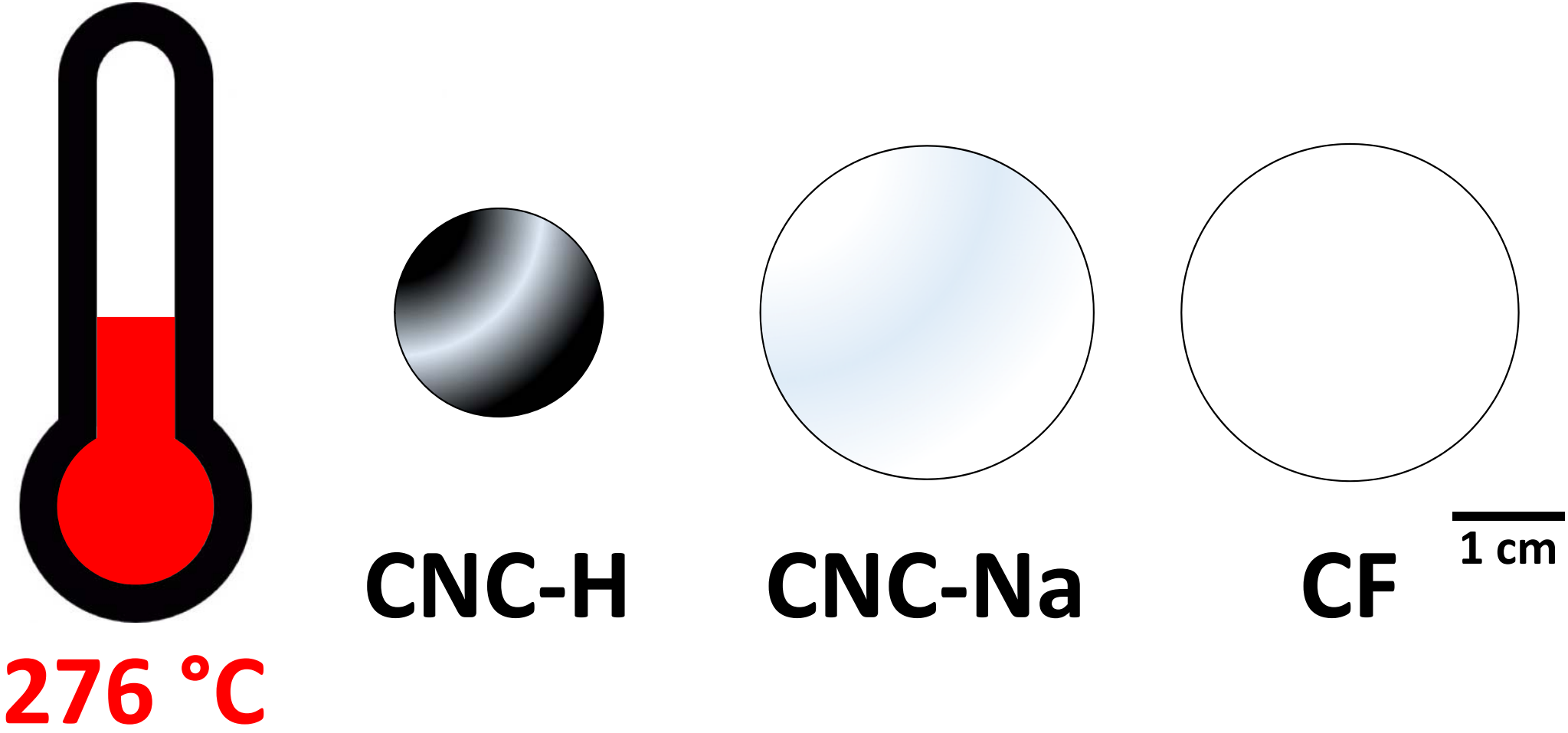

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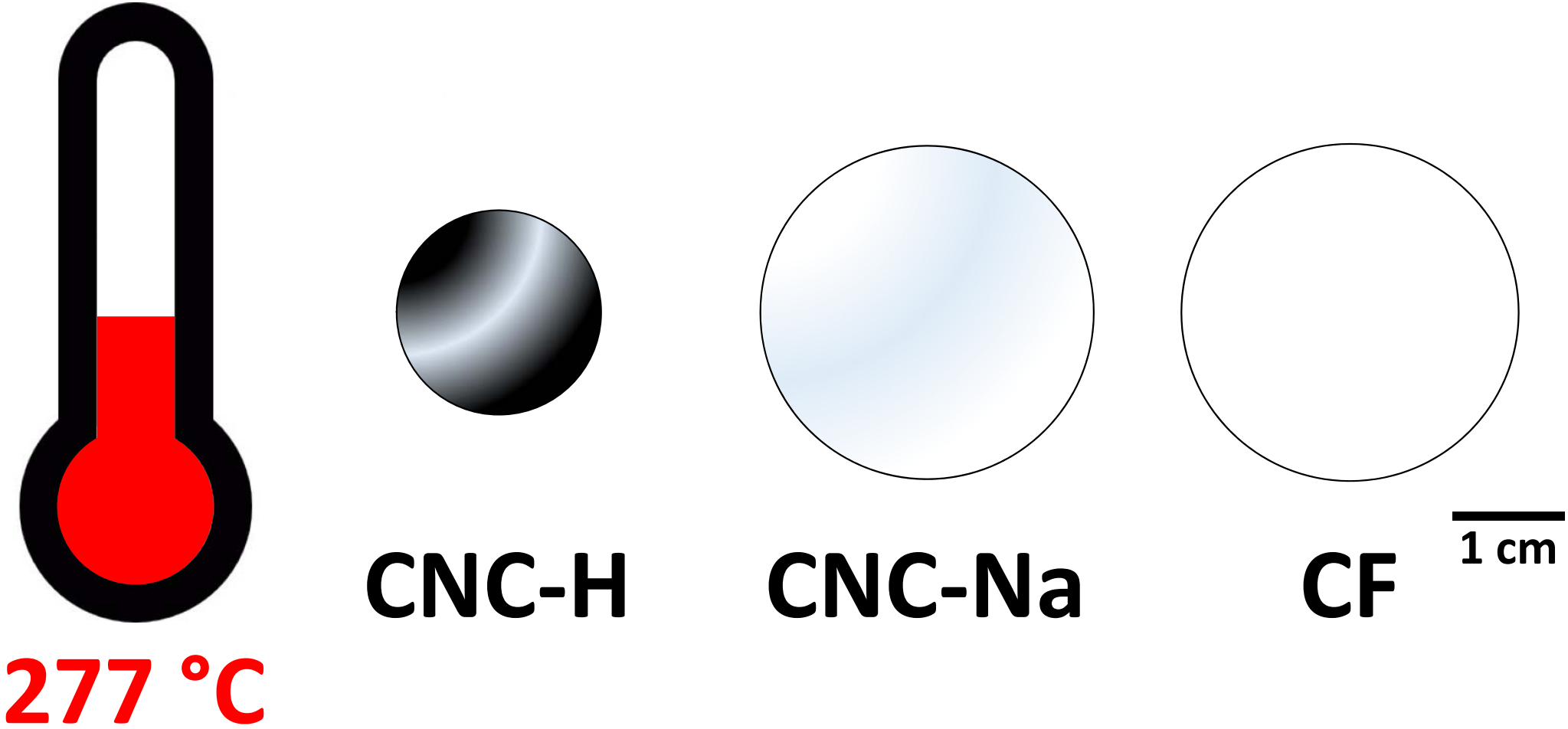

Results

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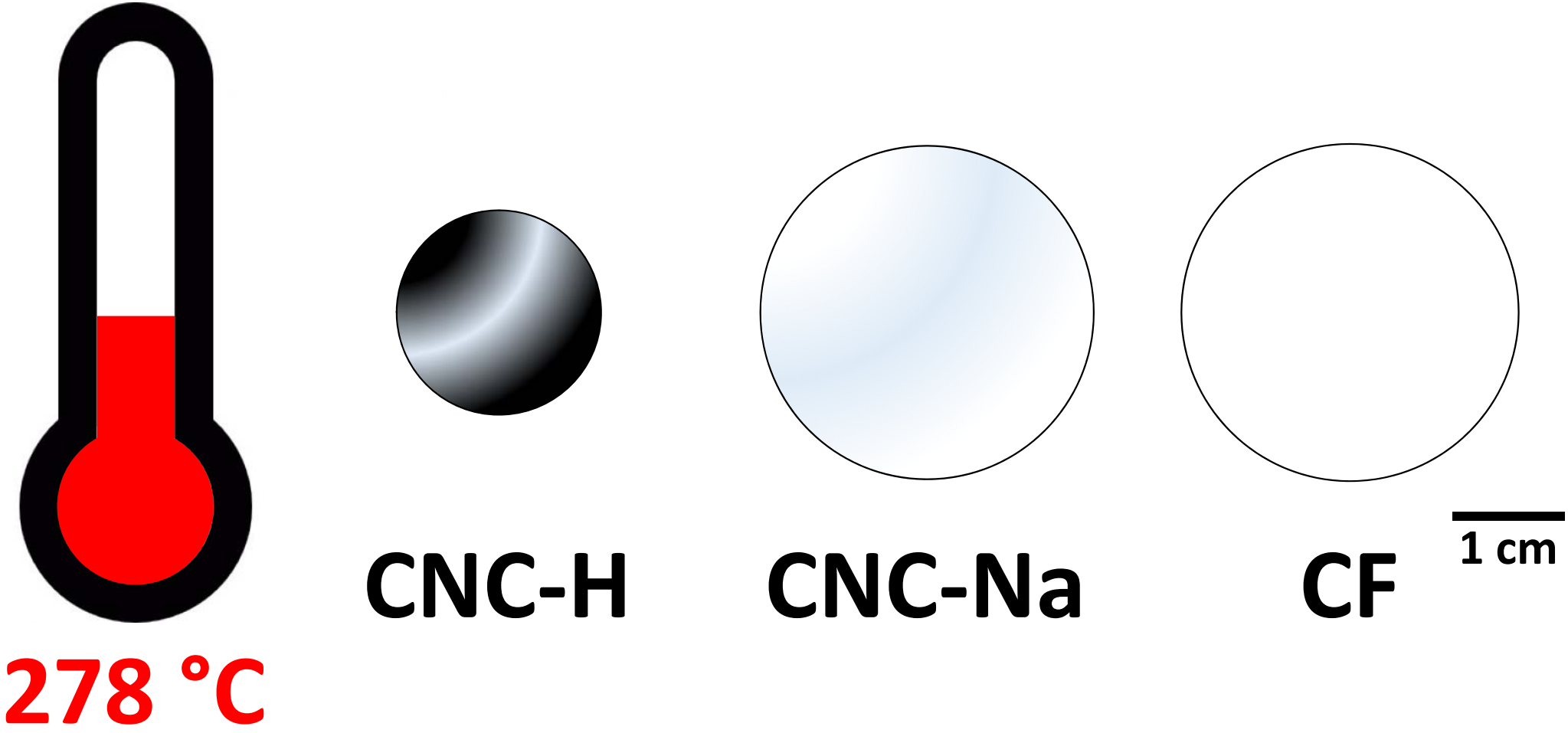

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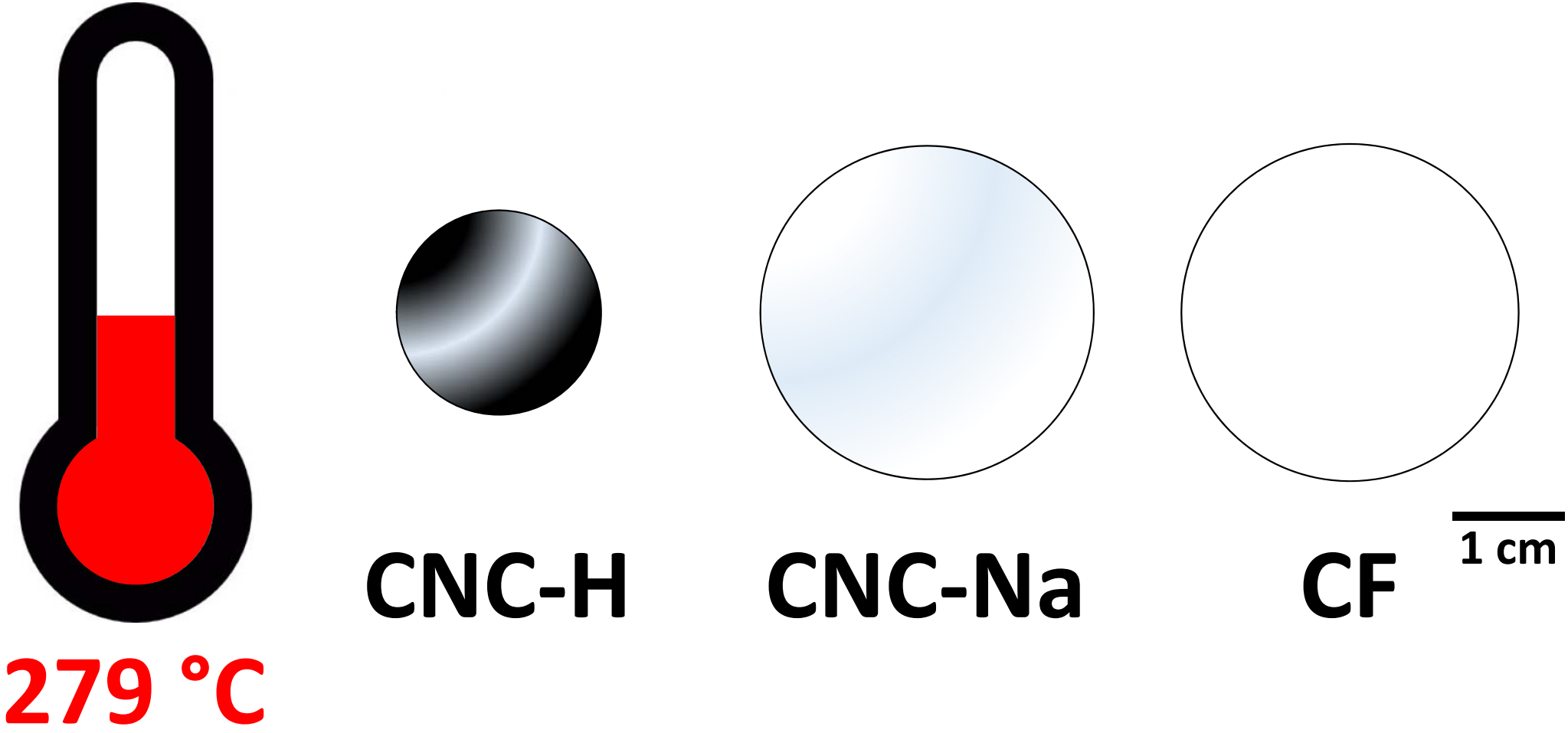

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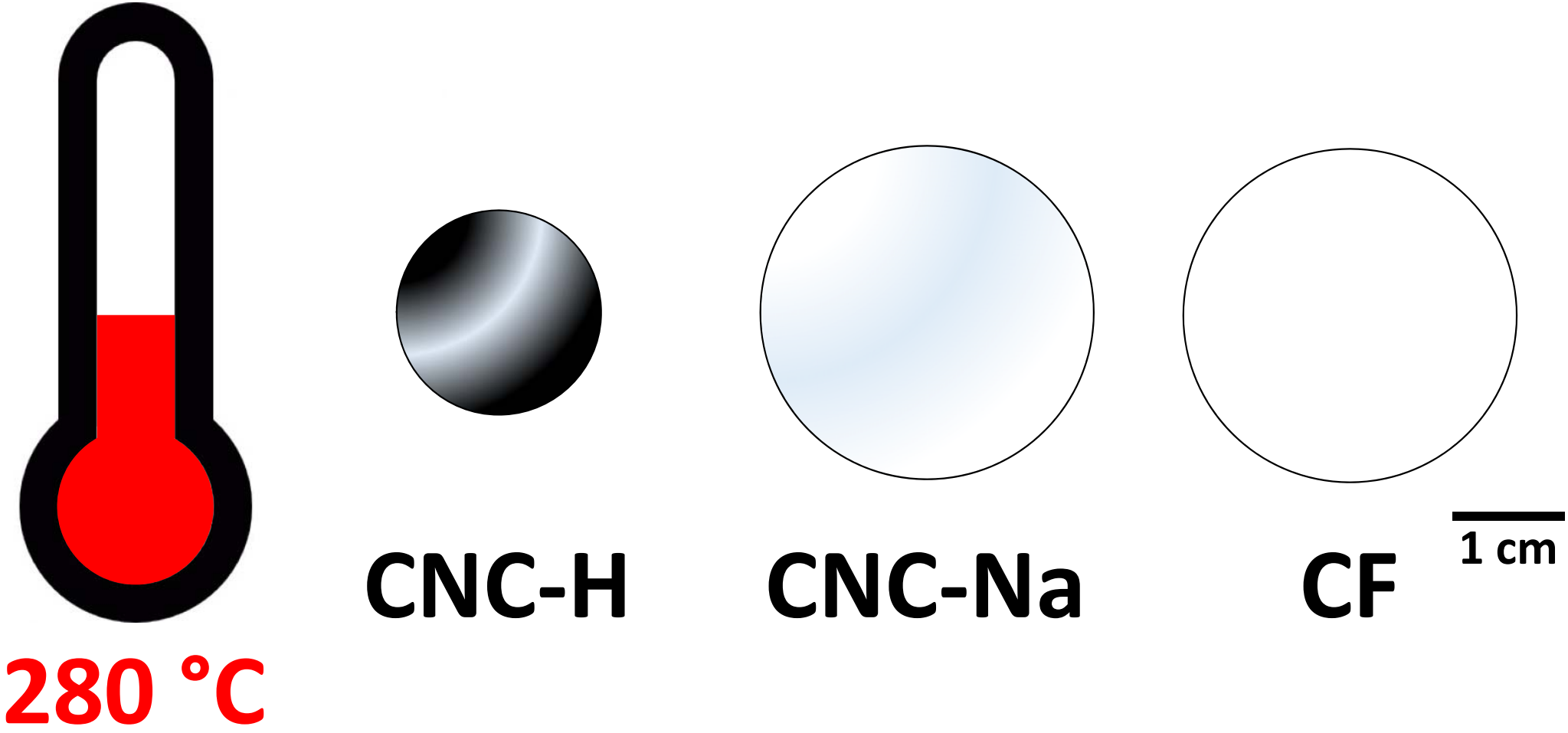

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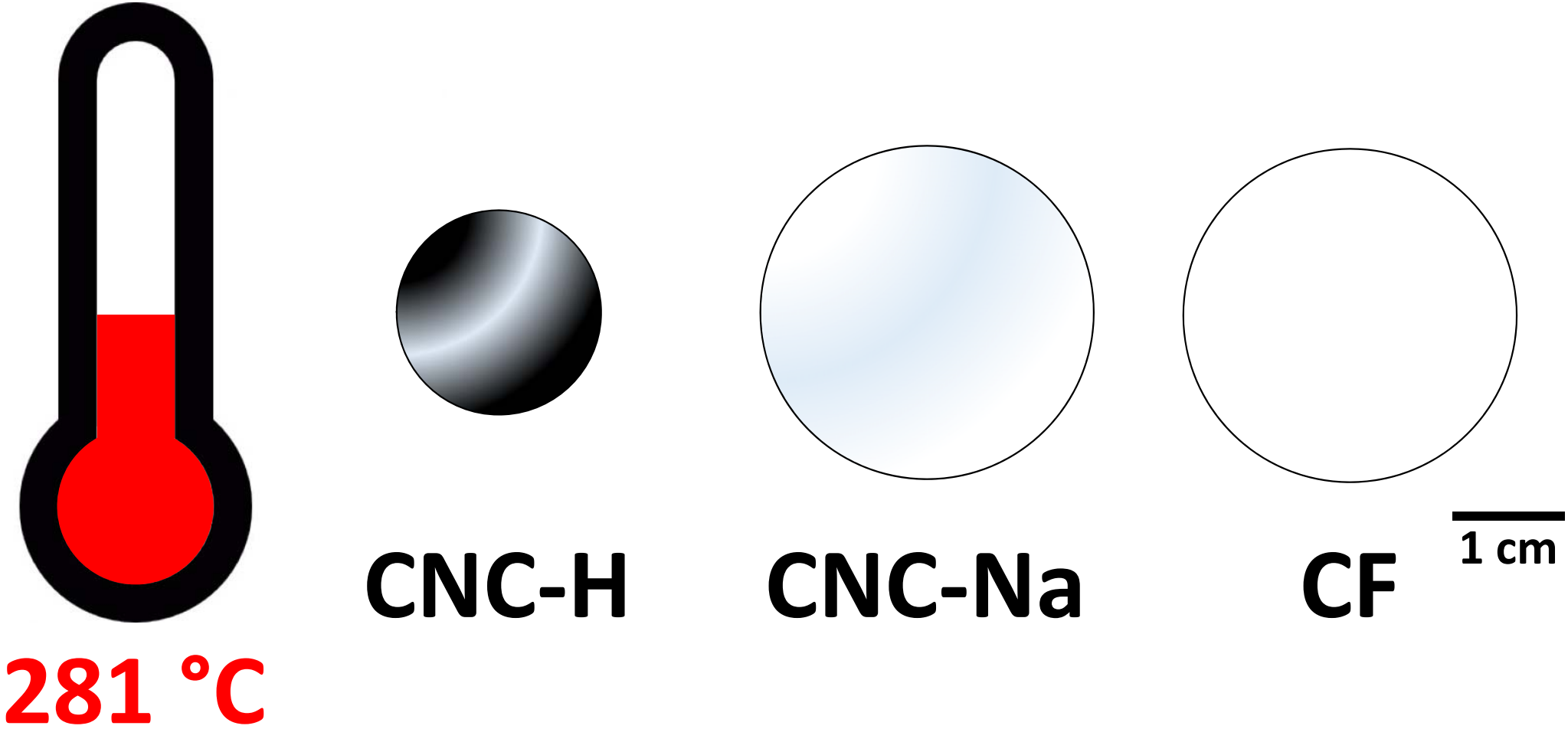
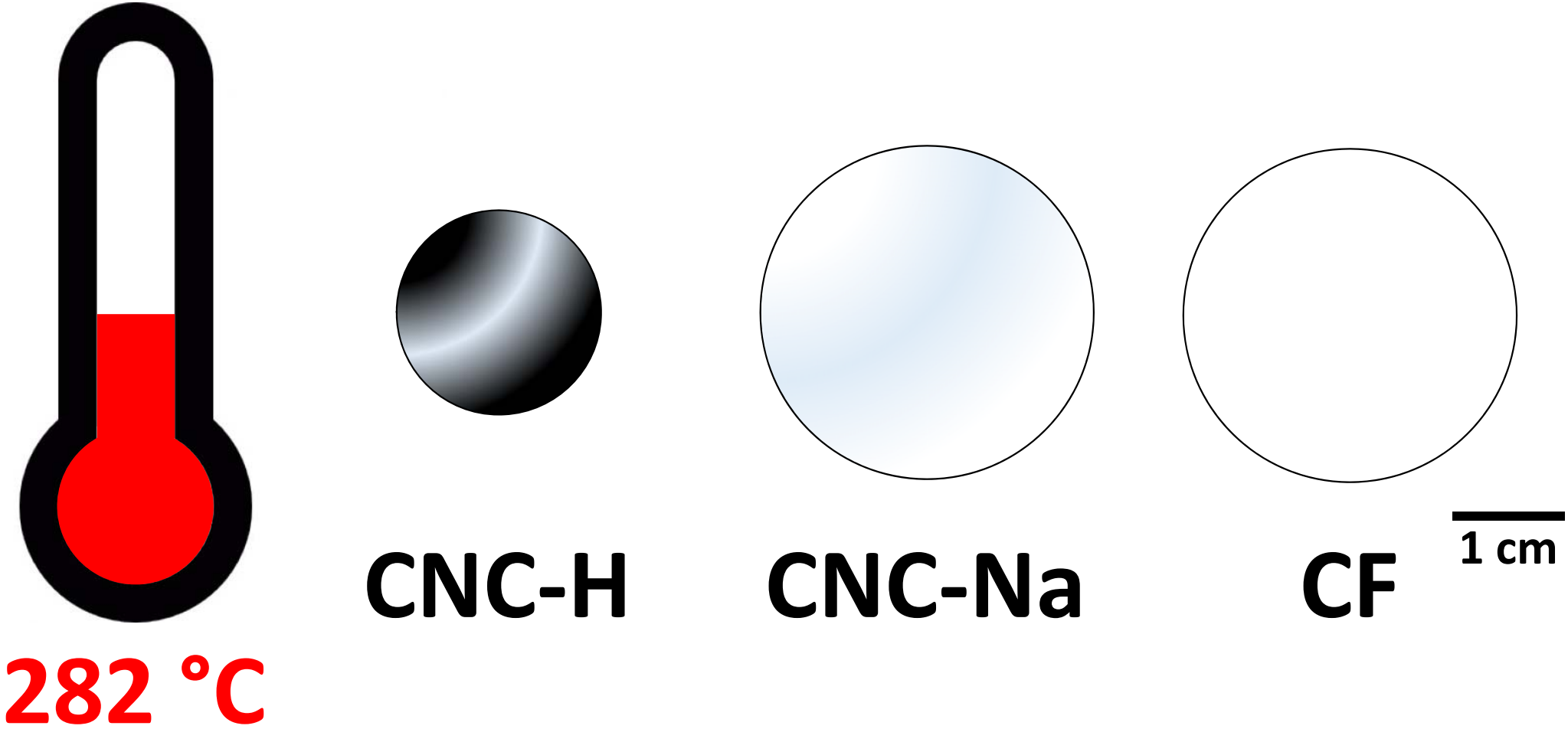


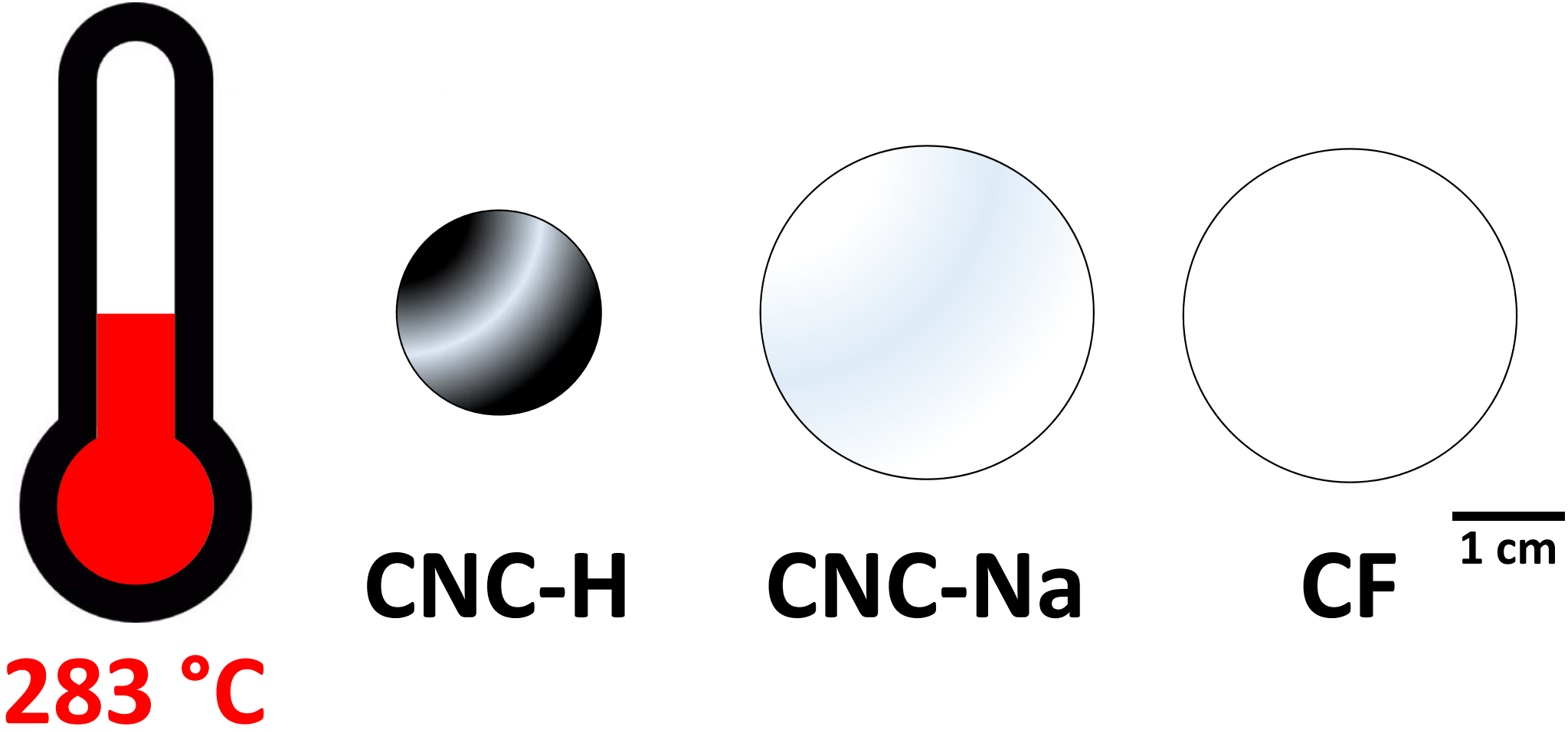
Results

THE UNIVERSITY OF BRITISH COLUMBIA



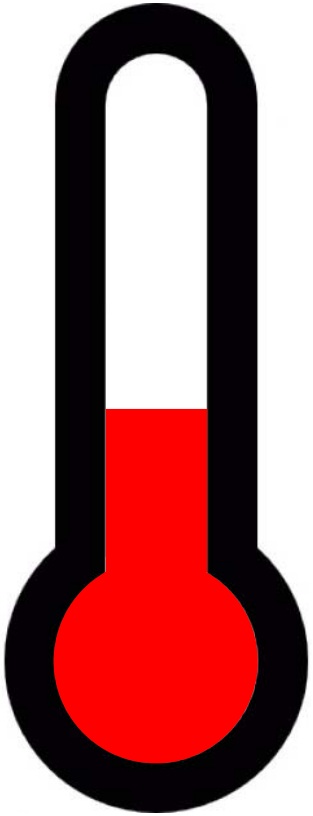
Results

THE UNIVERSITY OF BRITISH COLUMBIA

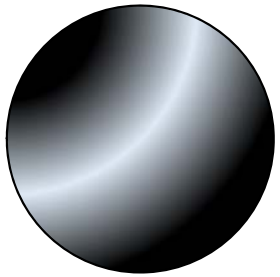


Results

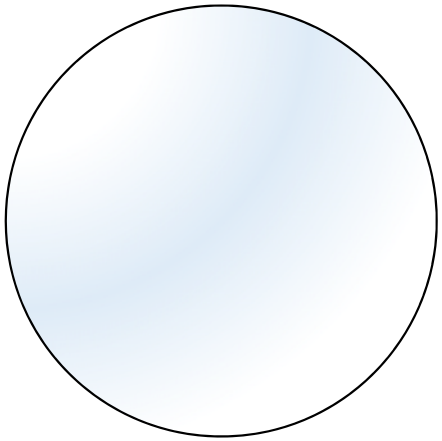
THE UNIVERSITY OF BRITISH COLUMBIA



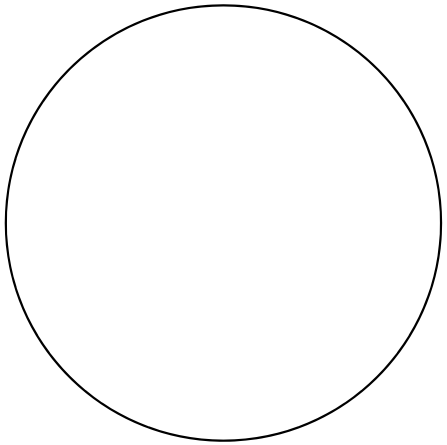
284 °C



CNC-H



CNC-Na

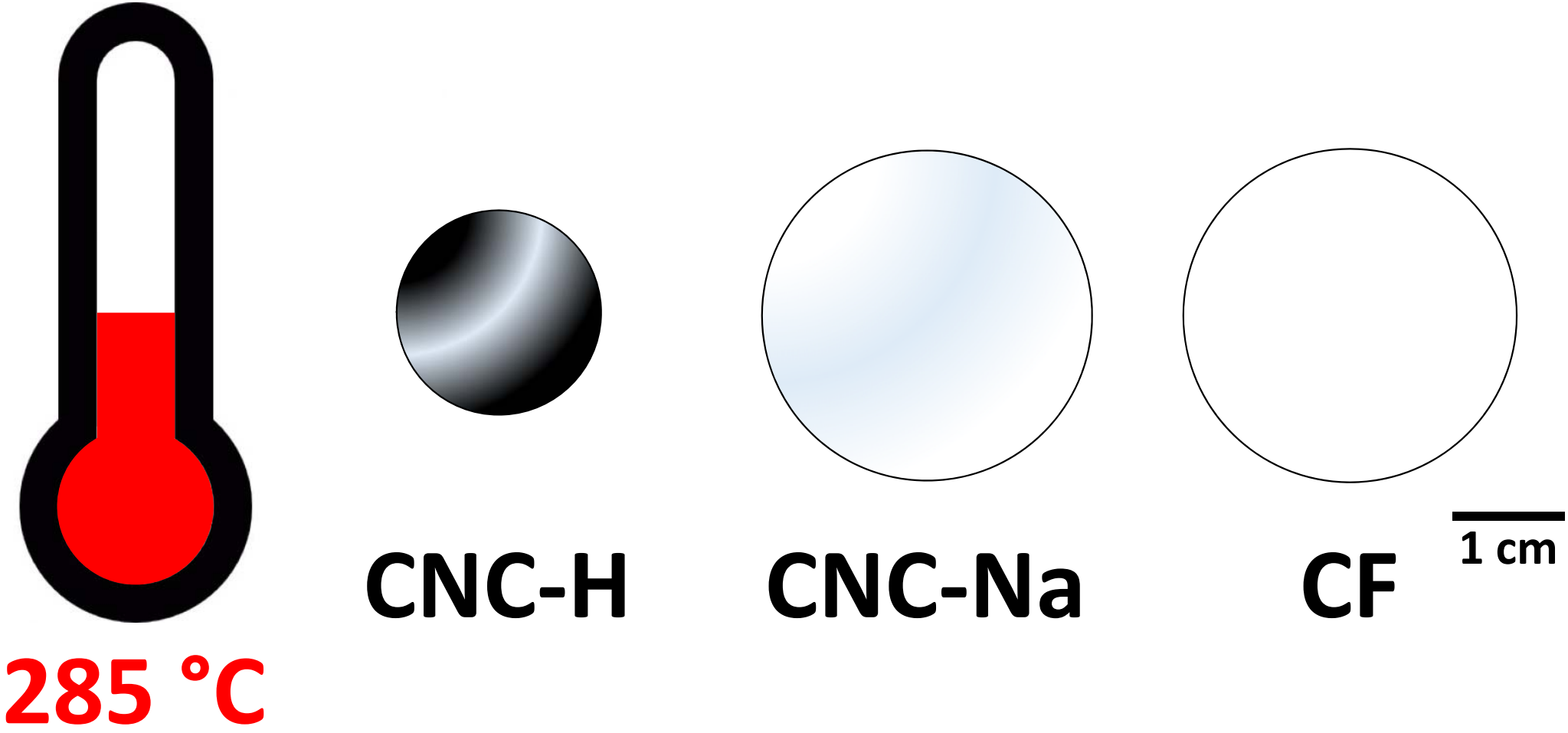


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



Results

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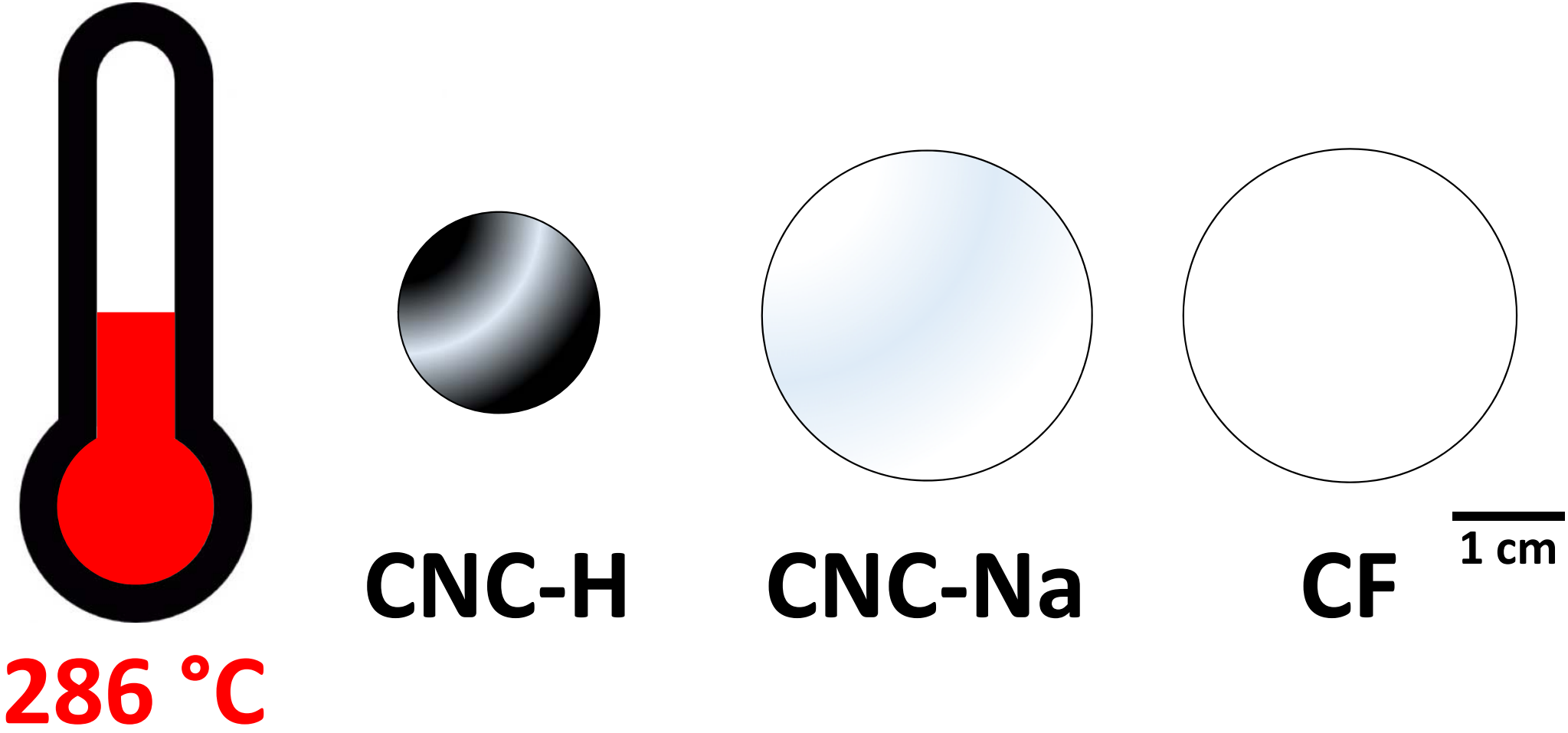

Results

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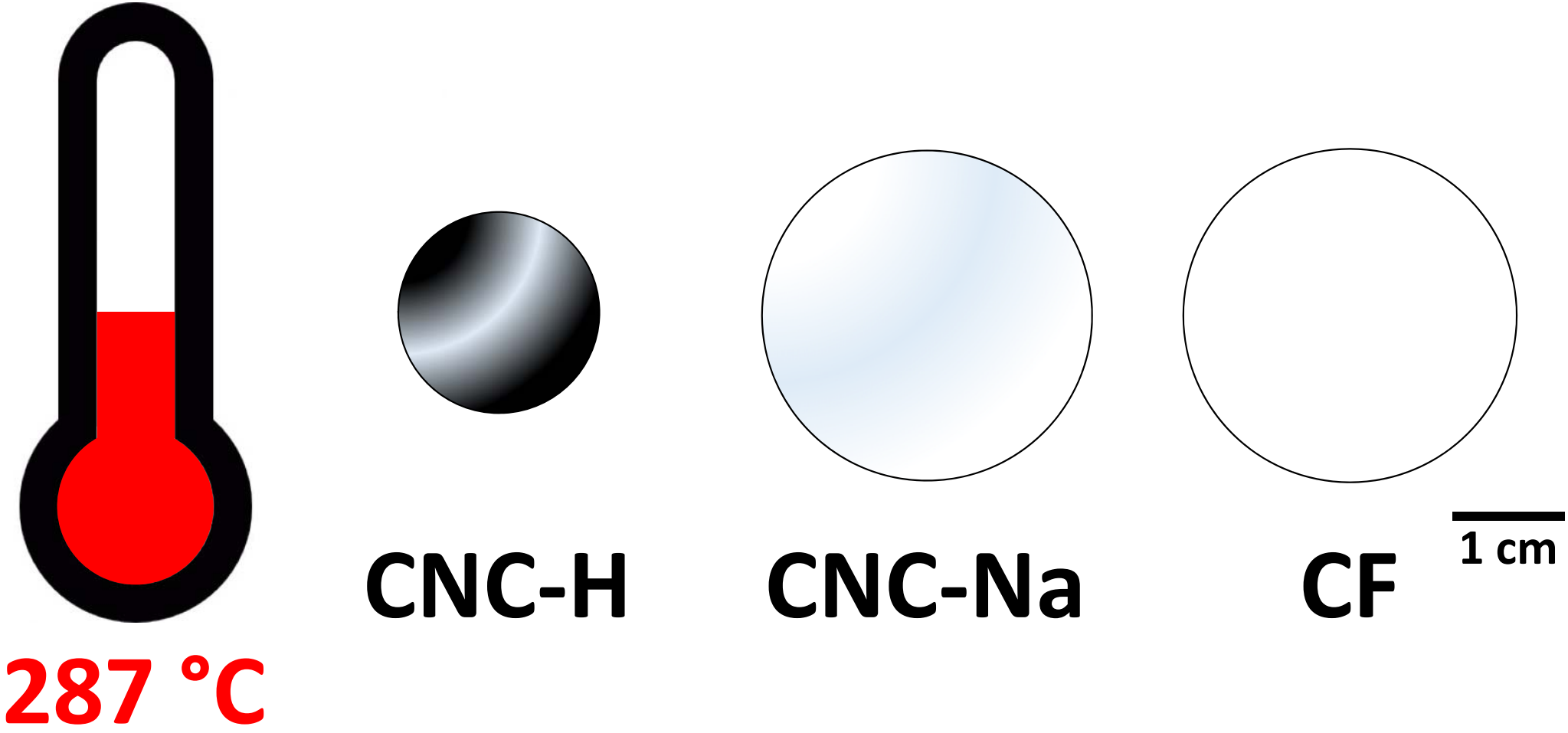

Results

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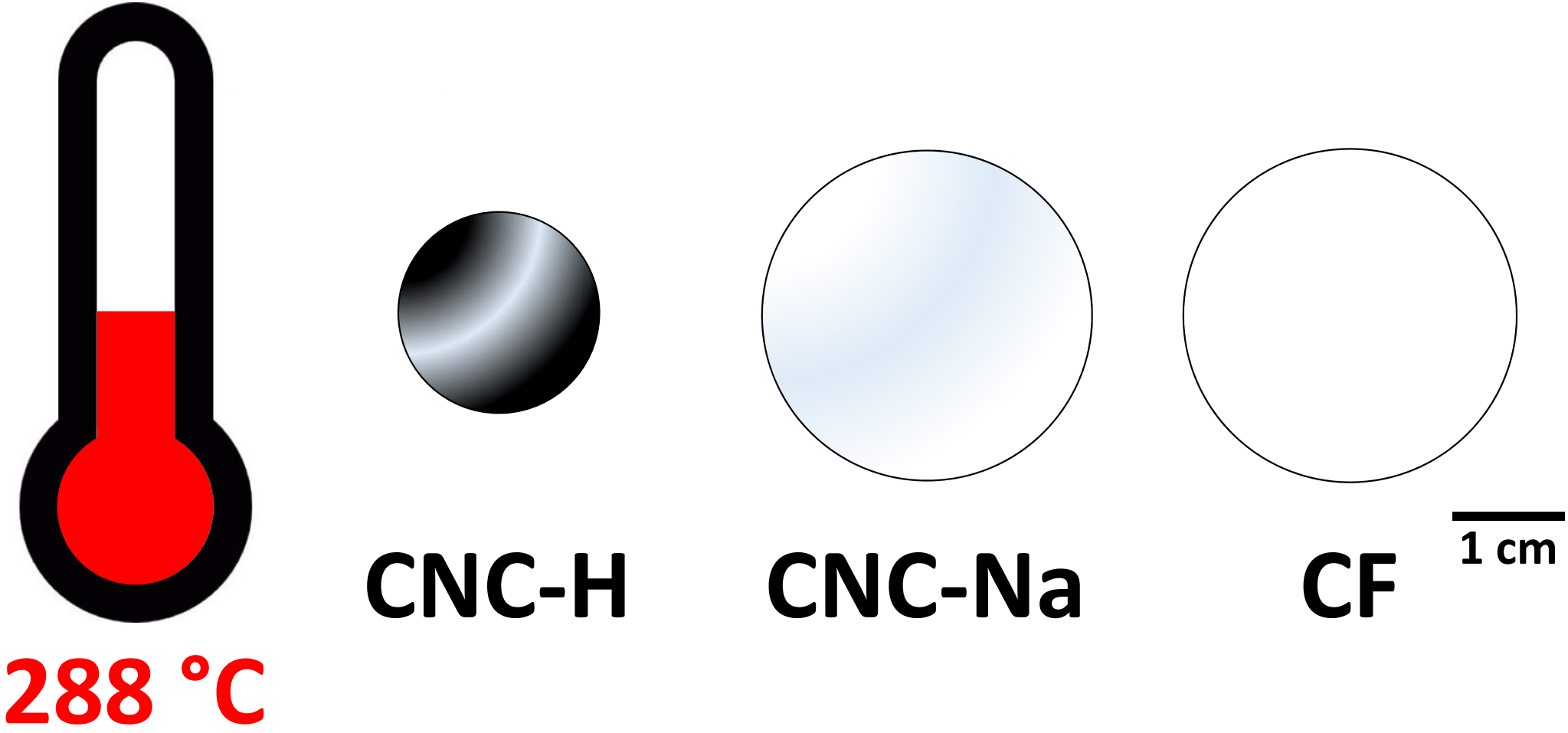

Results

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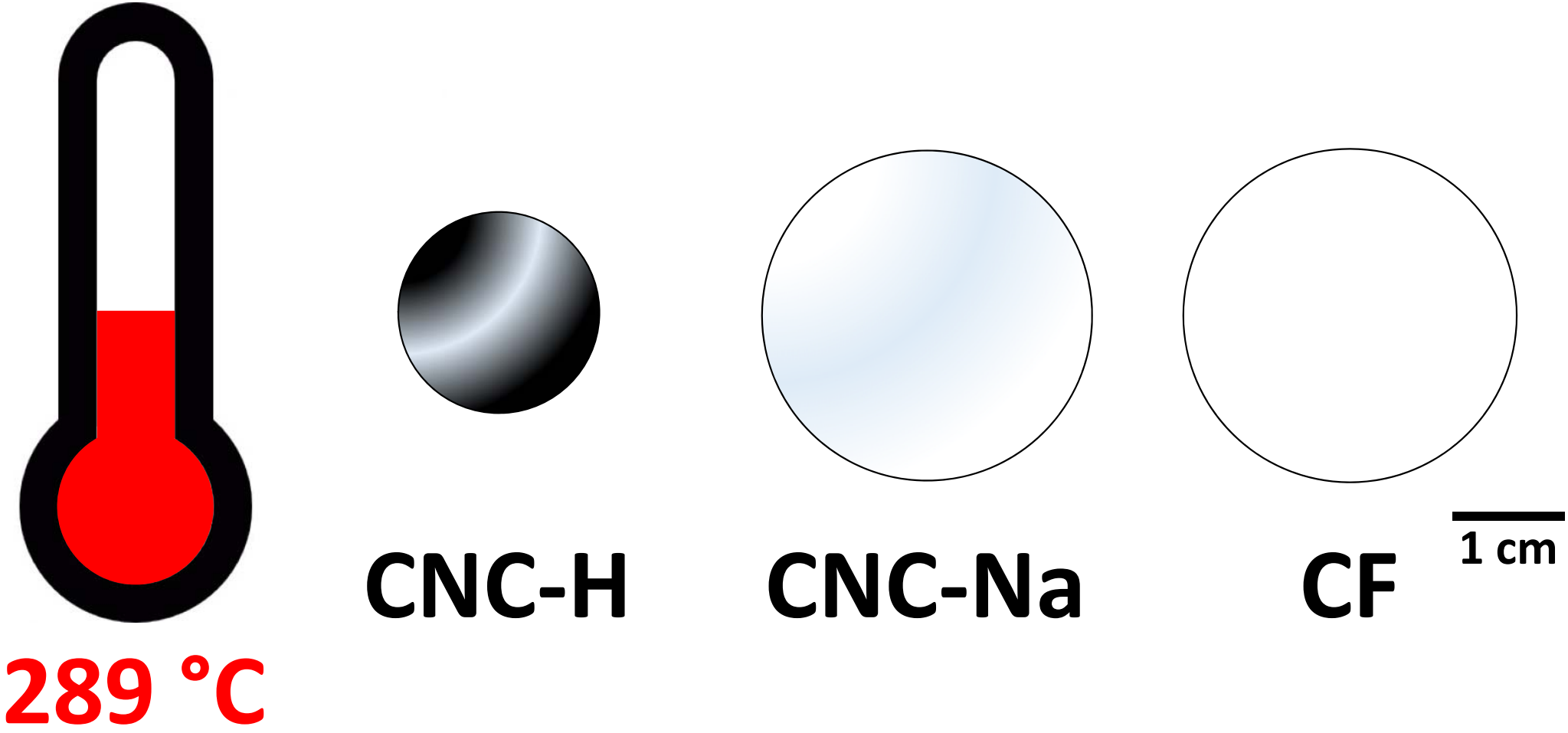

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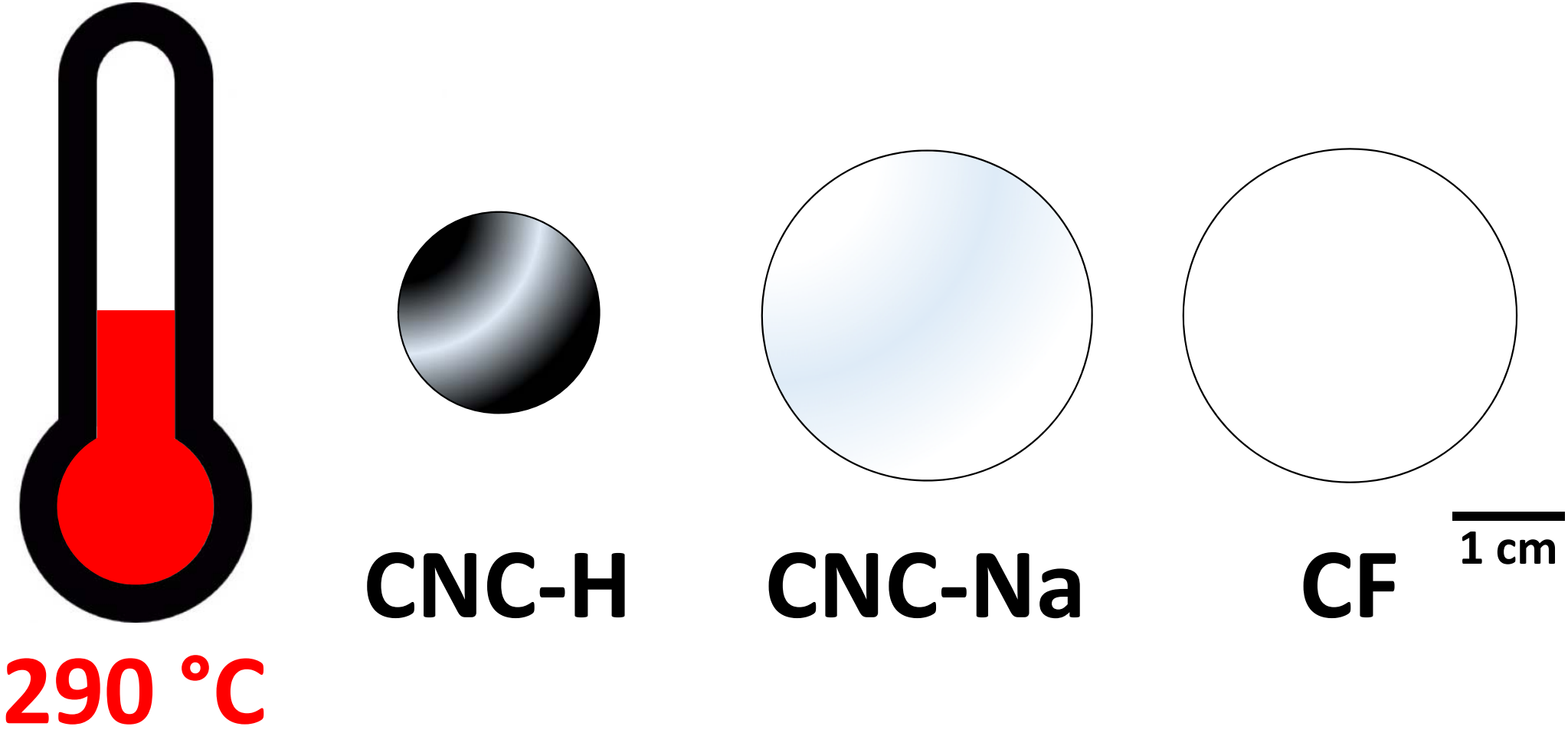

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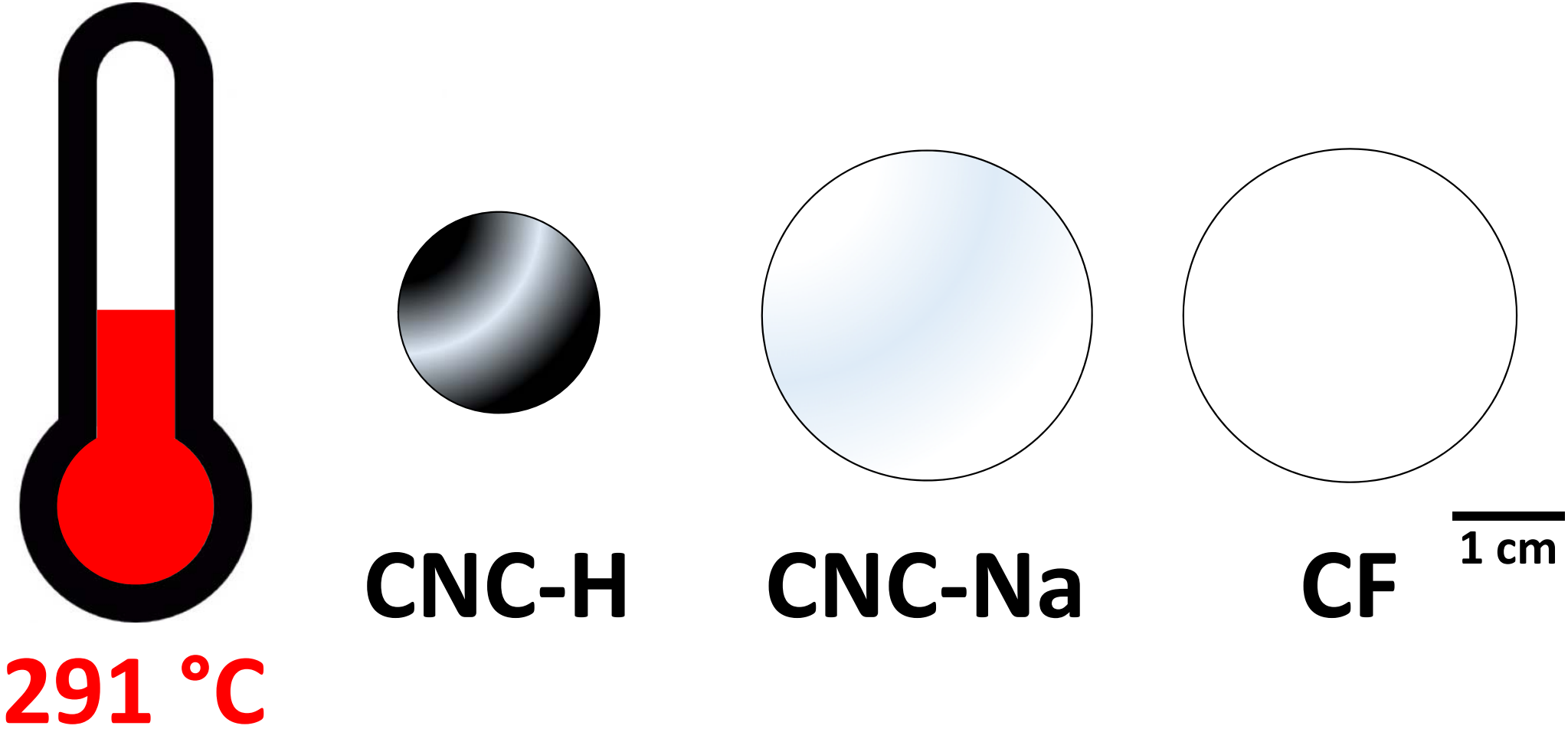

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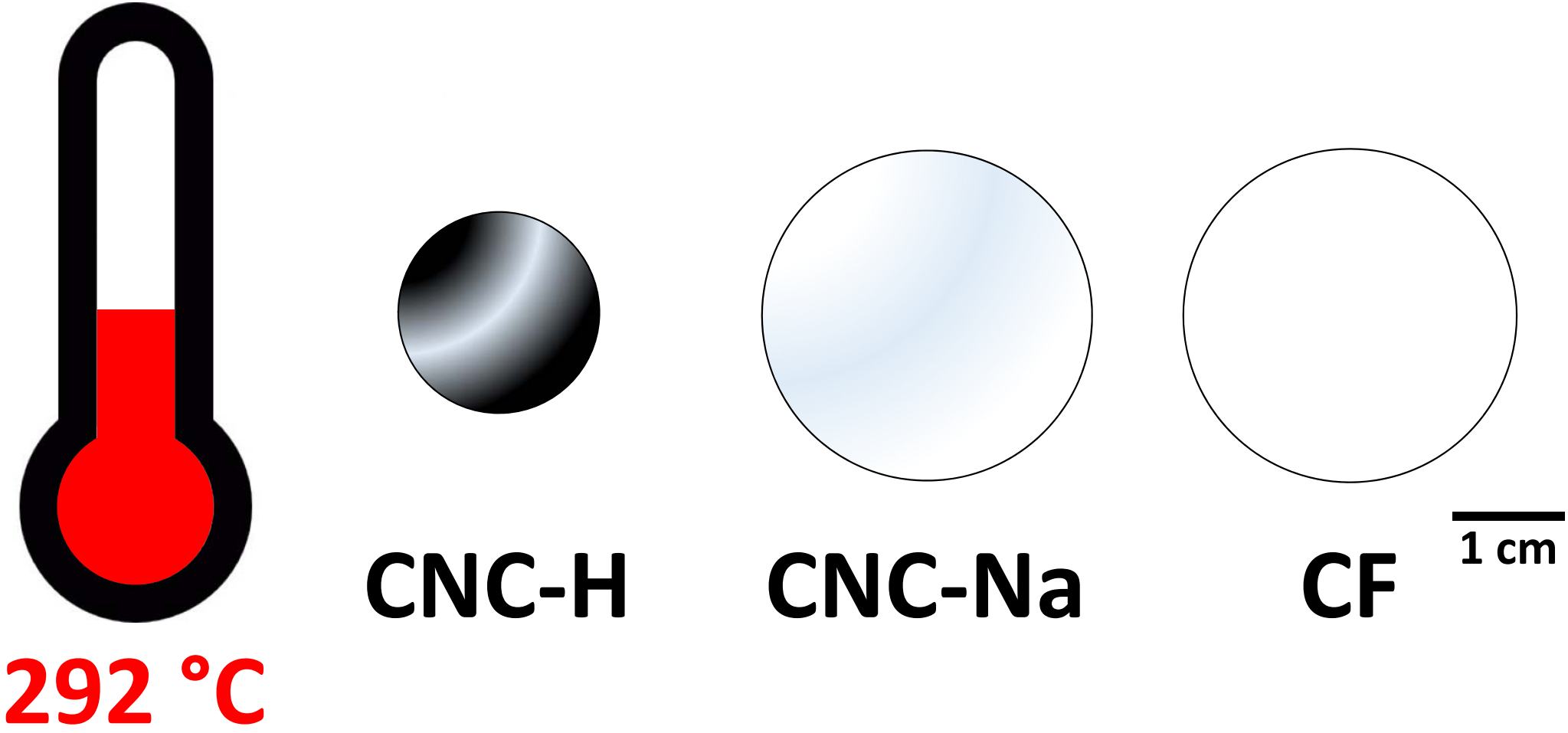

Results

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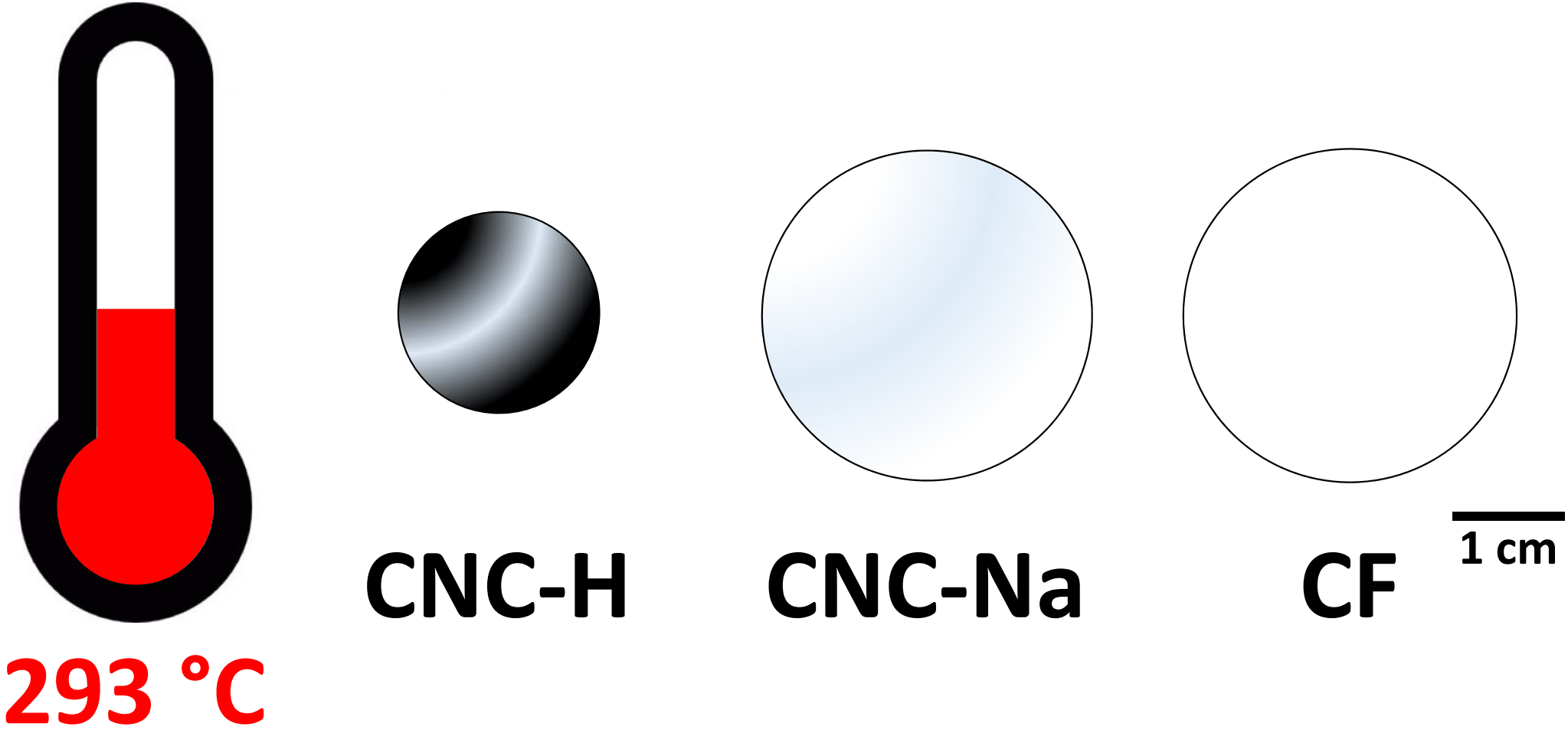

Results

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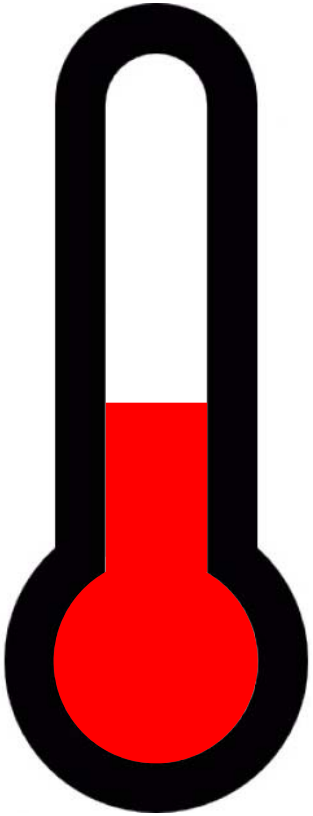
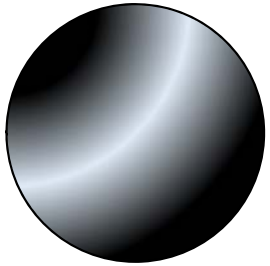
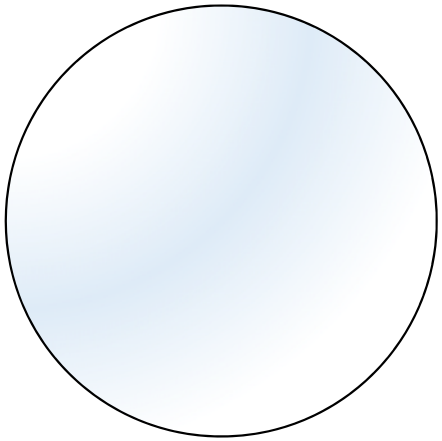


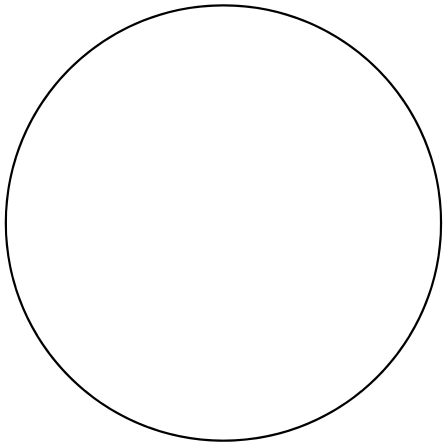
294 °C



CNC-H



CNC-Na

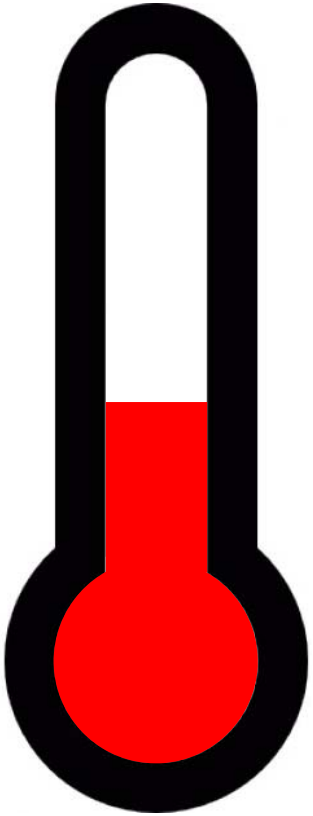


CF

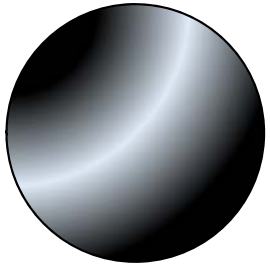
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



295 °C



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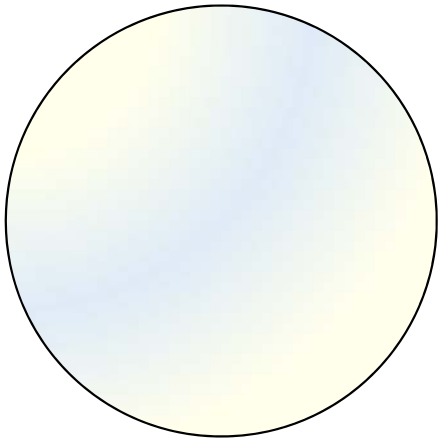

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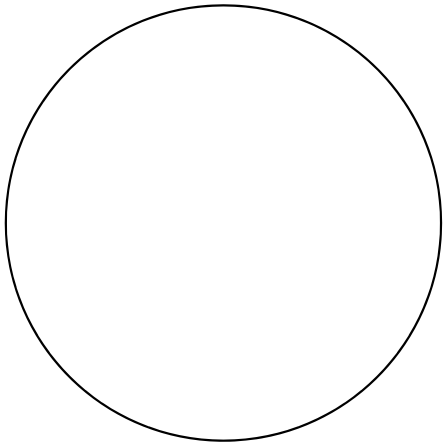
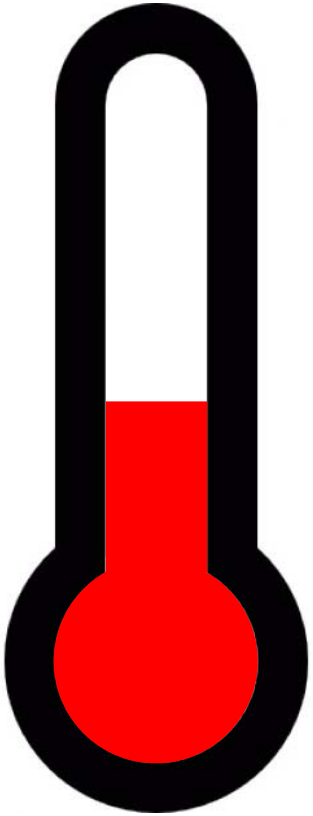


CF

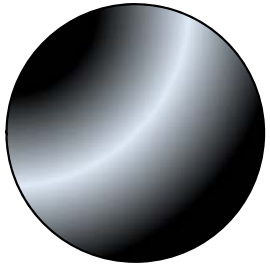
1 cm

Results

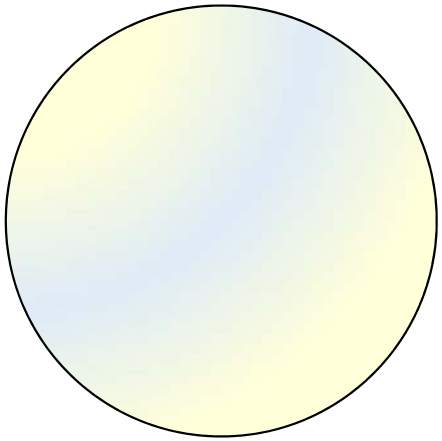
THE UNIVERSITY OF BRITISH COLUMBIA



296 °C



CNC-H



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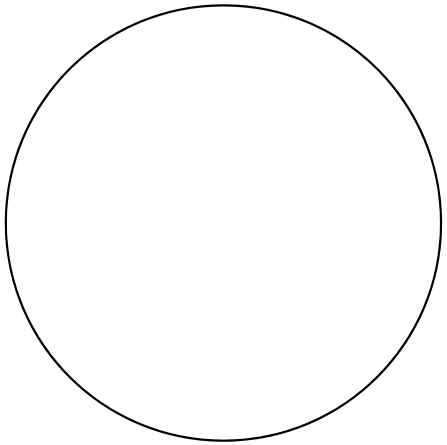
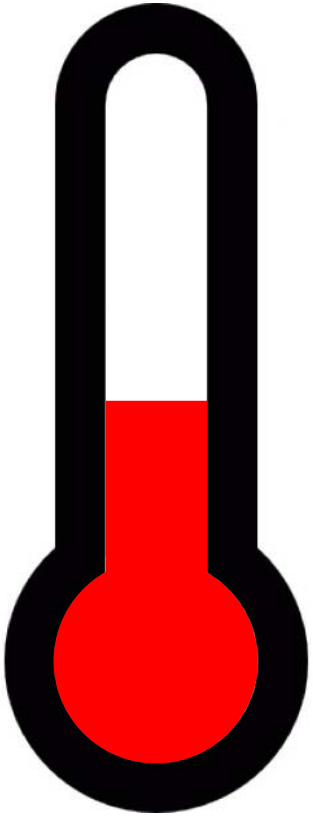


CF

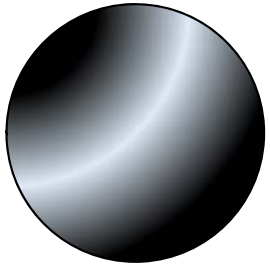
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



297 °C



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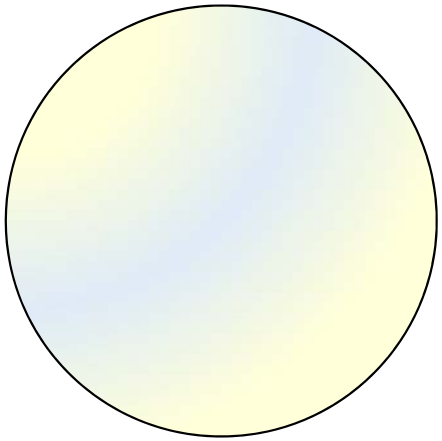

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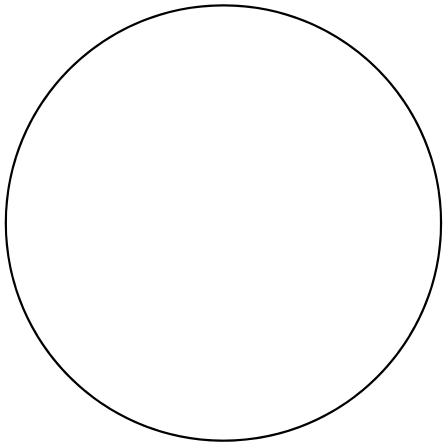
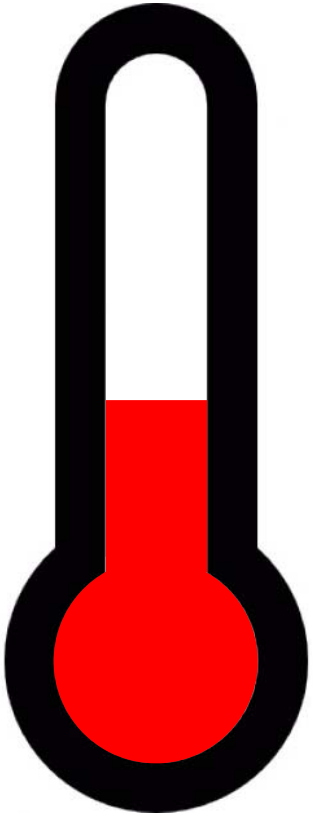


CF

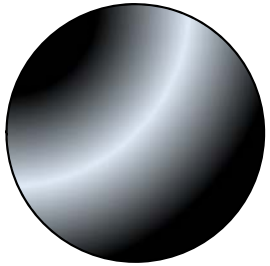
1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



298 °C



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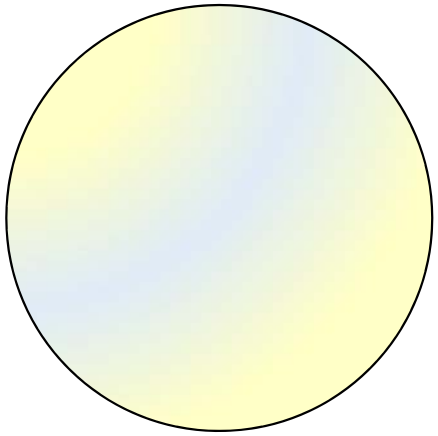

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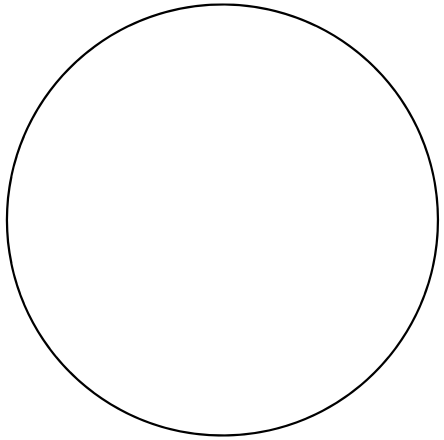
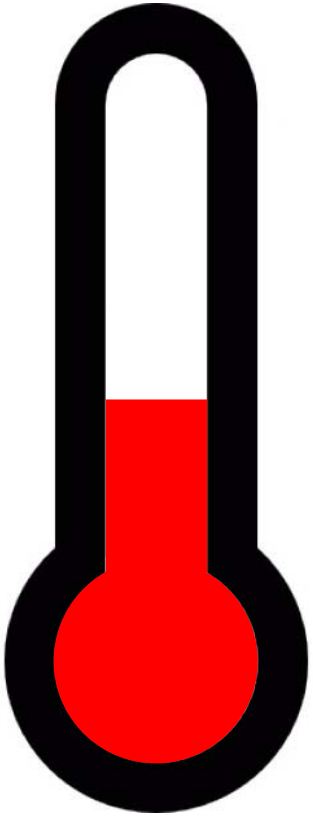


CF

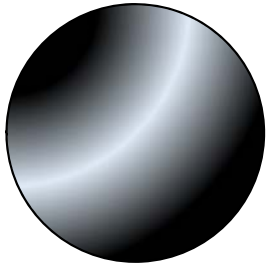
1 cm

Results

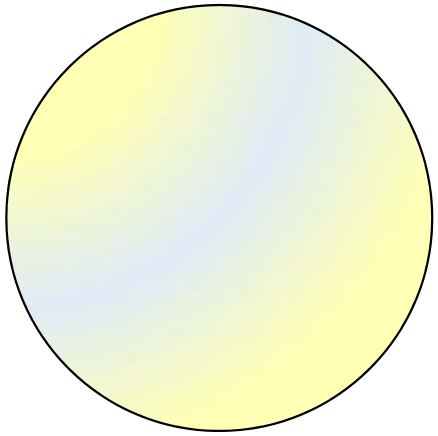
THE UNIVERSITY OF BRITISH COLUMBIA



299 °C



CNC-H



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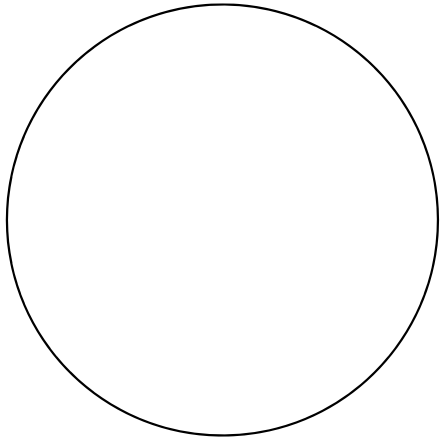
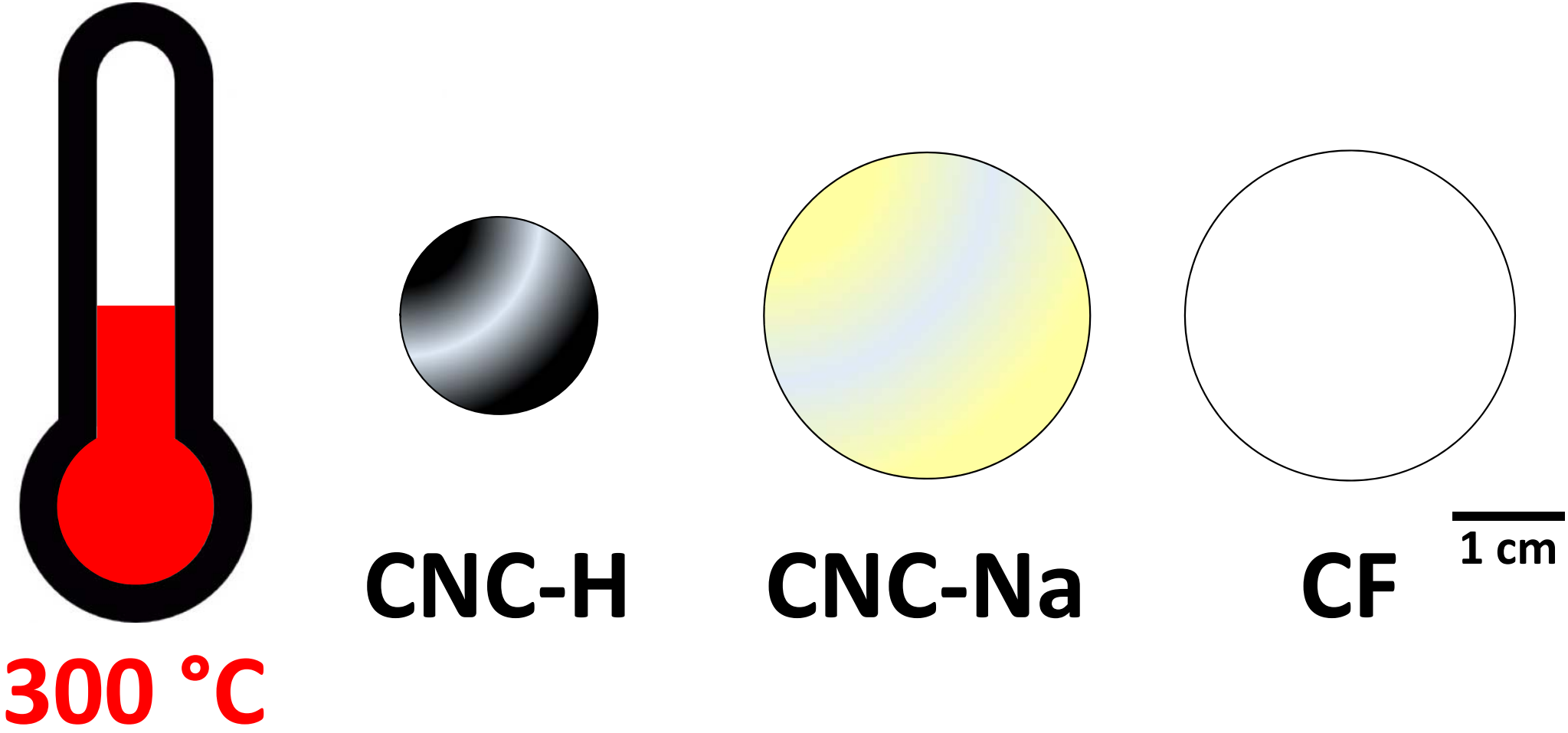


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



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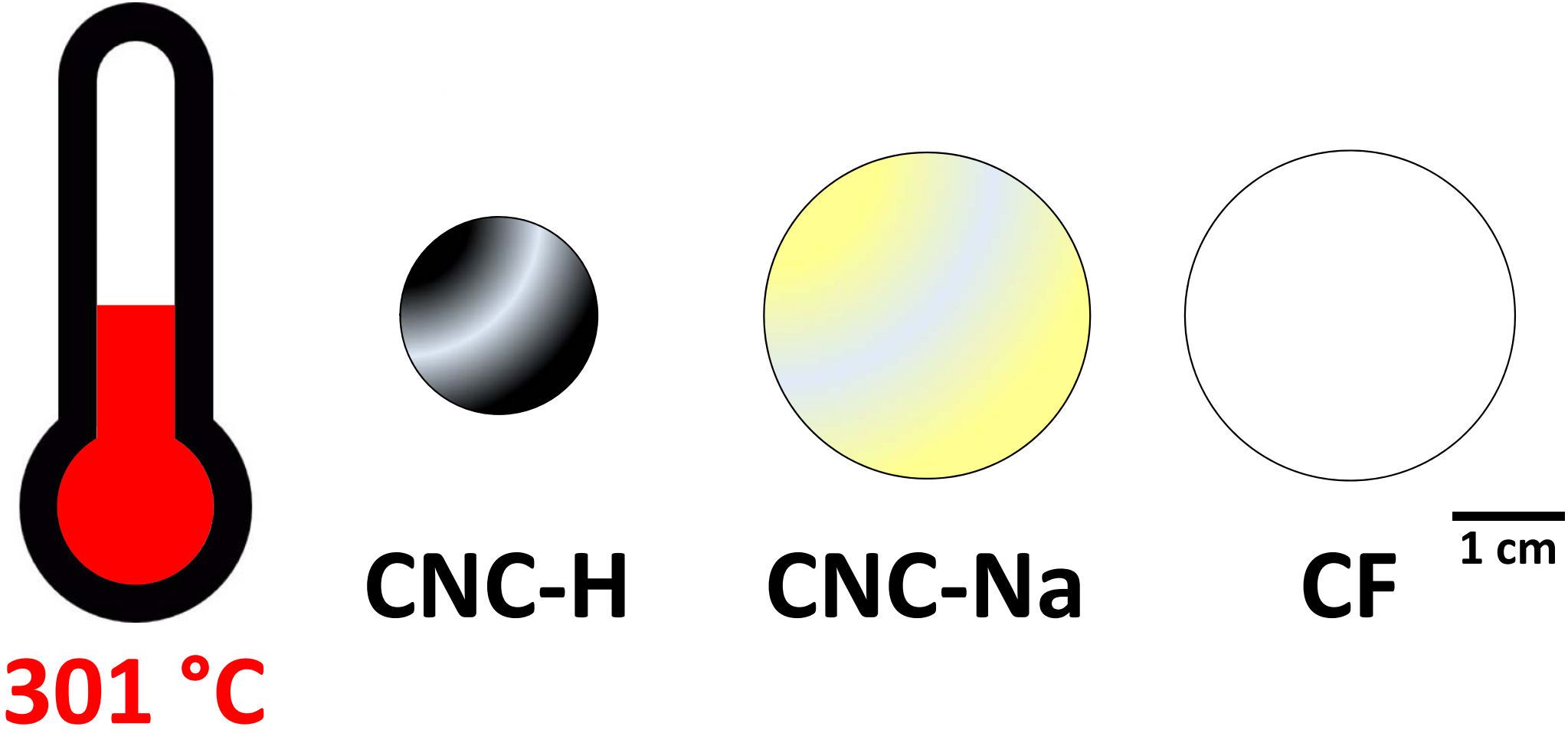

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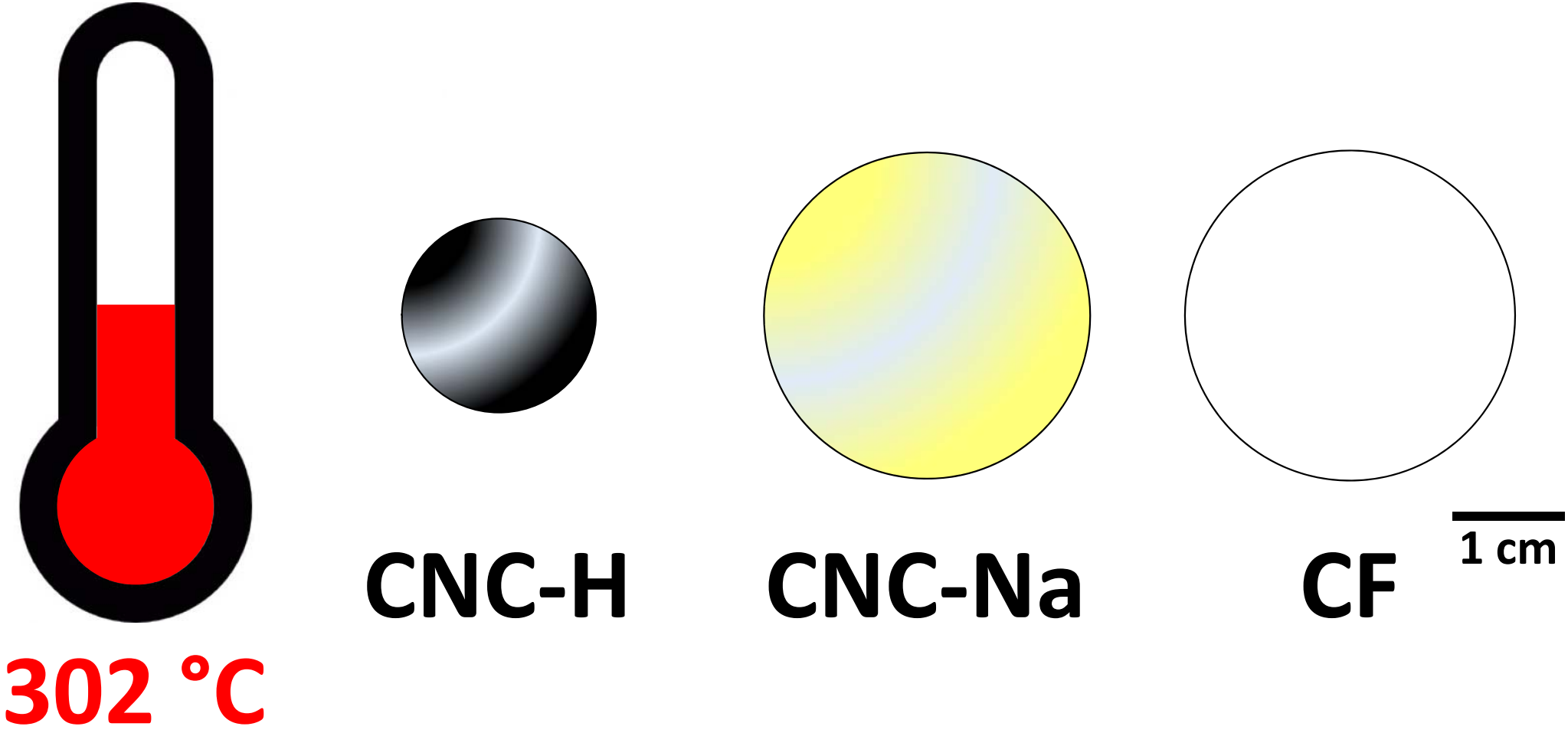

Results

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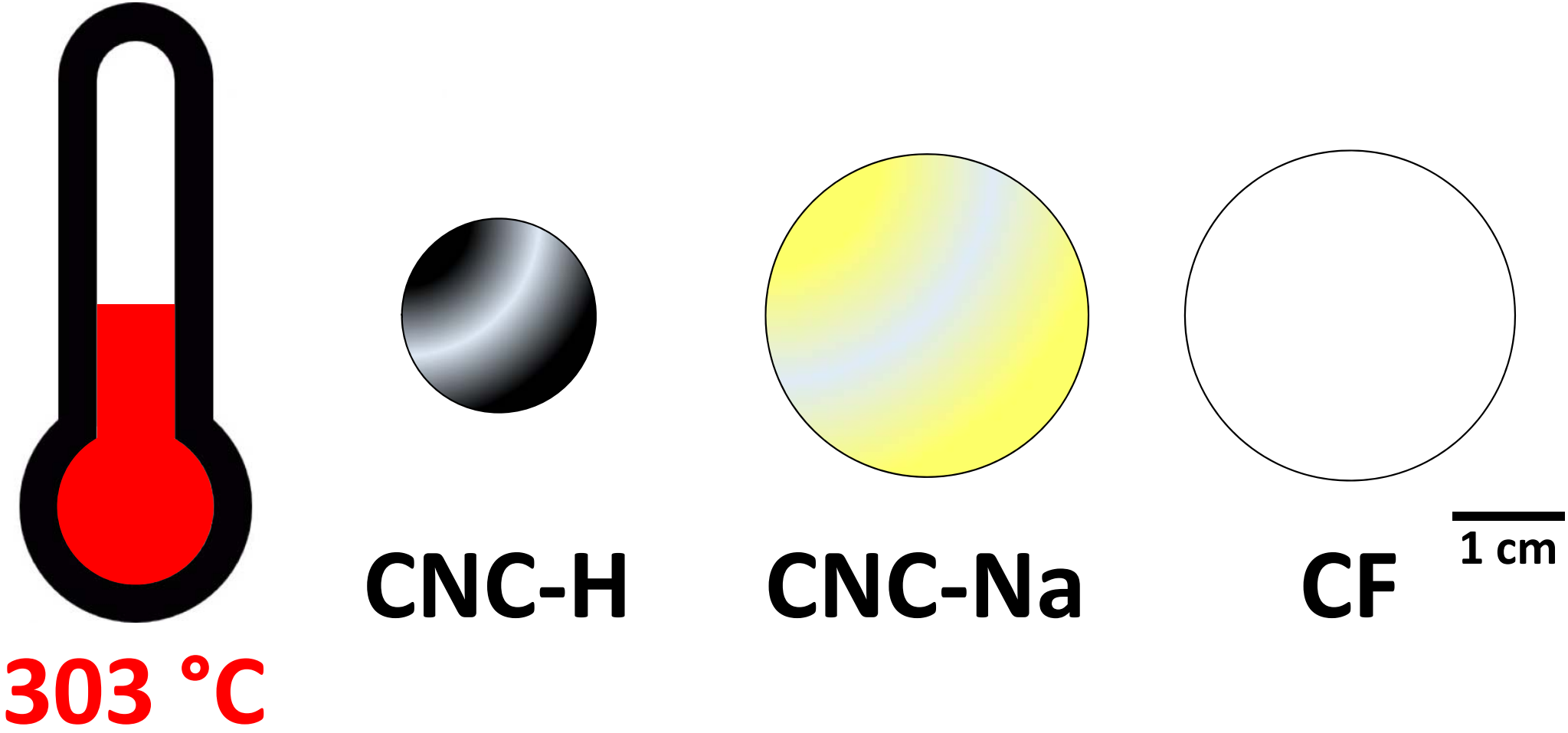

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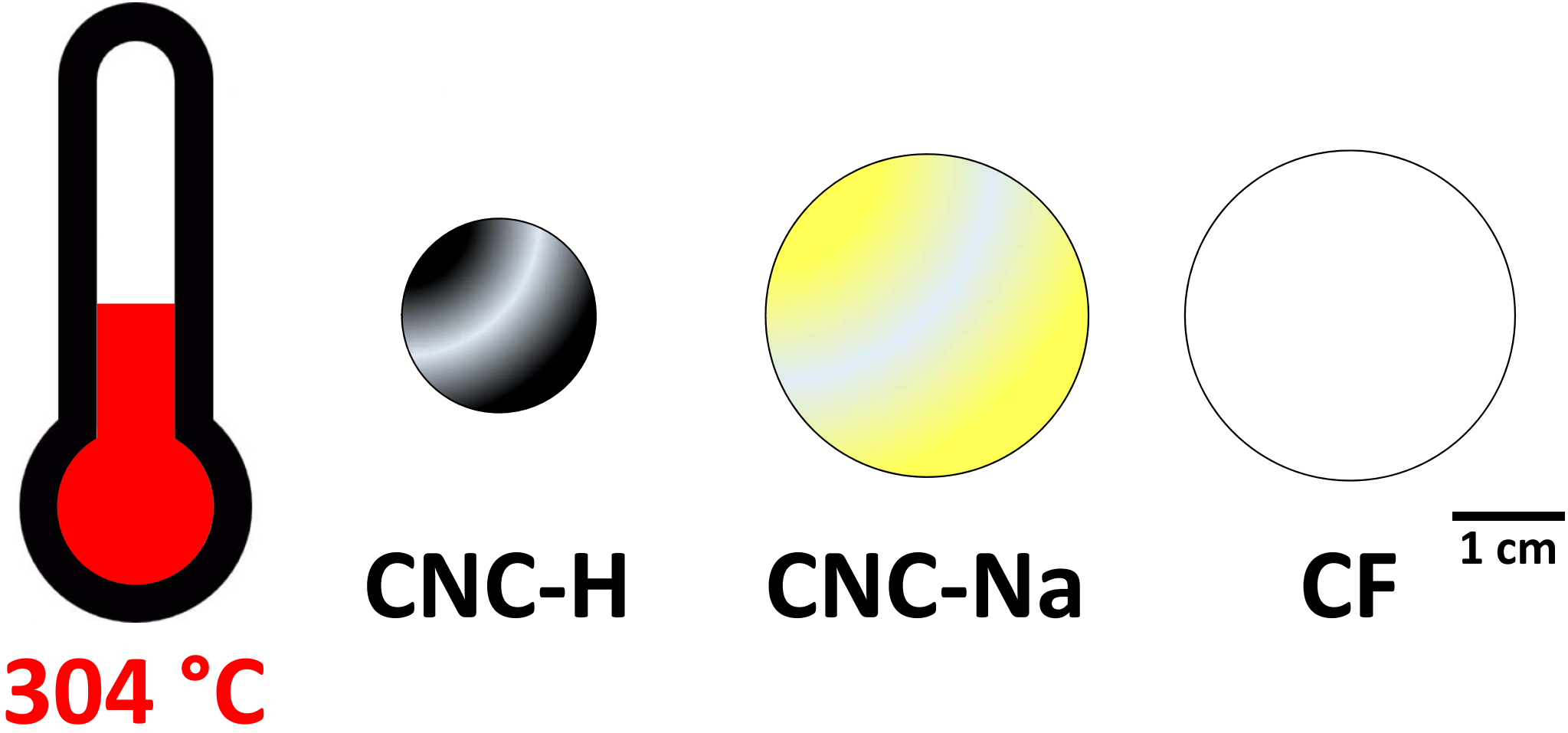

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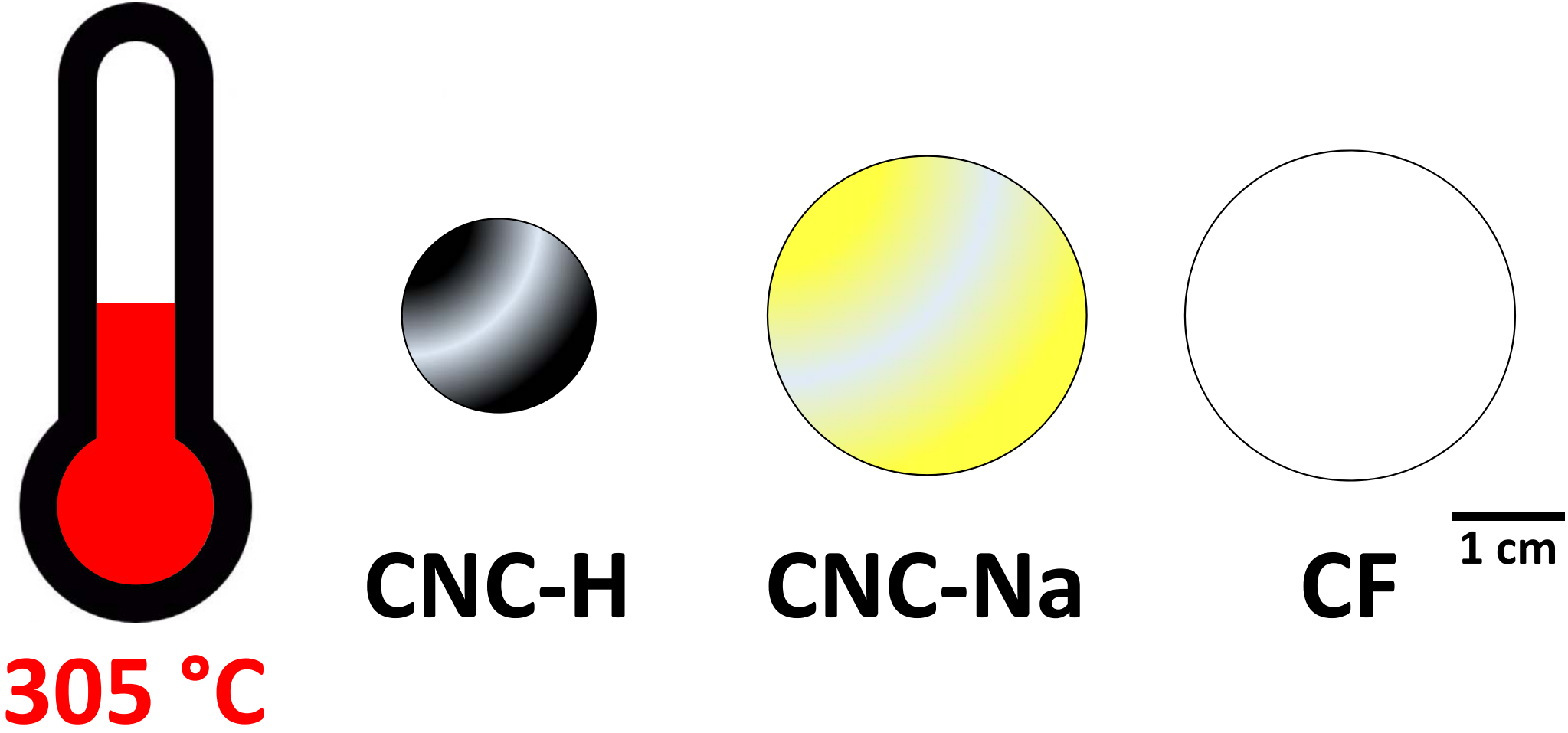

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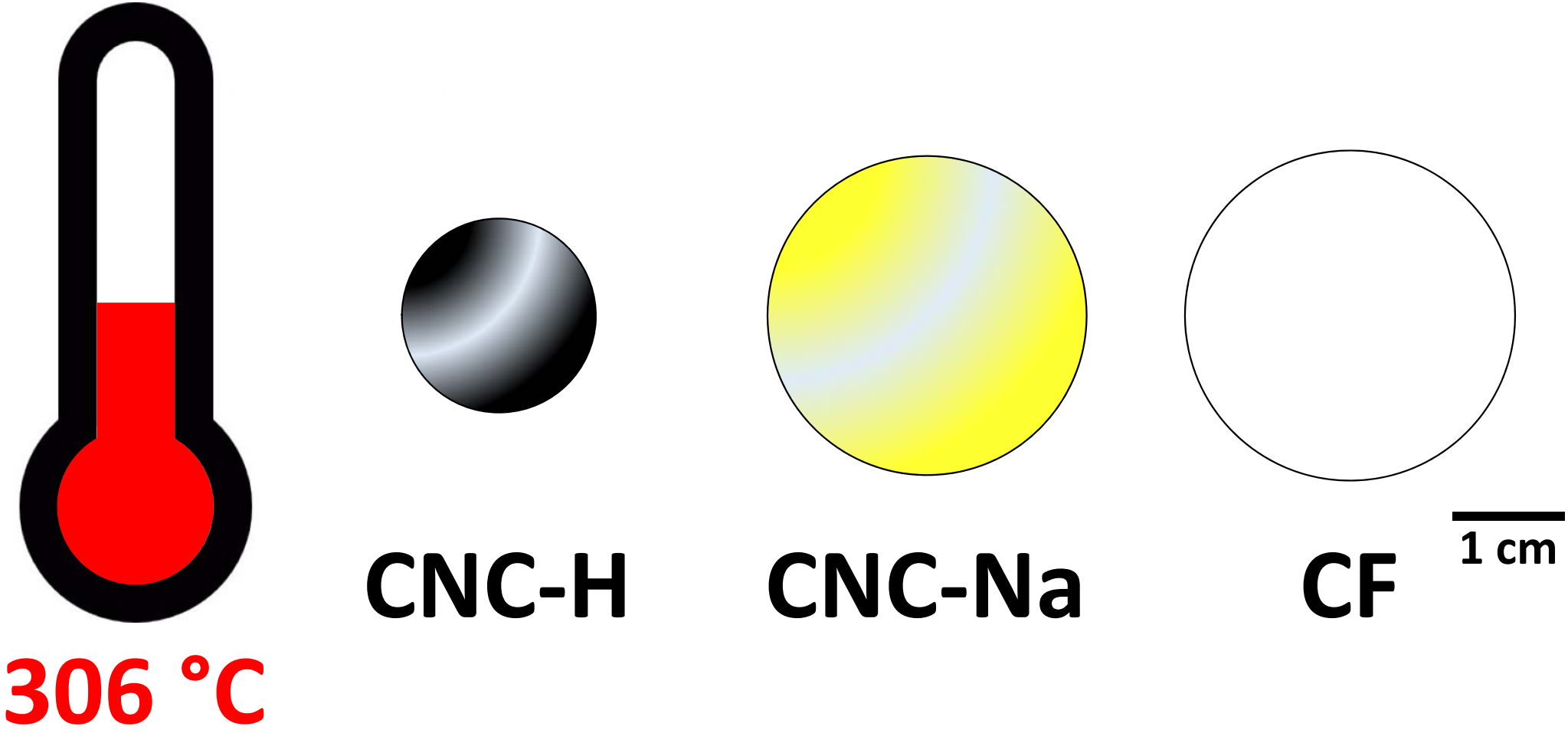

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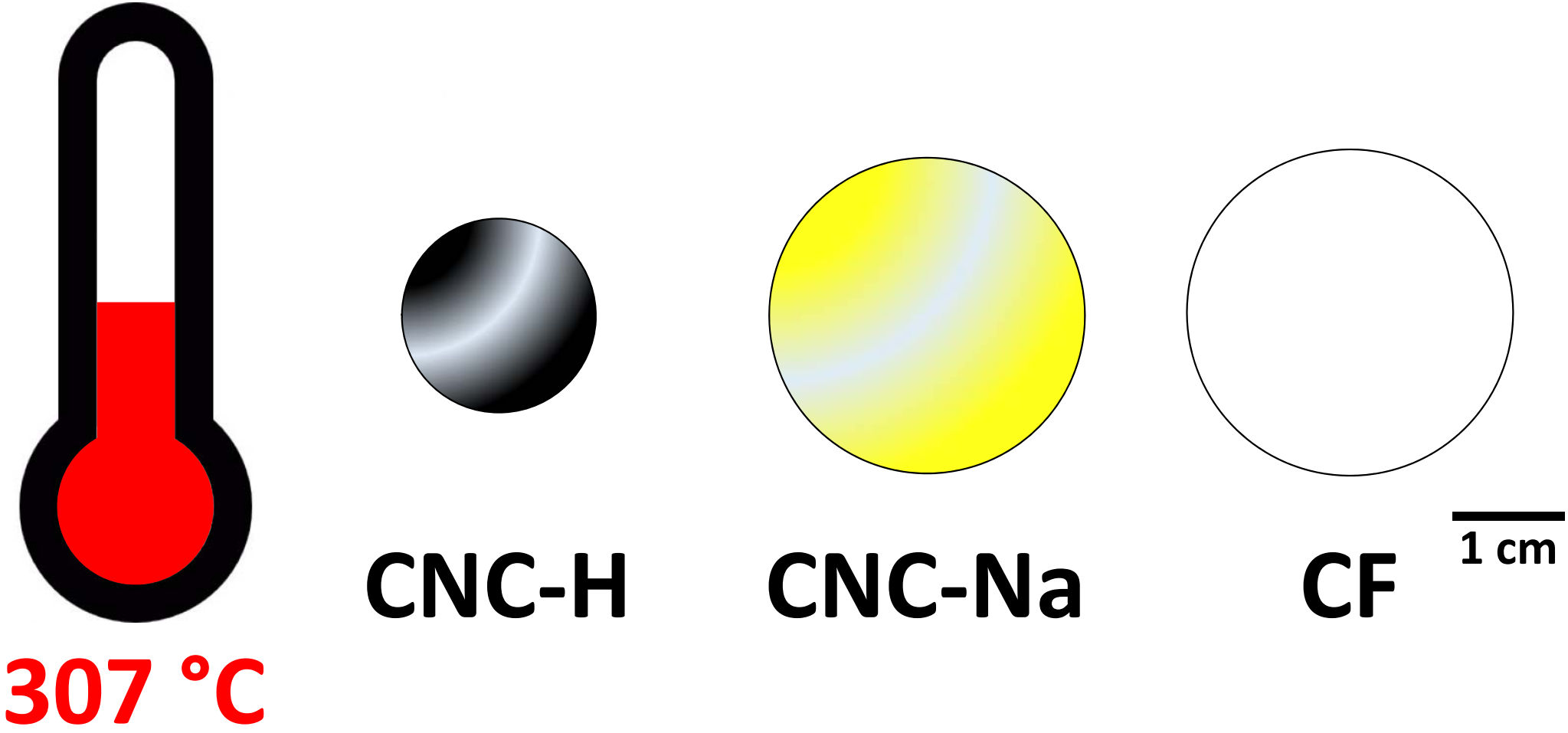

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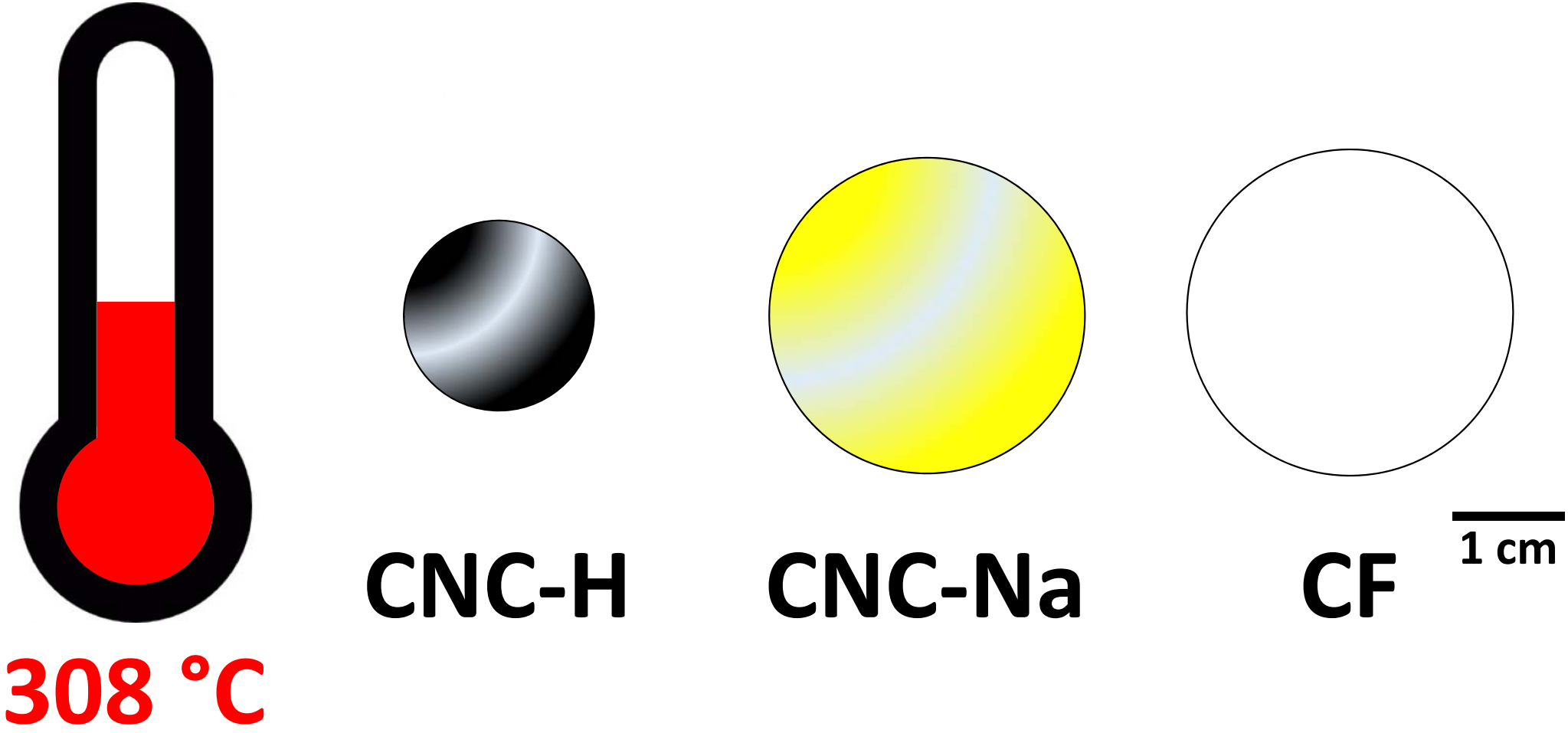

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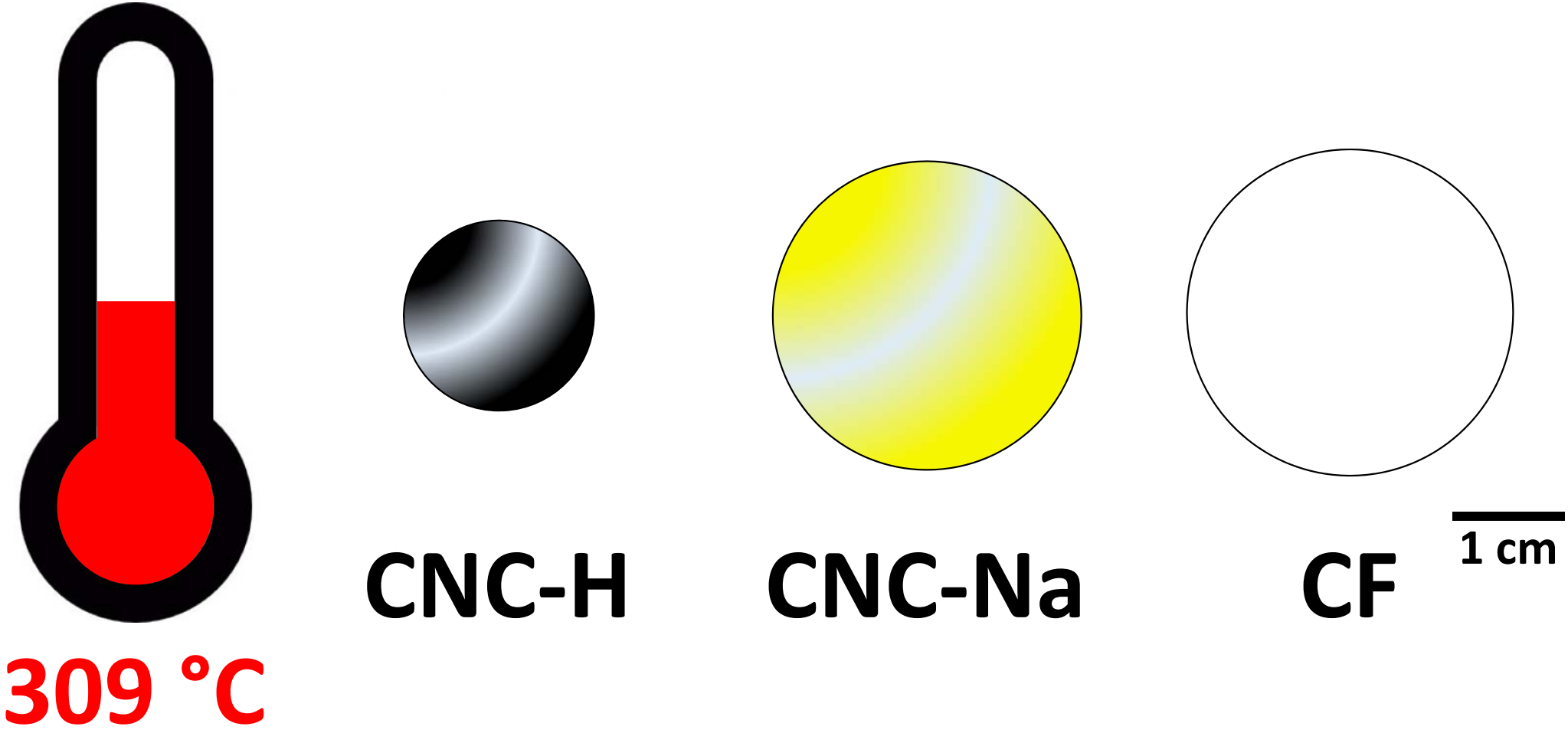

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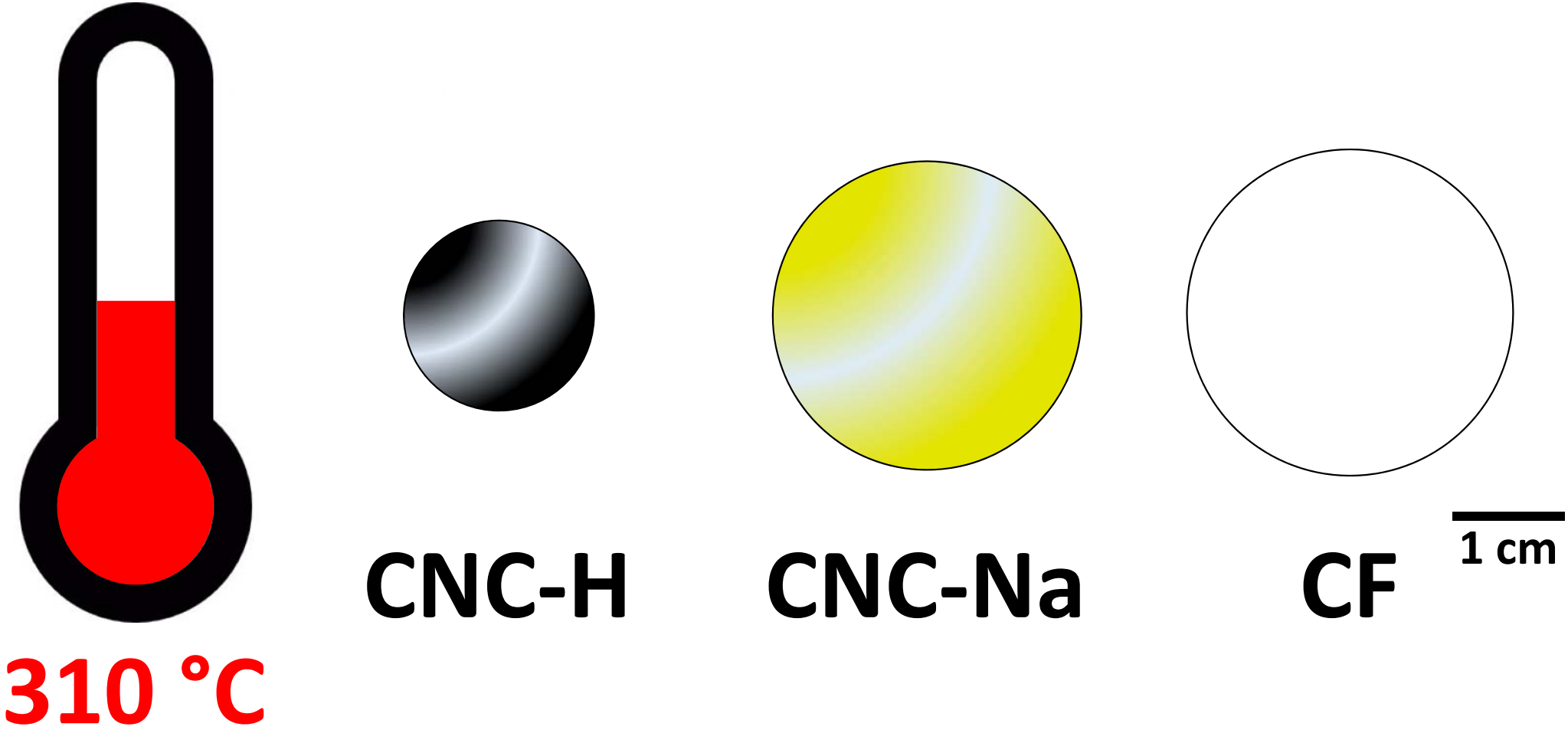

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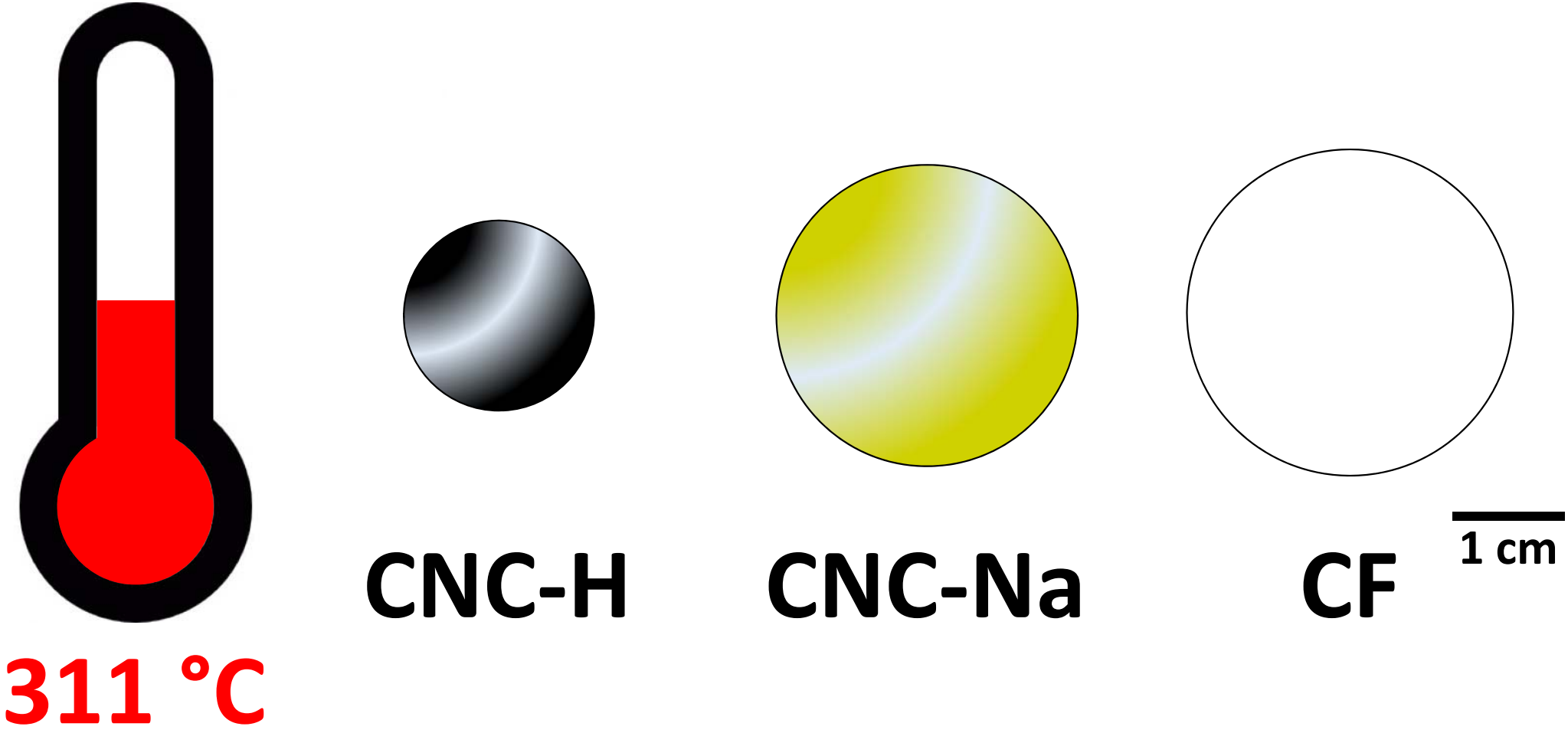

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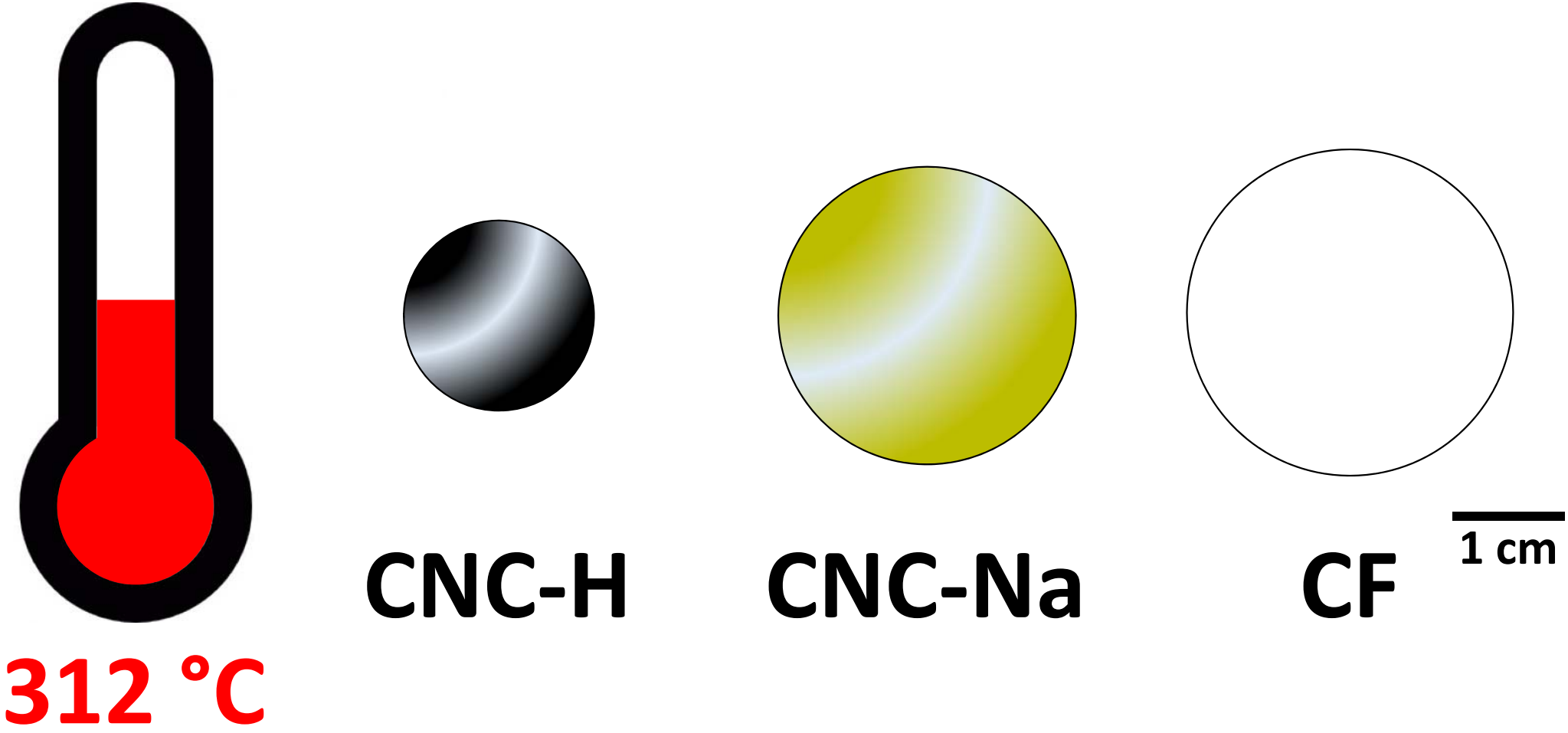

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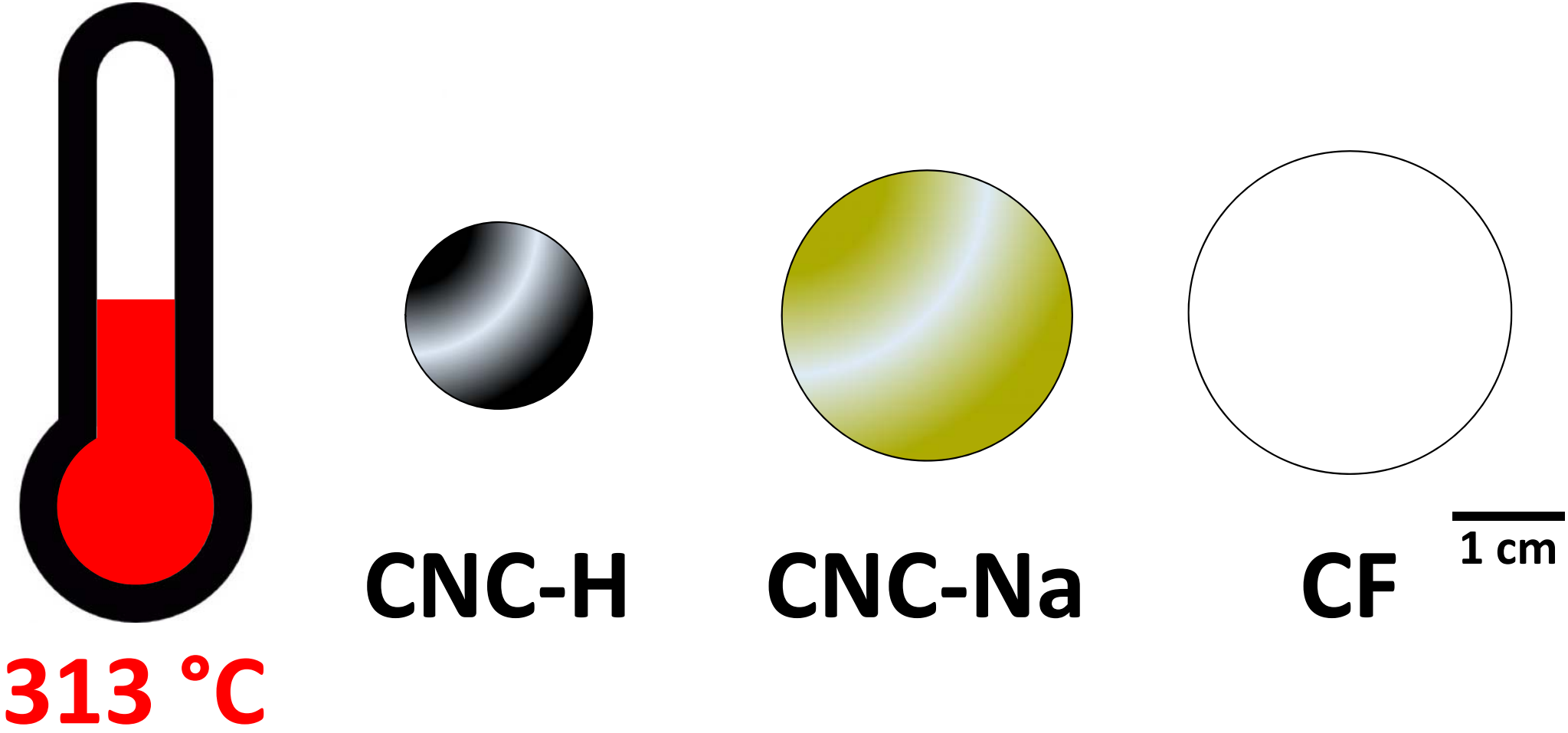

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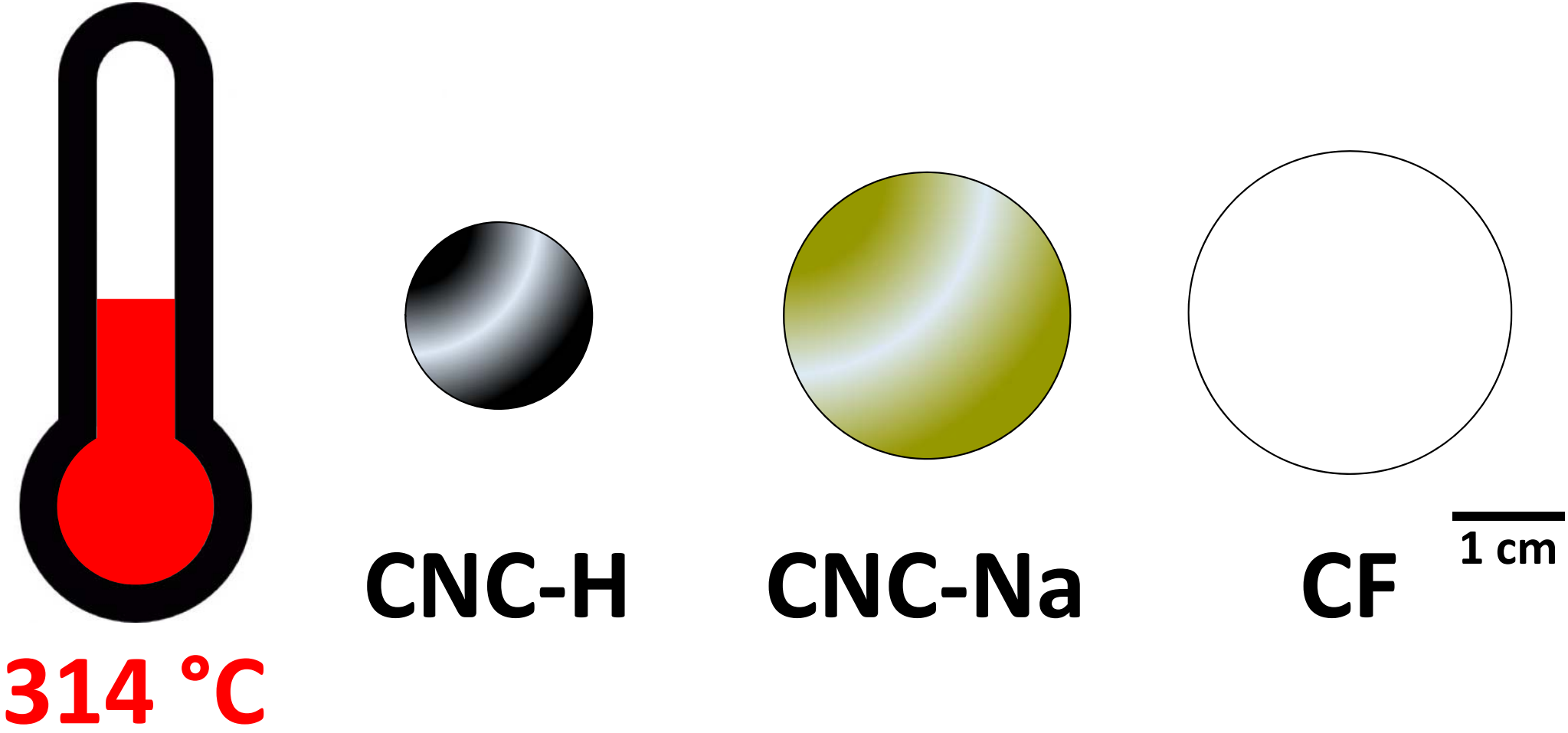

Results

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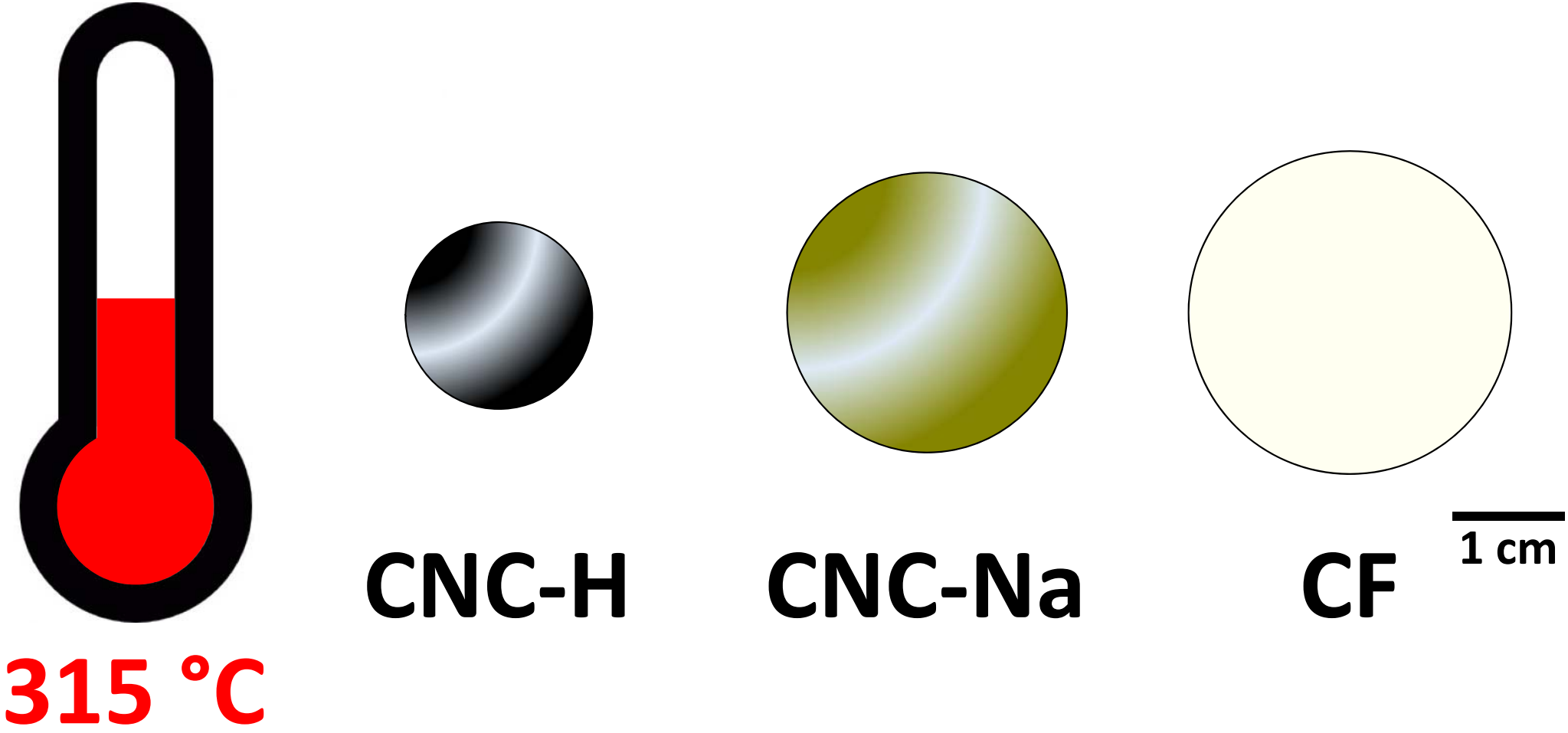

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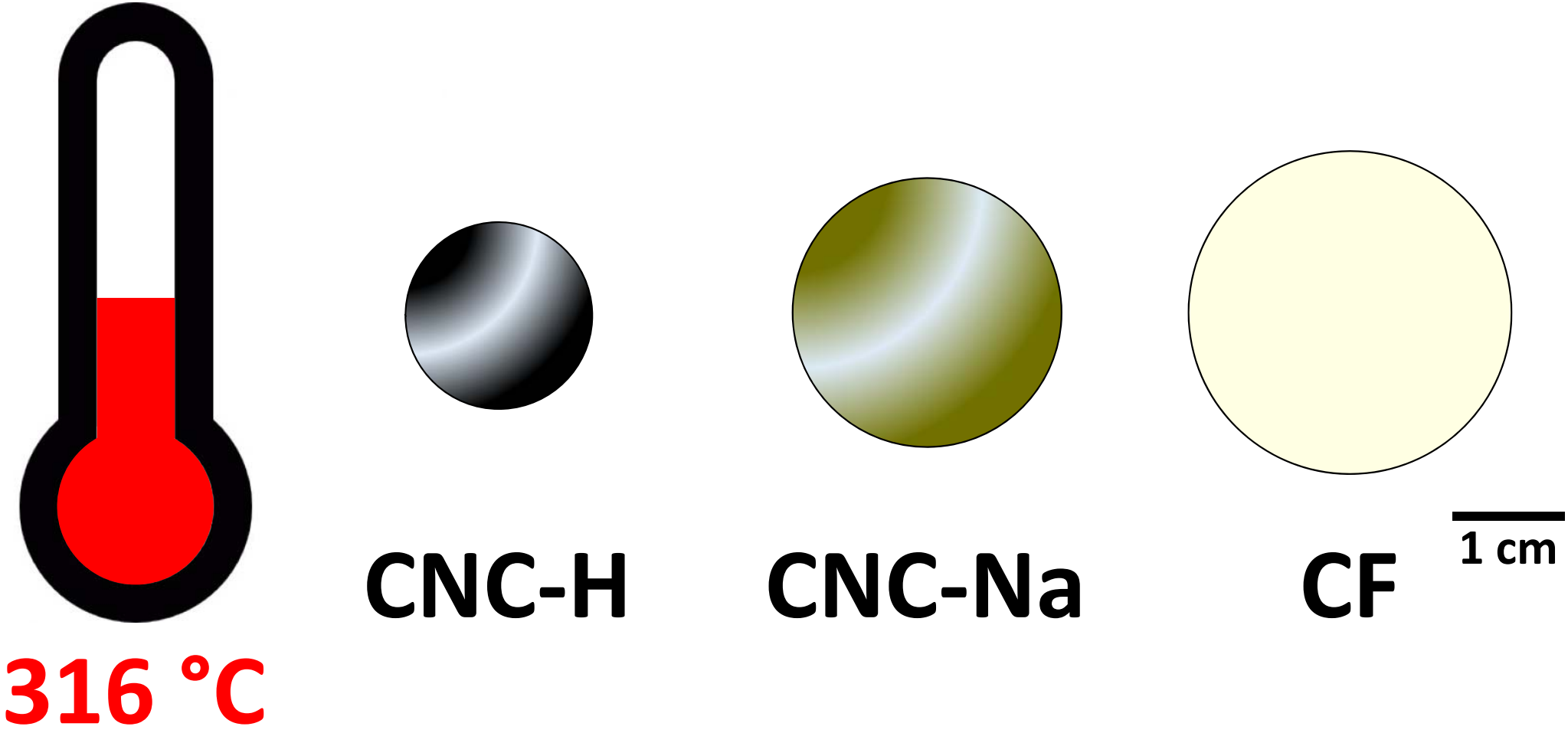

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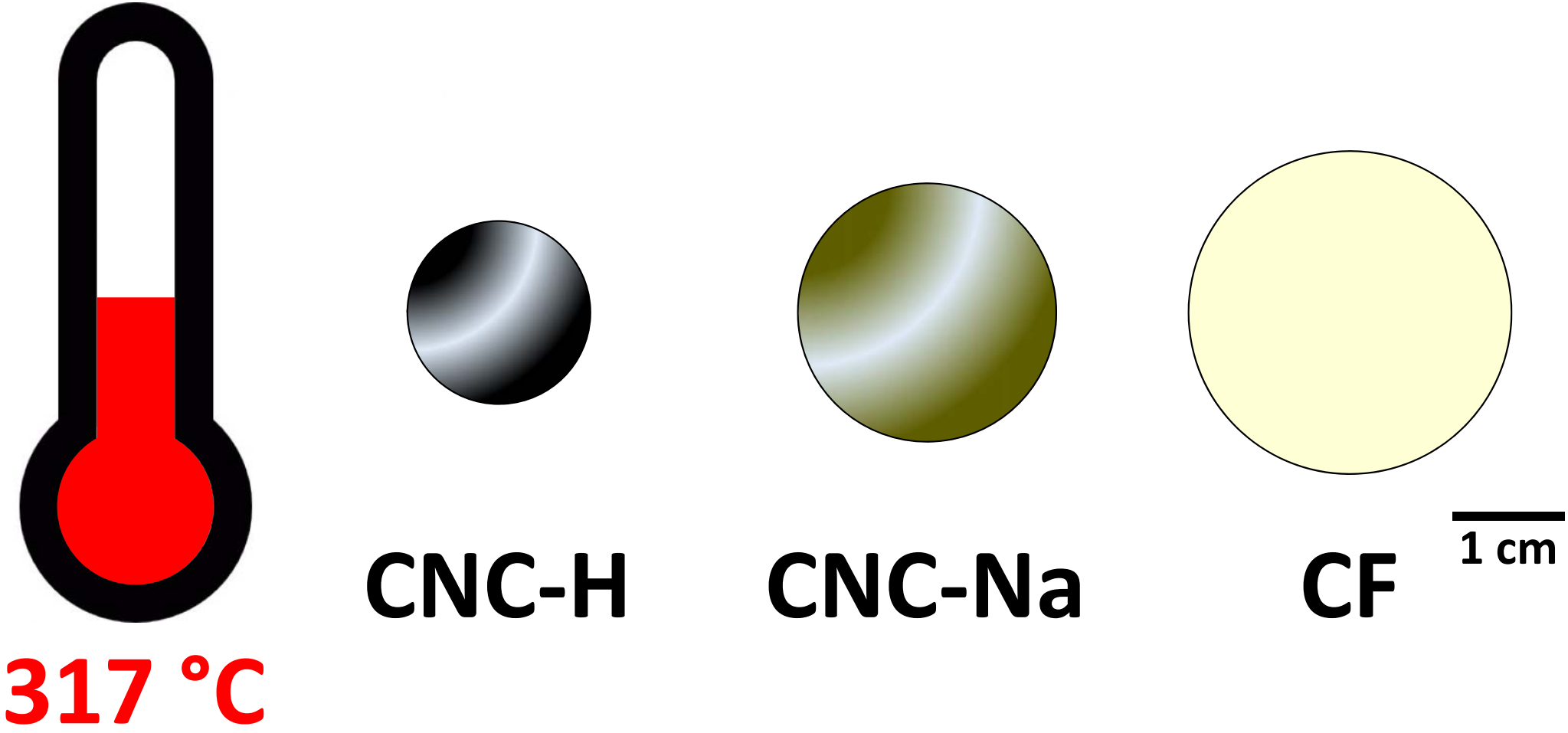

Results

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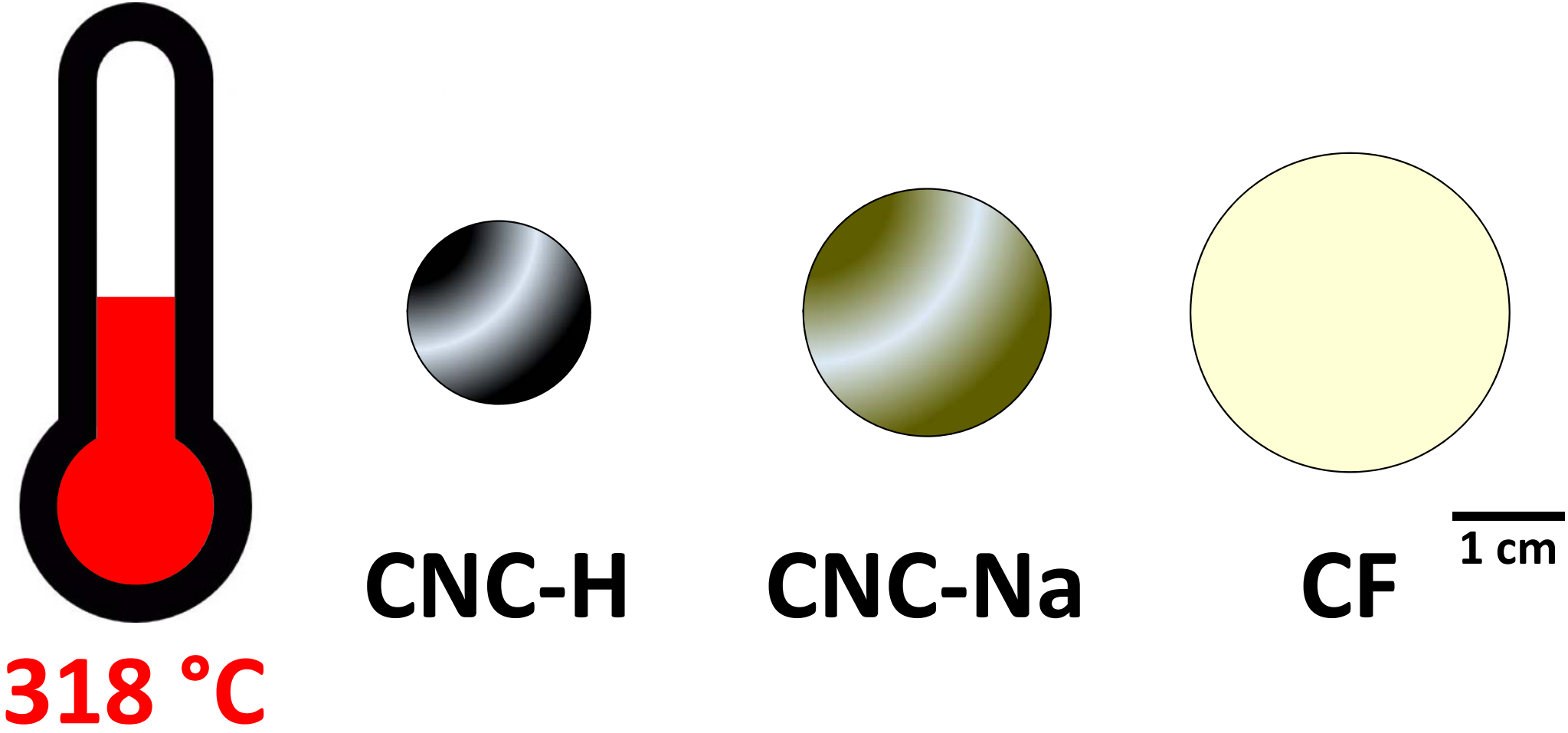
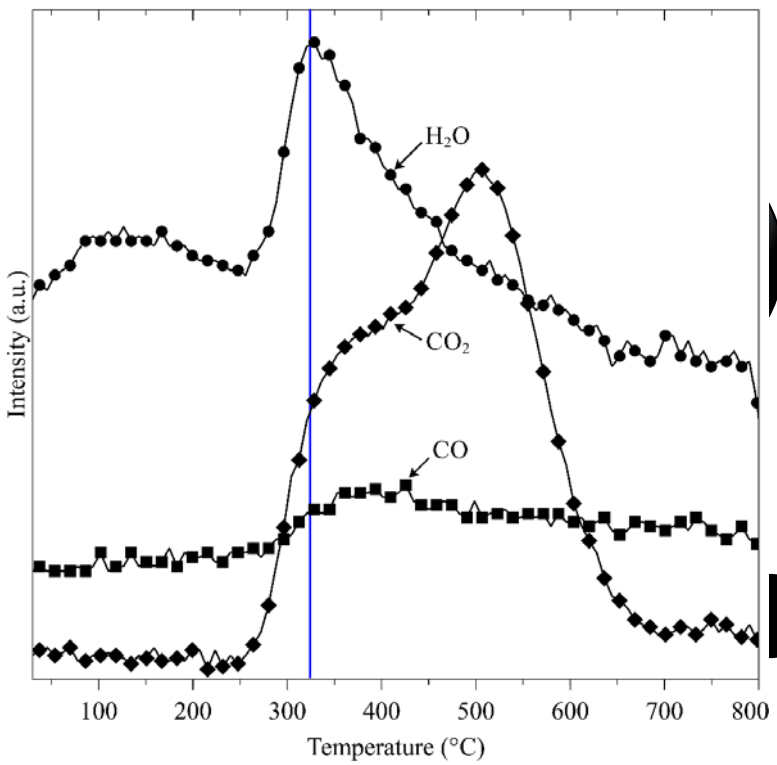
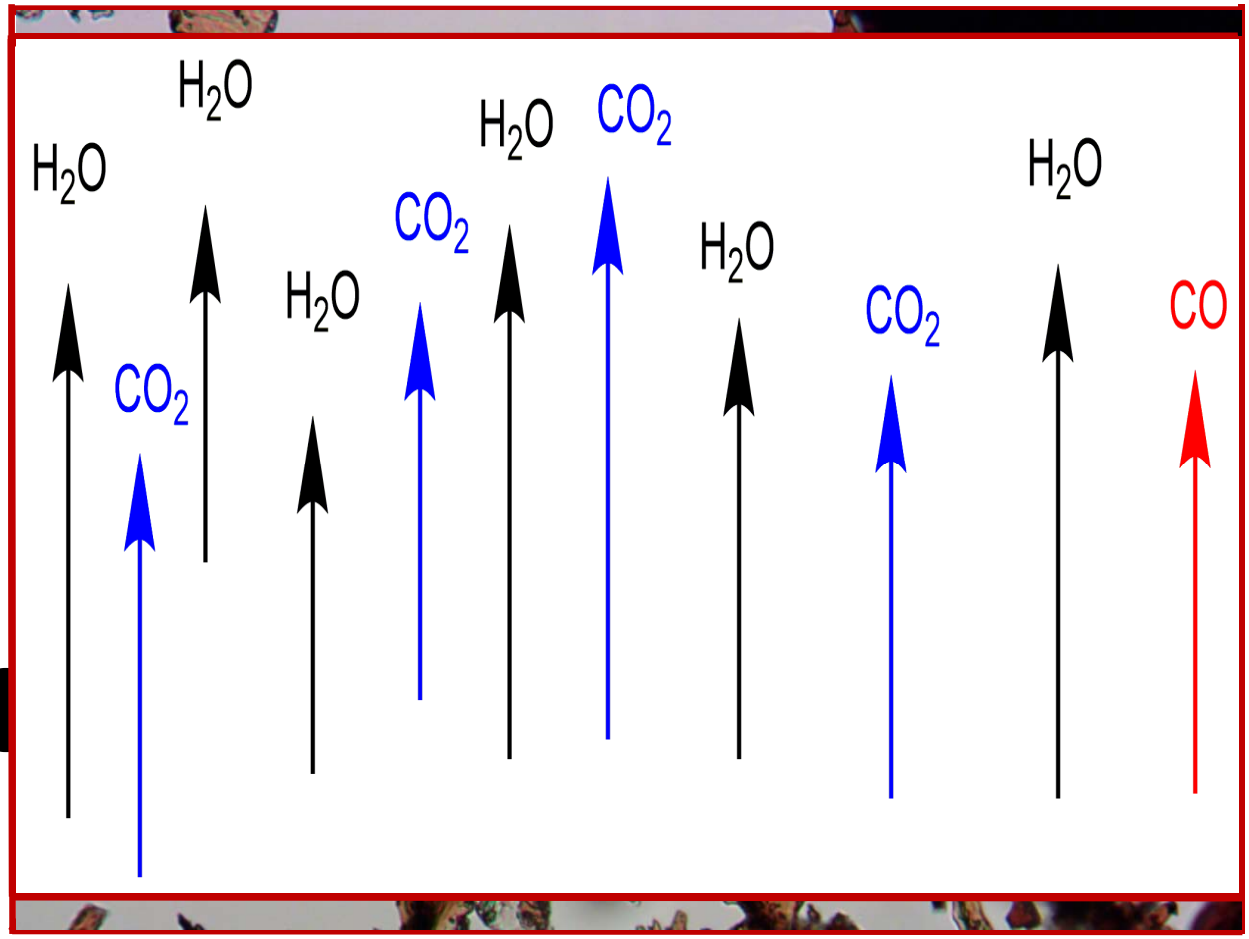


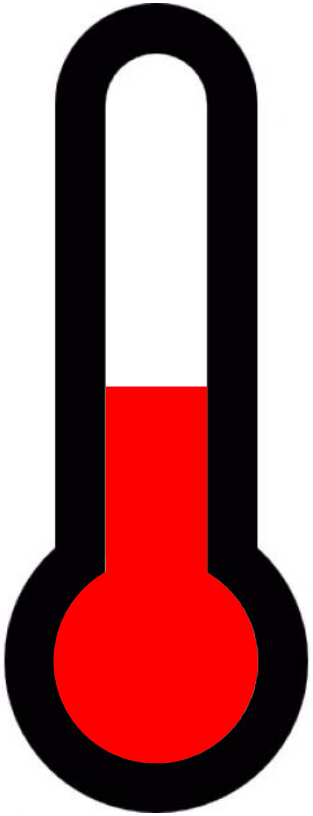
Results


H₂O
CO₂
CO
Intensity (a.u.)
Temperature (°C)
100
200
300
400
500
600
700
800

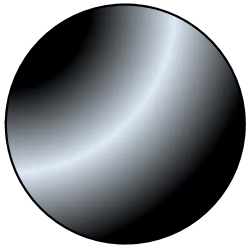

H2O
CO2
H2O
H2O
CO2
H2O
CO2
H2O
CO2
H2O
CO

Results

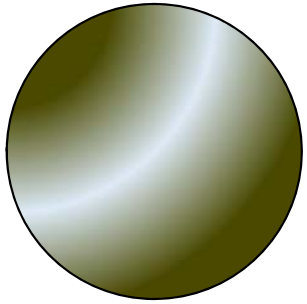
THE UNIVERSITY OF BRITISH COLUMBIA



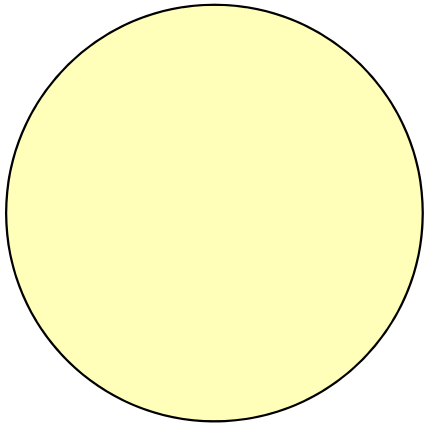
320 °C



CNC-H



CNC-Na

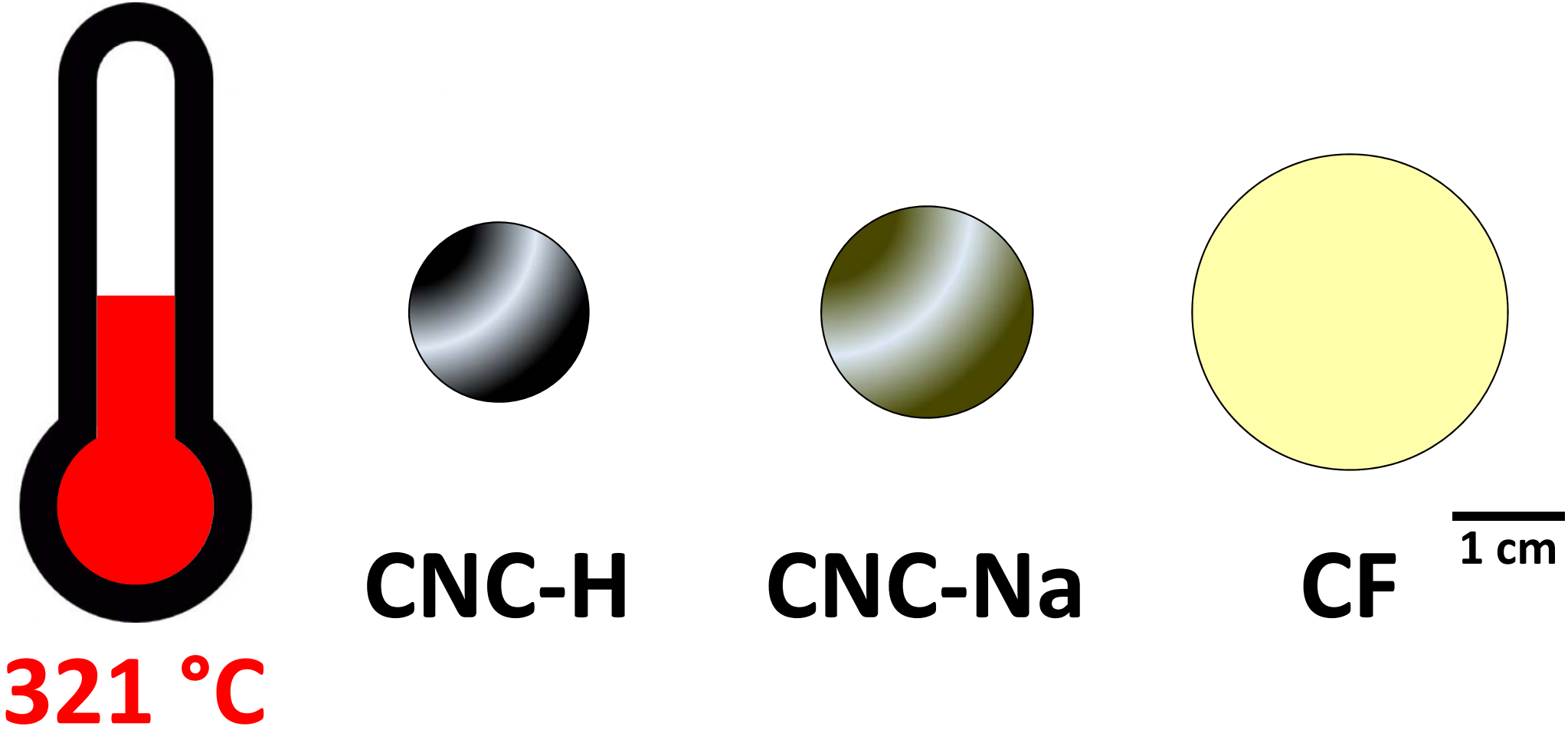


CF

1 cm

Results

THE UNIVERSITY OF BRITISH COLUMBIA



Results

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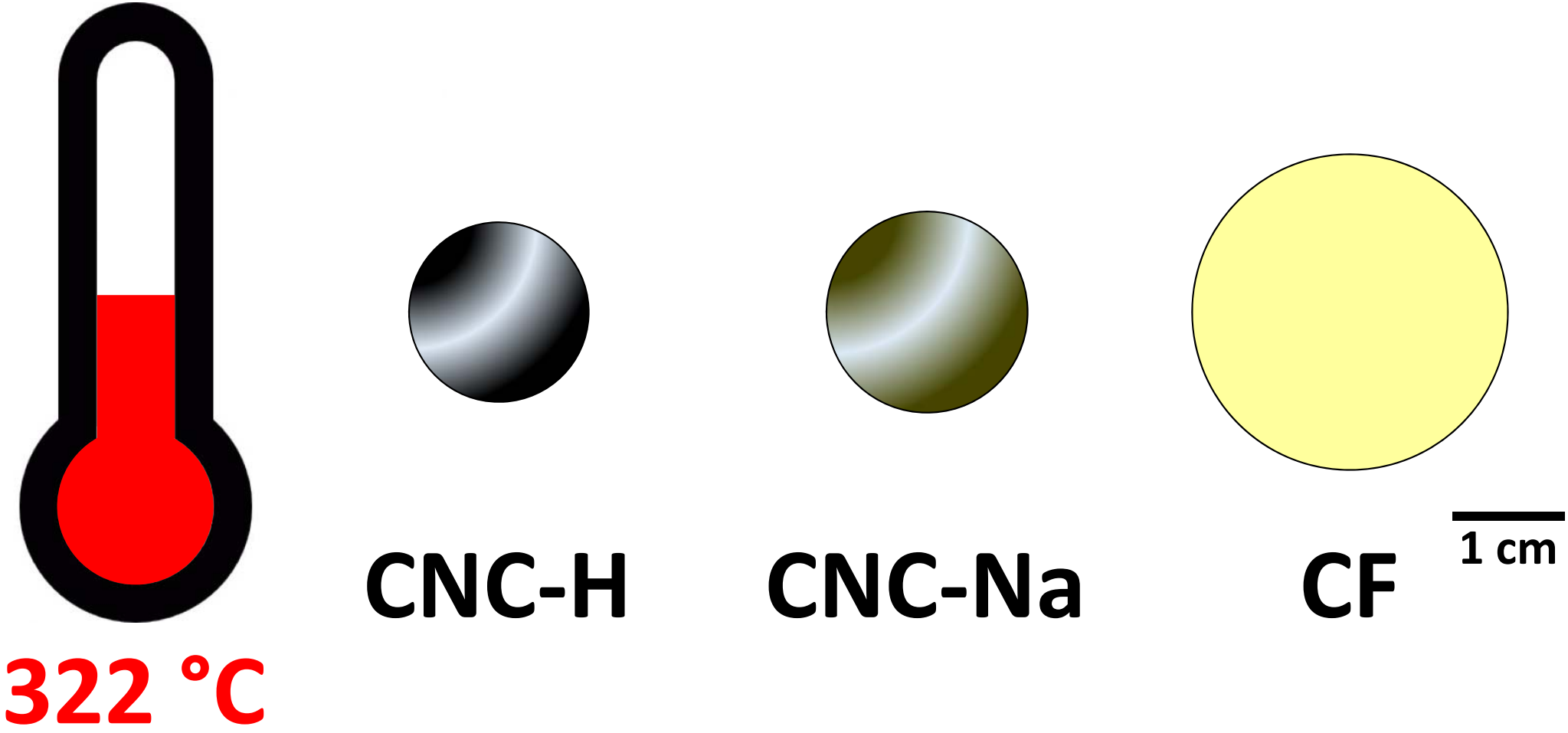

Results

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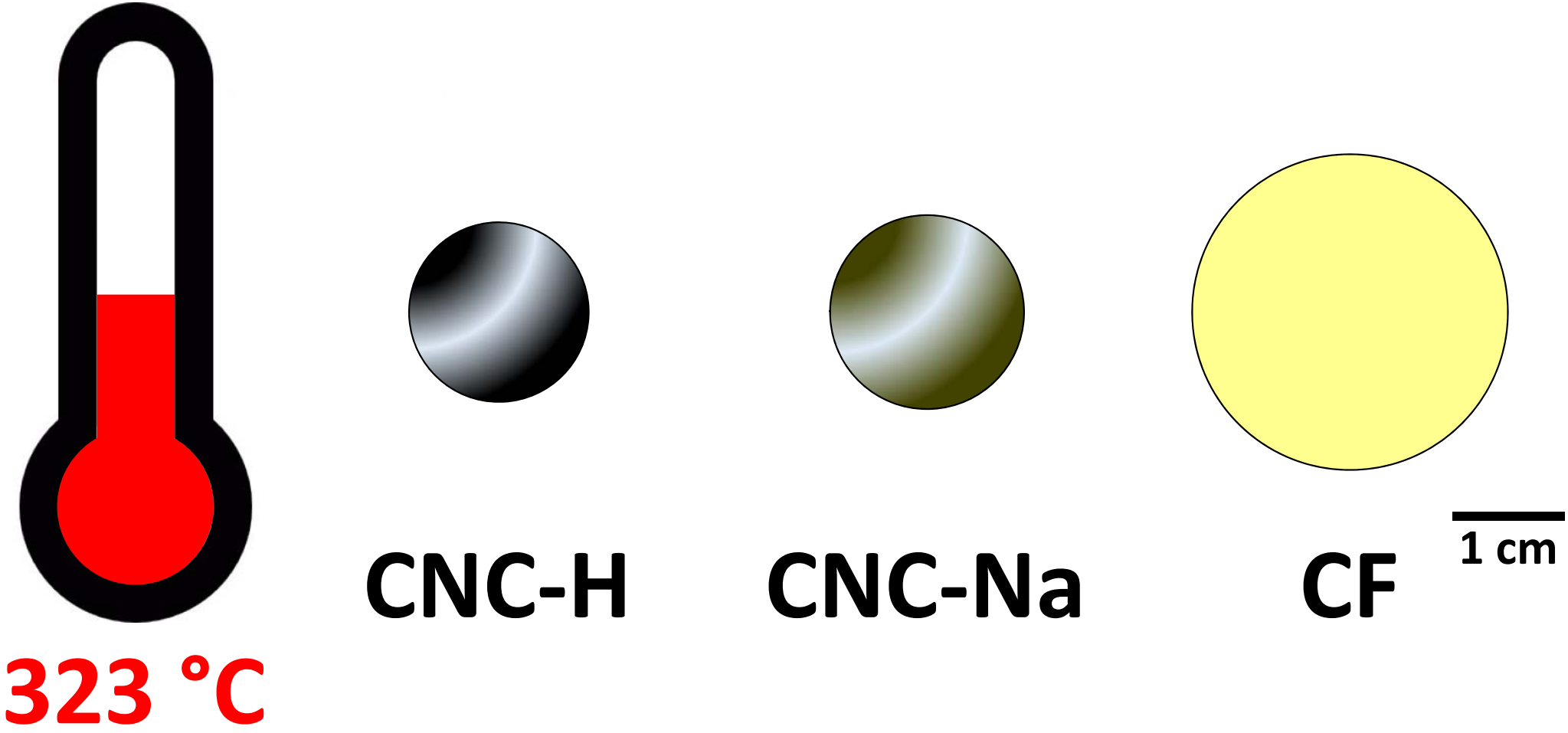

Results

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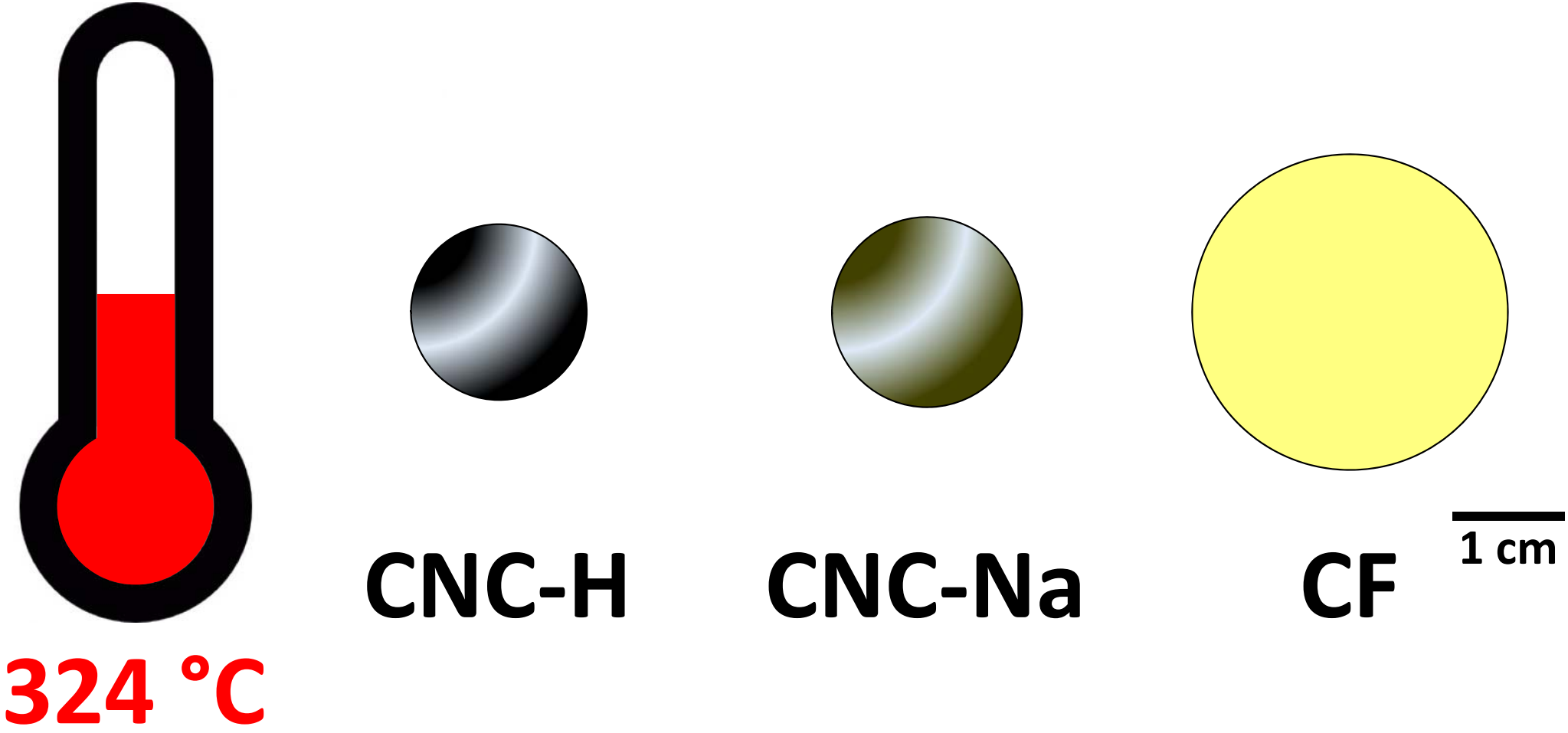

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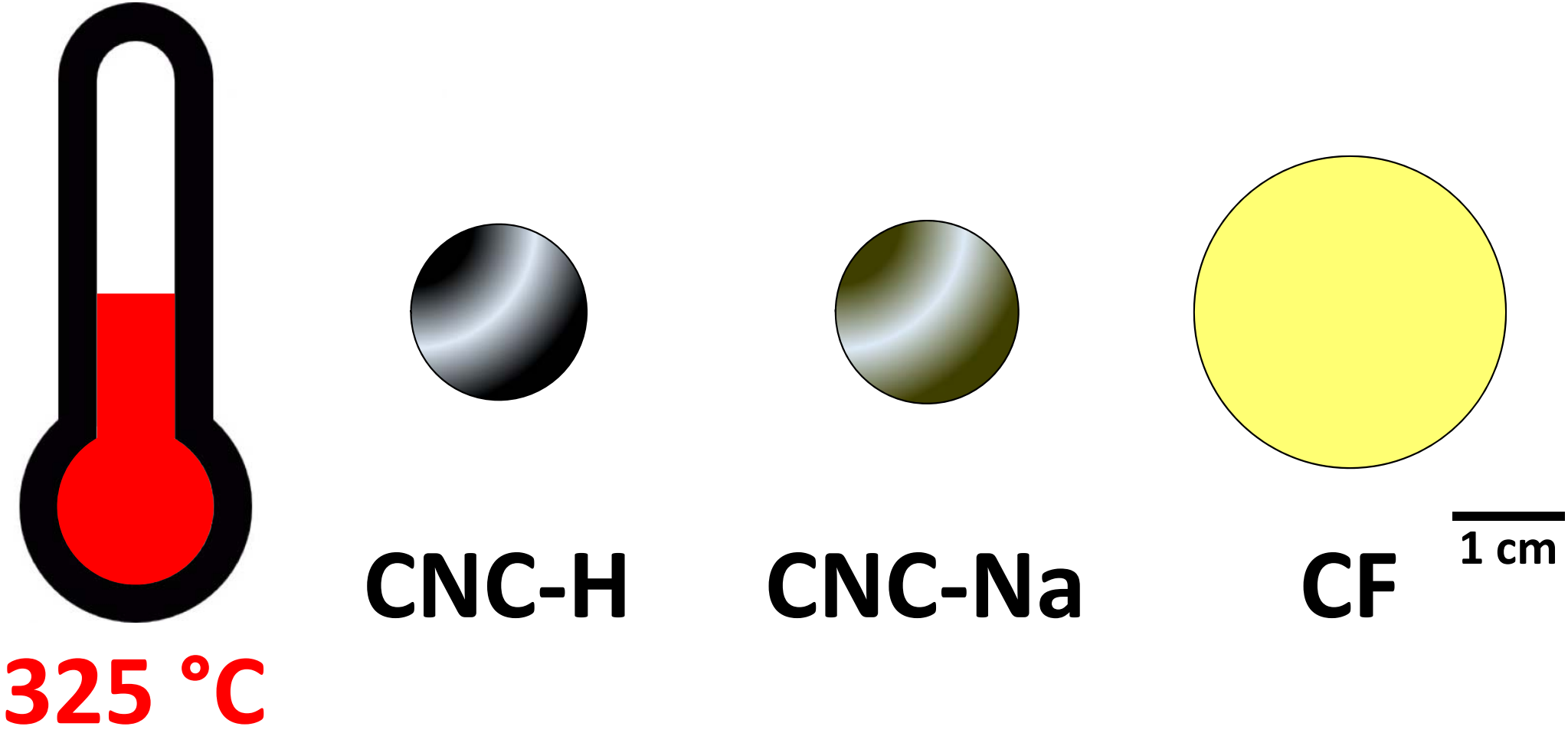

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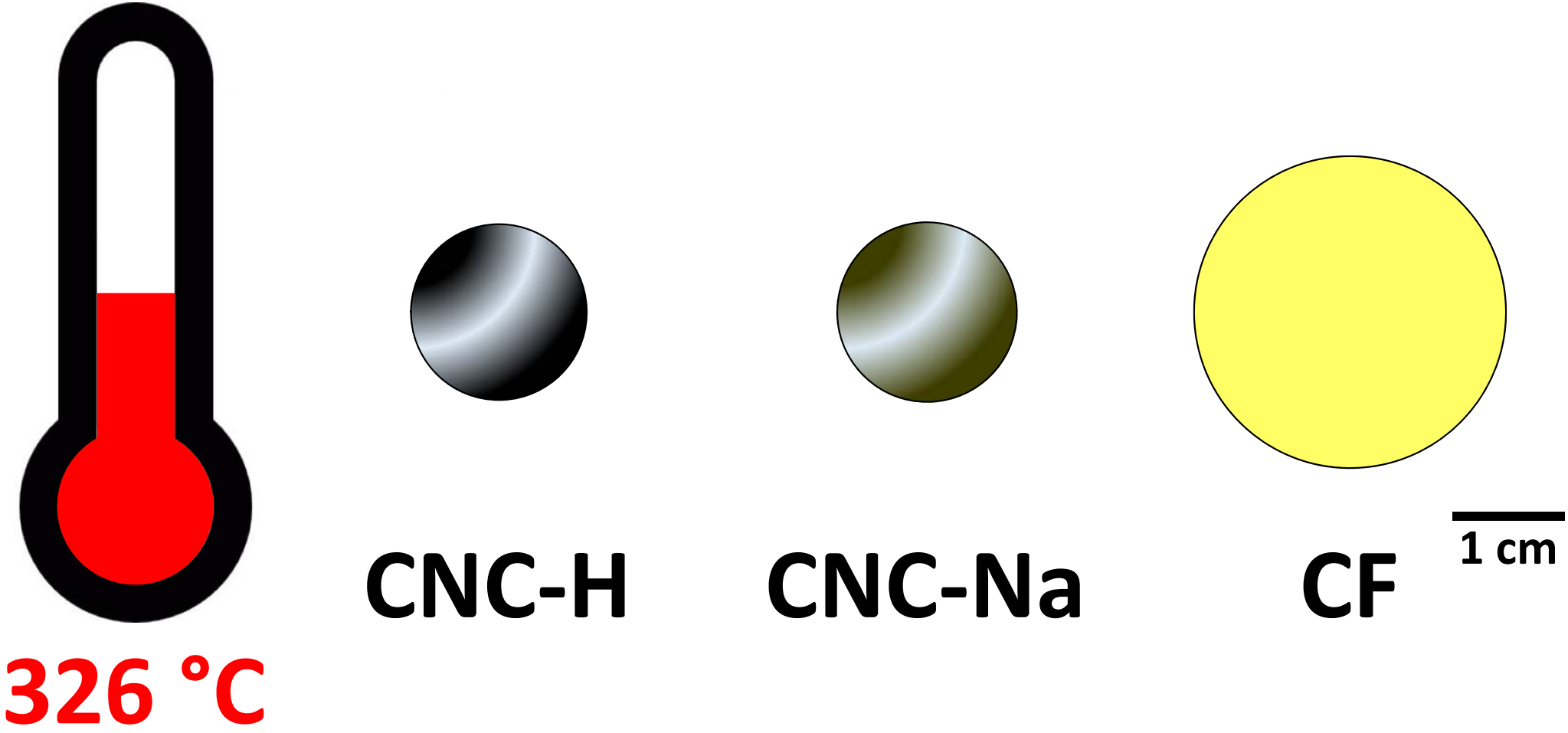

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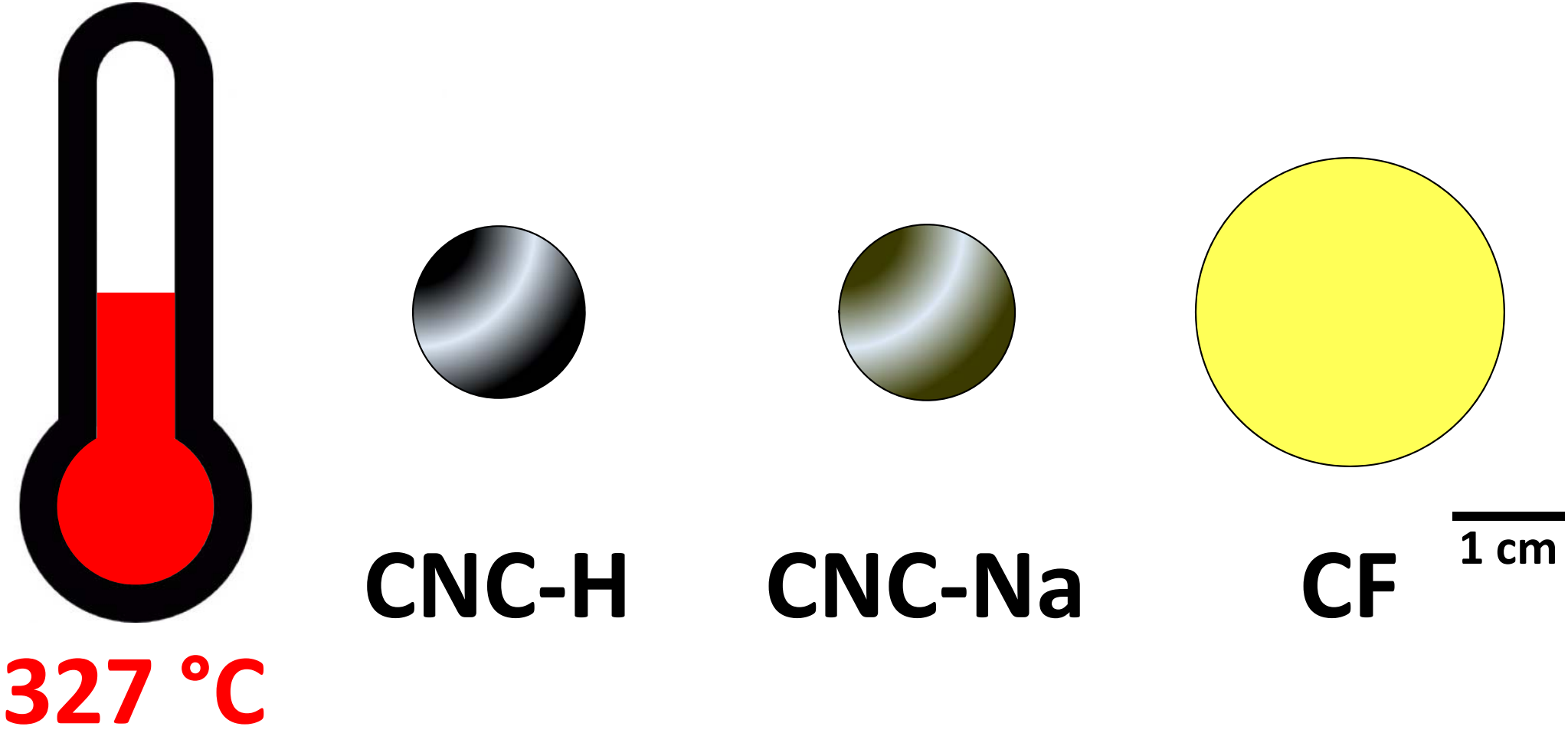

Results

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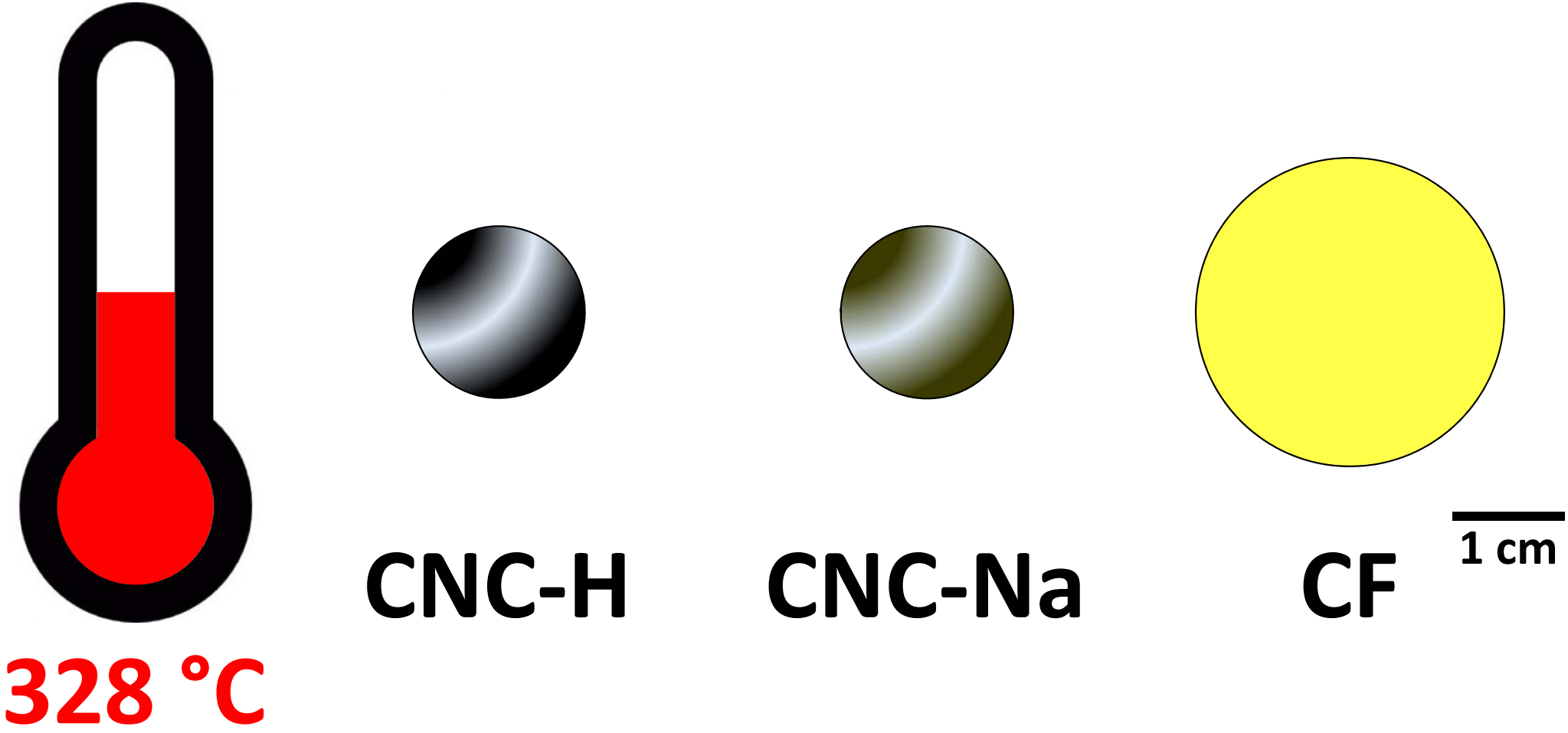

Results

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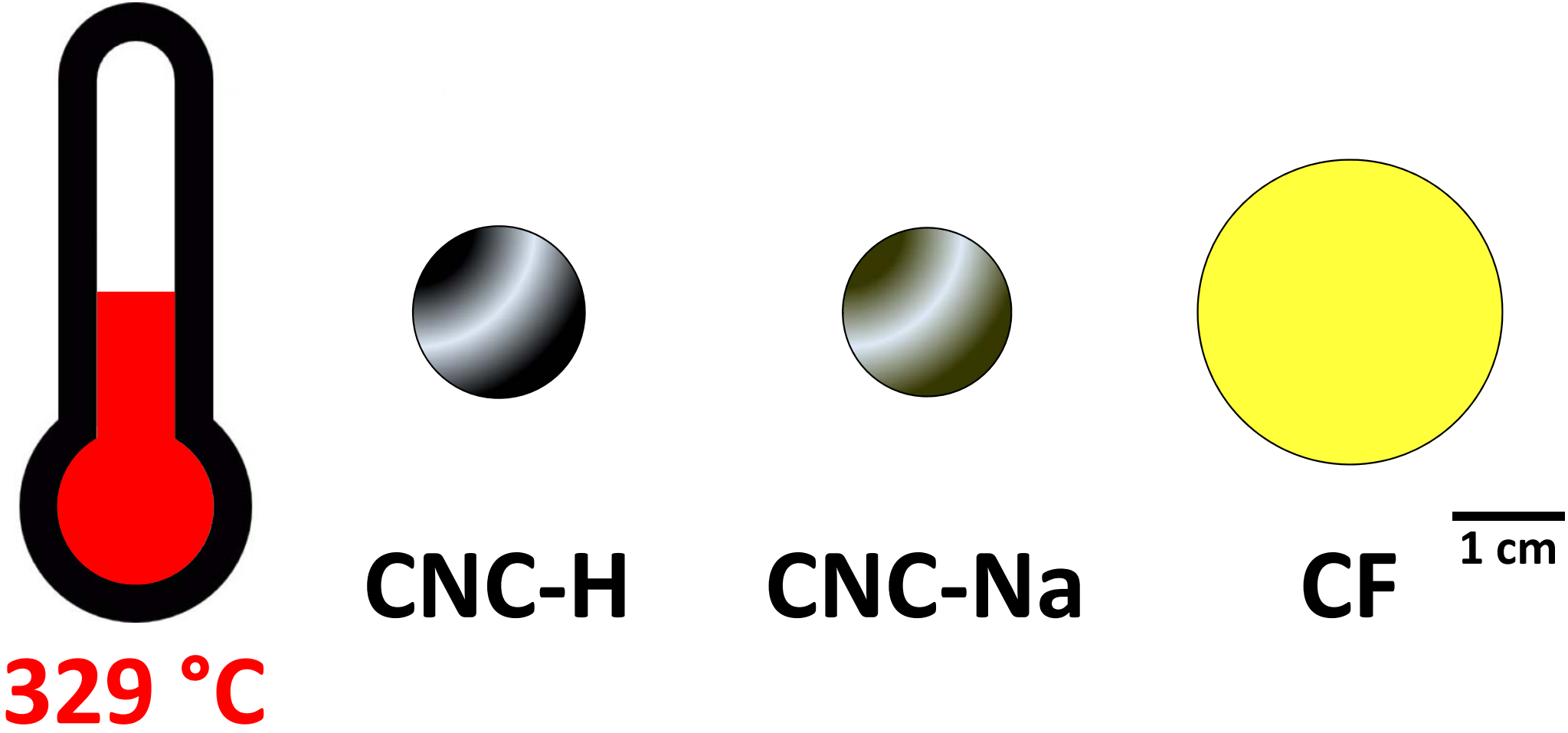

Results

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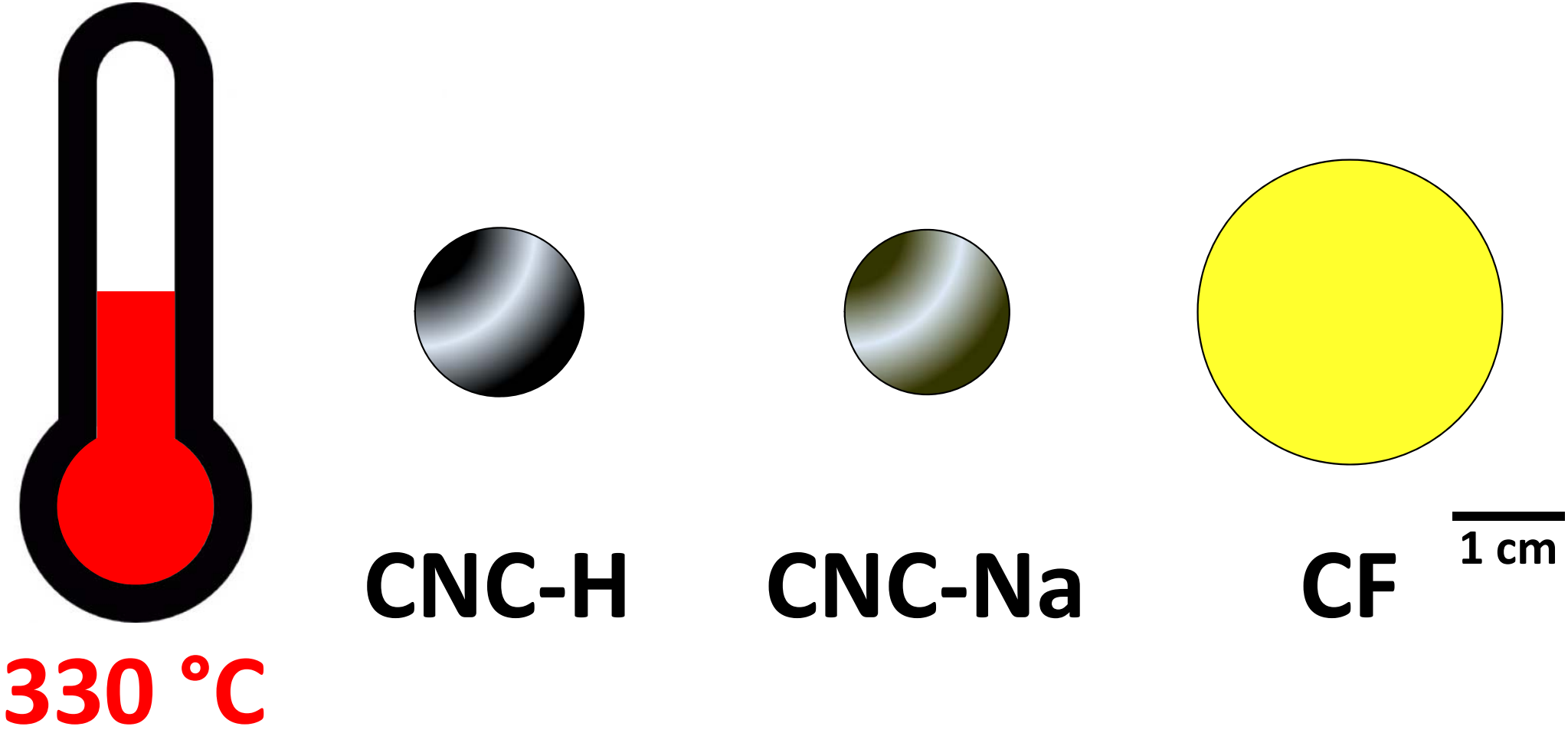

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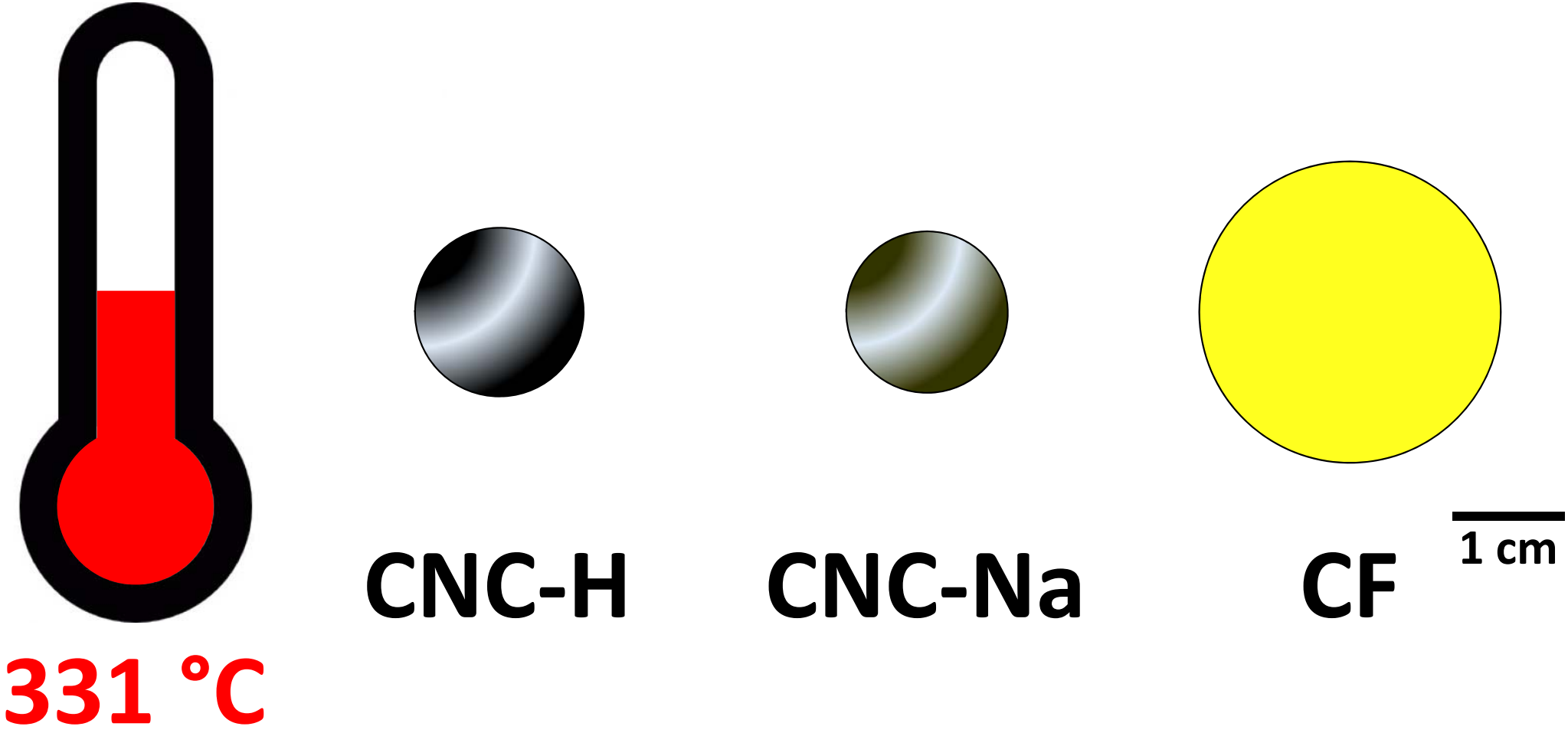

Results

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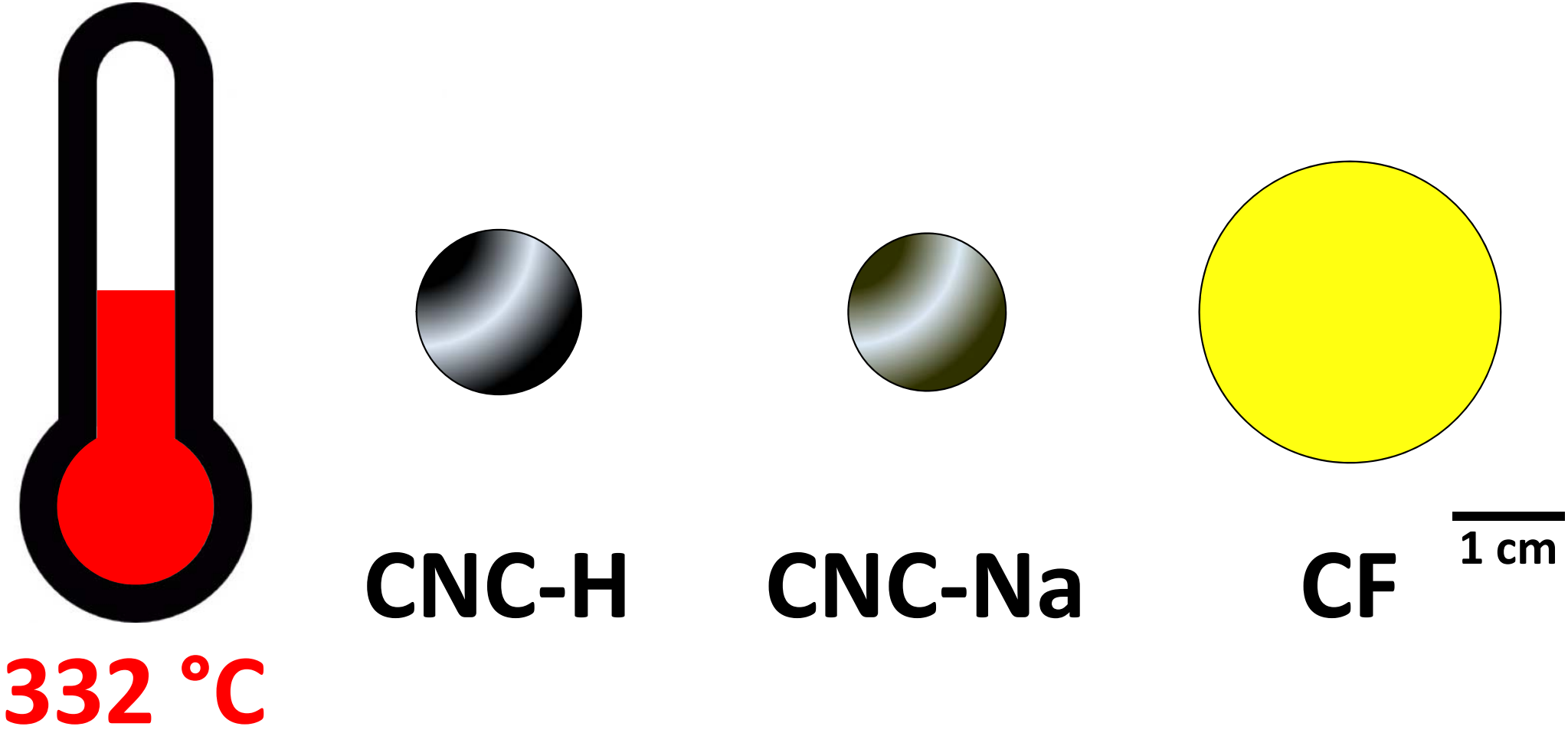

Results

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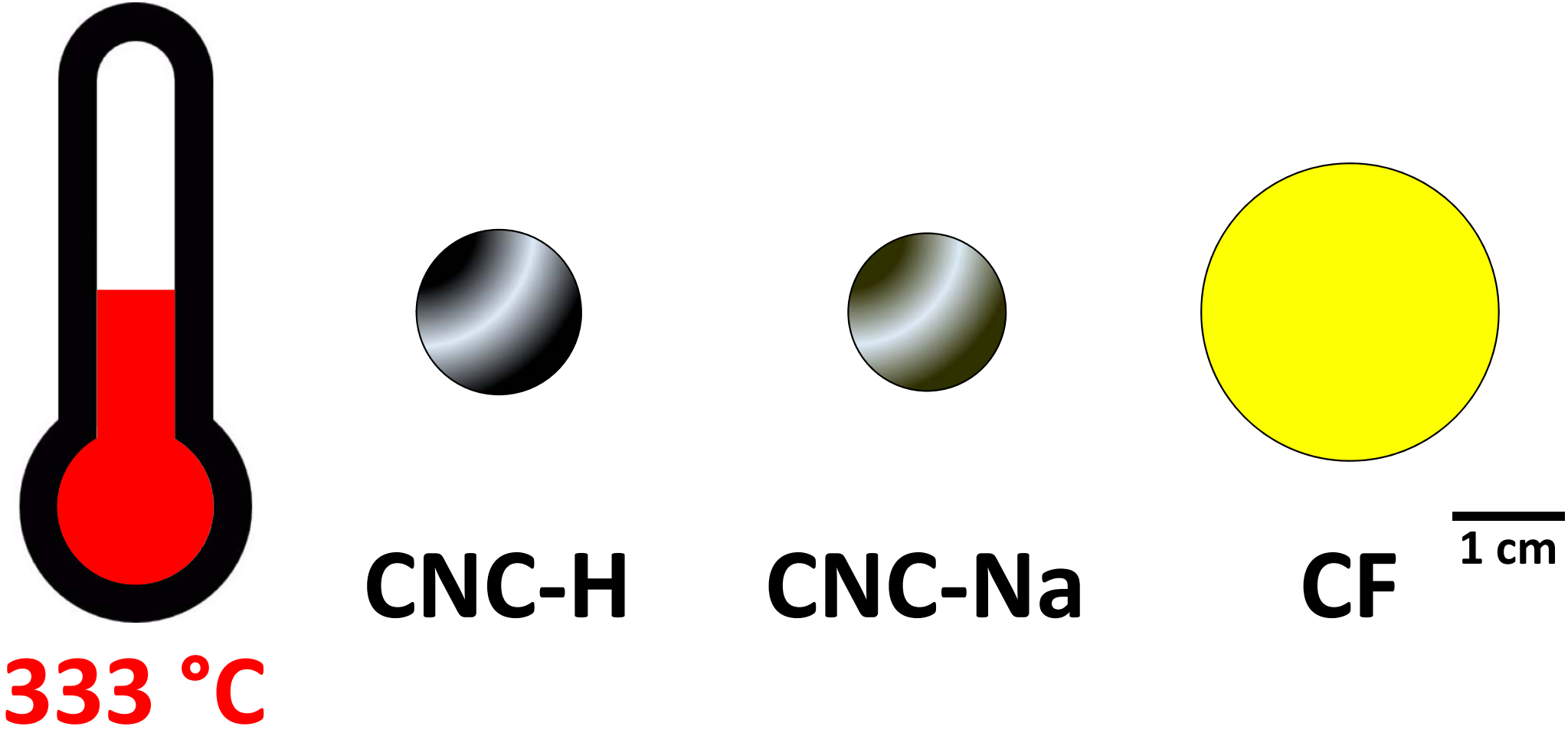

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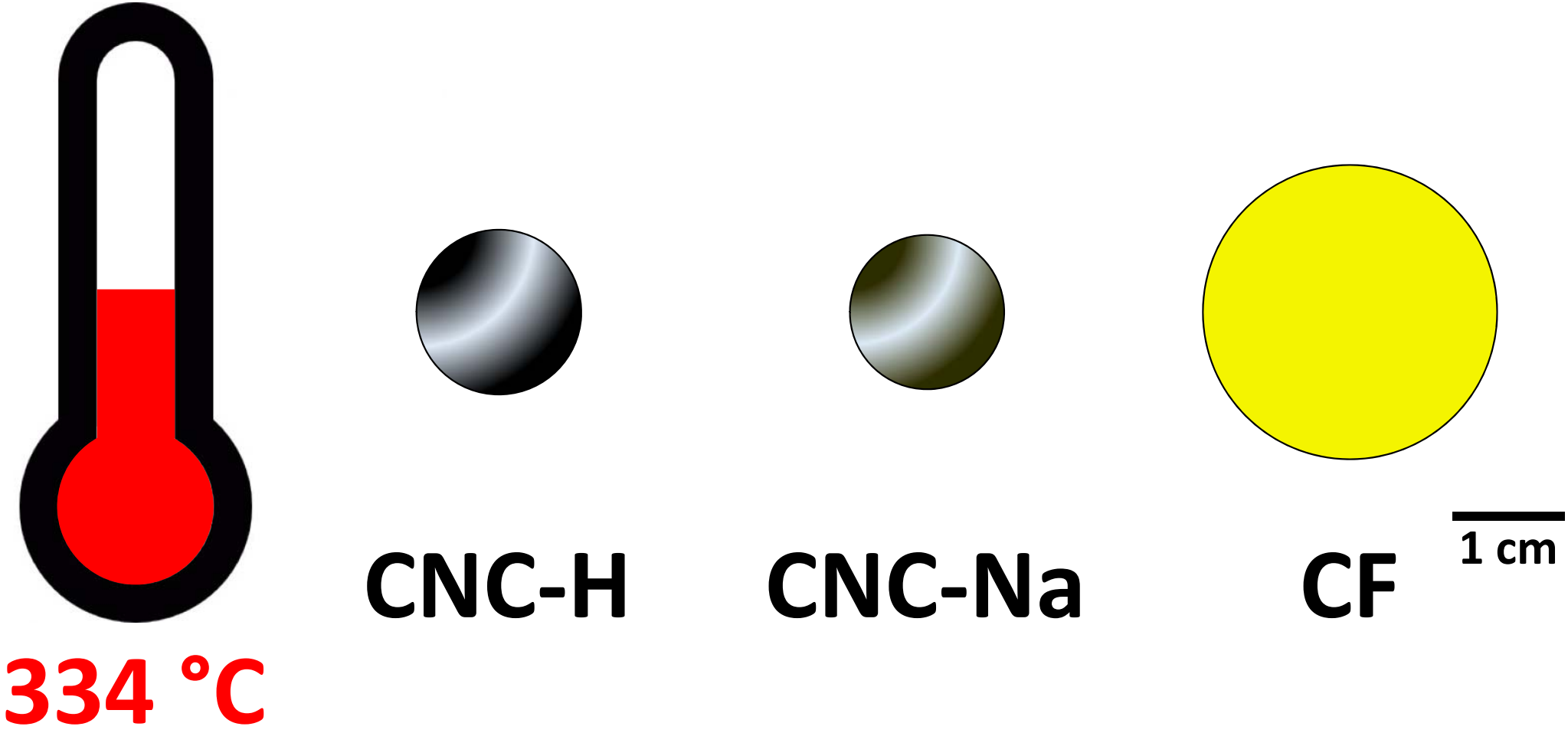

Results

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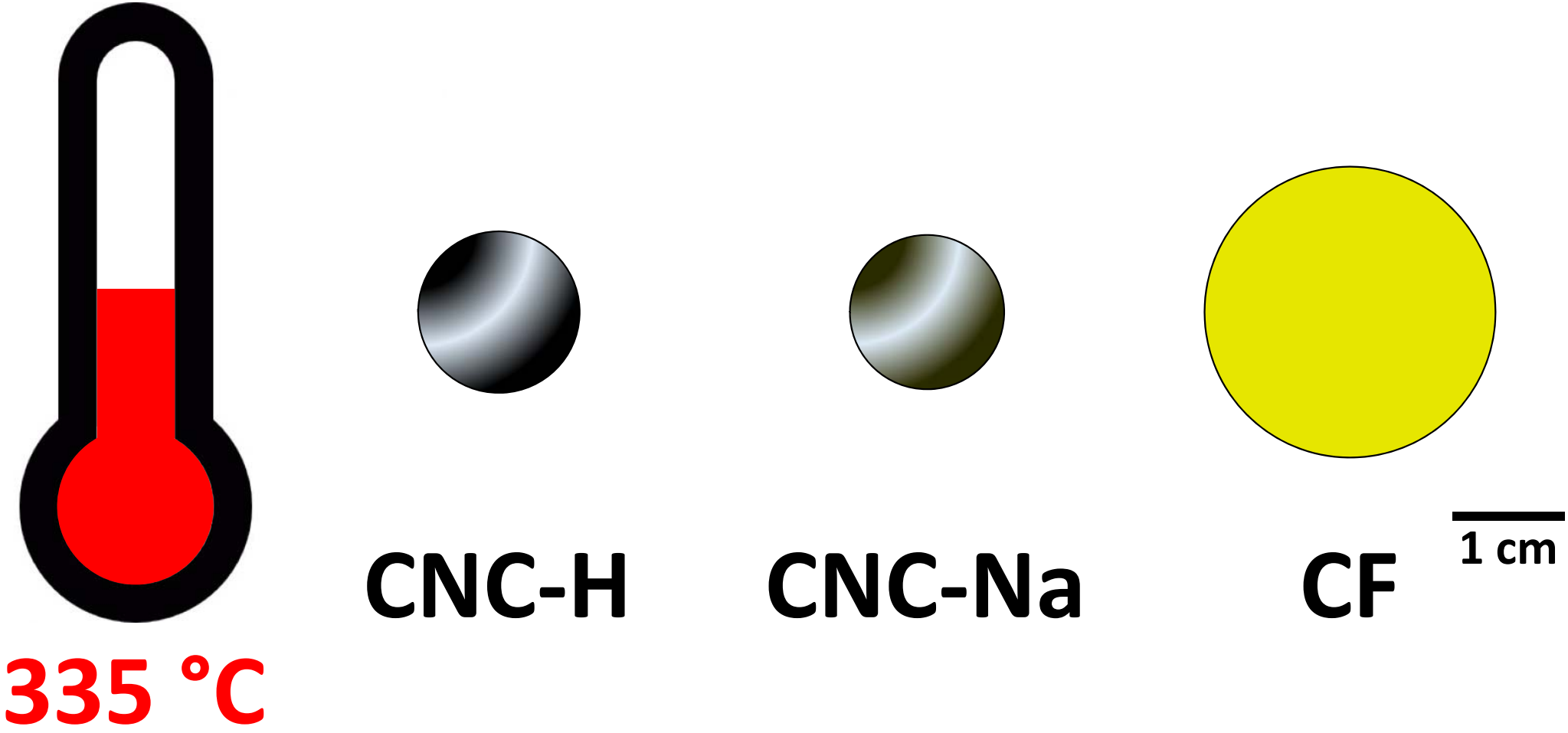

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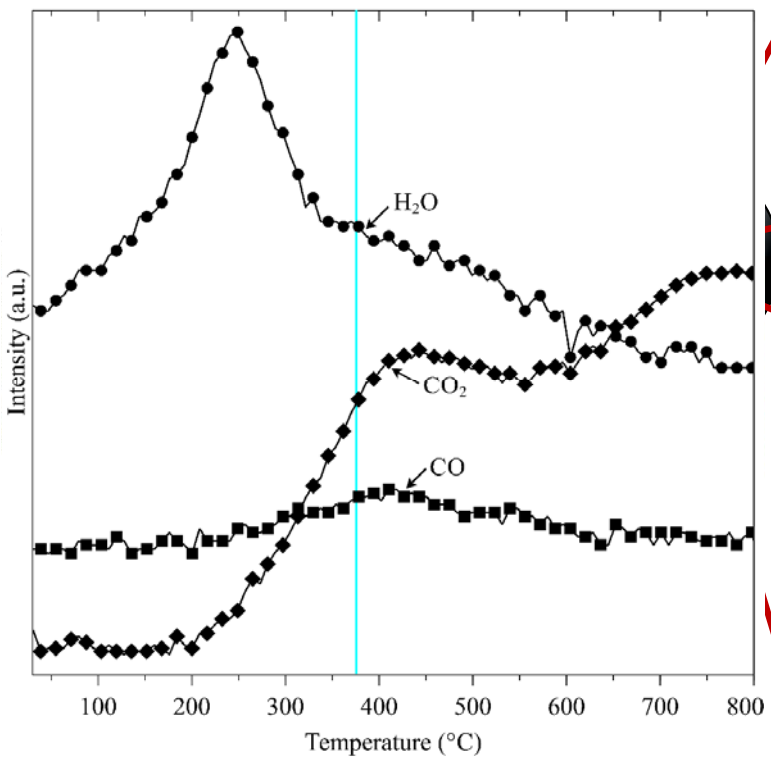
H₂O
CO₂
CO
Intensity (a.u.)
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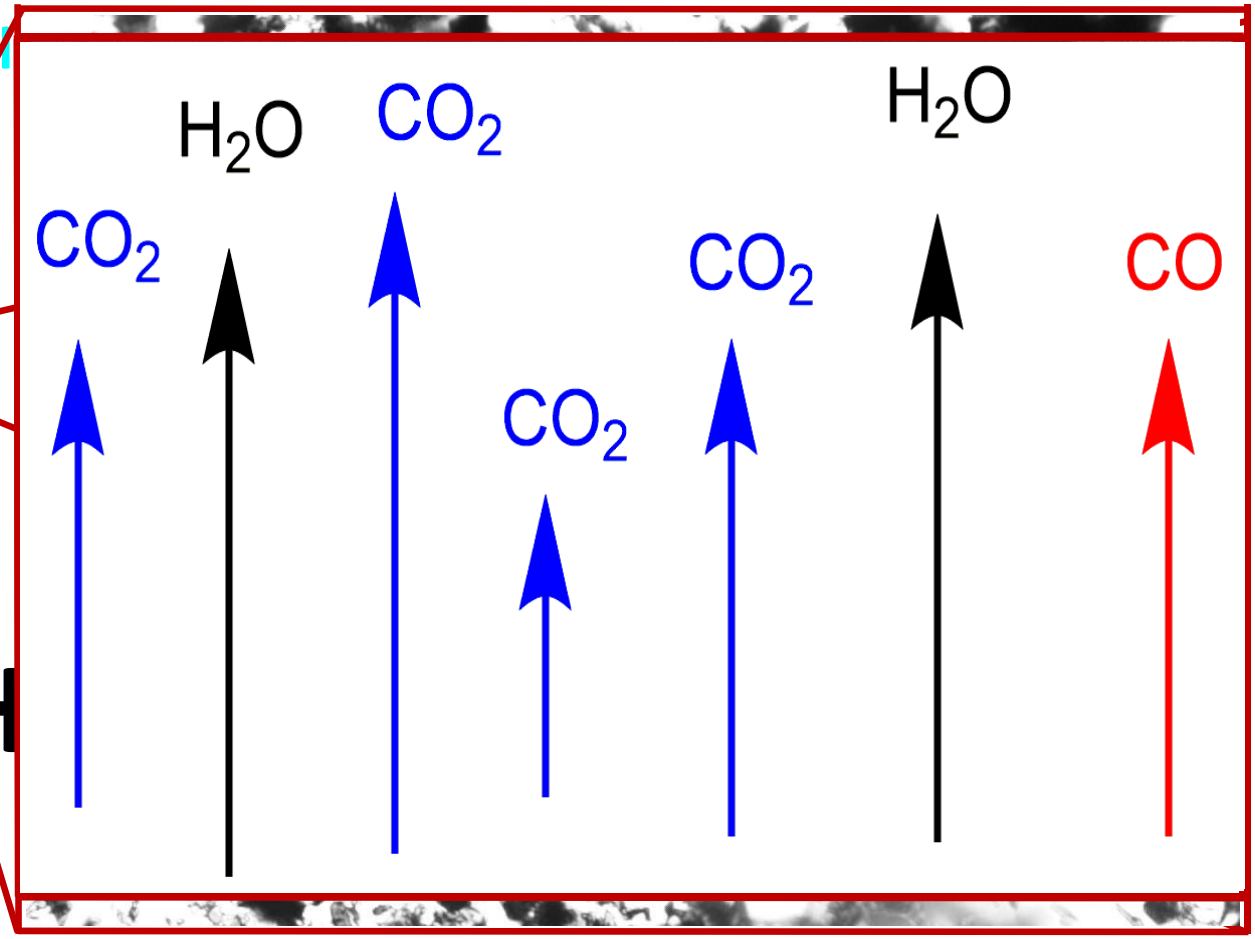
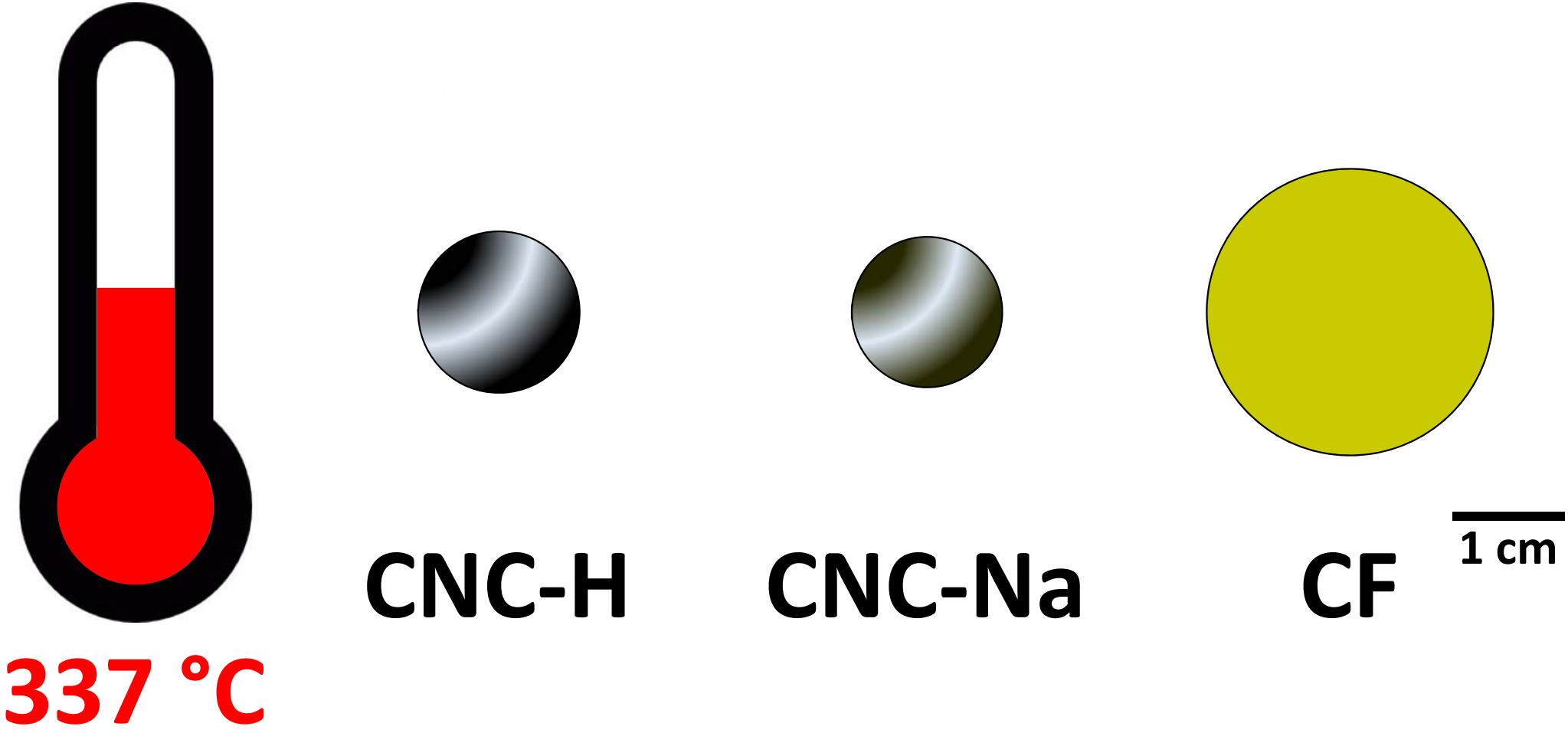
Temperature (°C)


CO2
H2O
CO2
CO2
CO2
H2O
CO

Results

THE UNIVERSITY OF BRITISH COLUMBIA



Results

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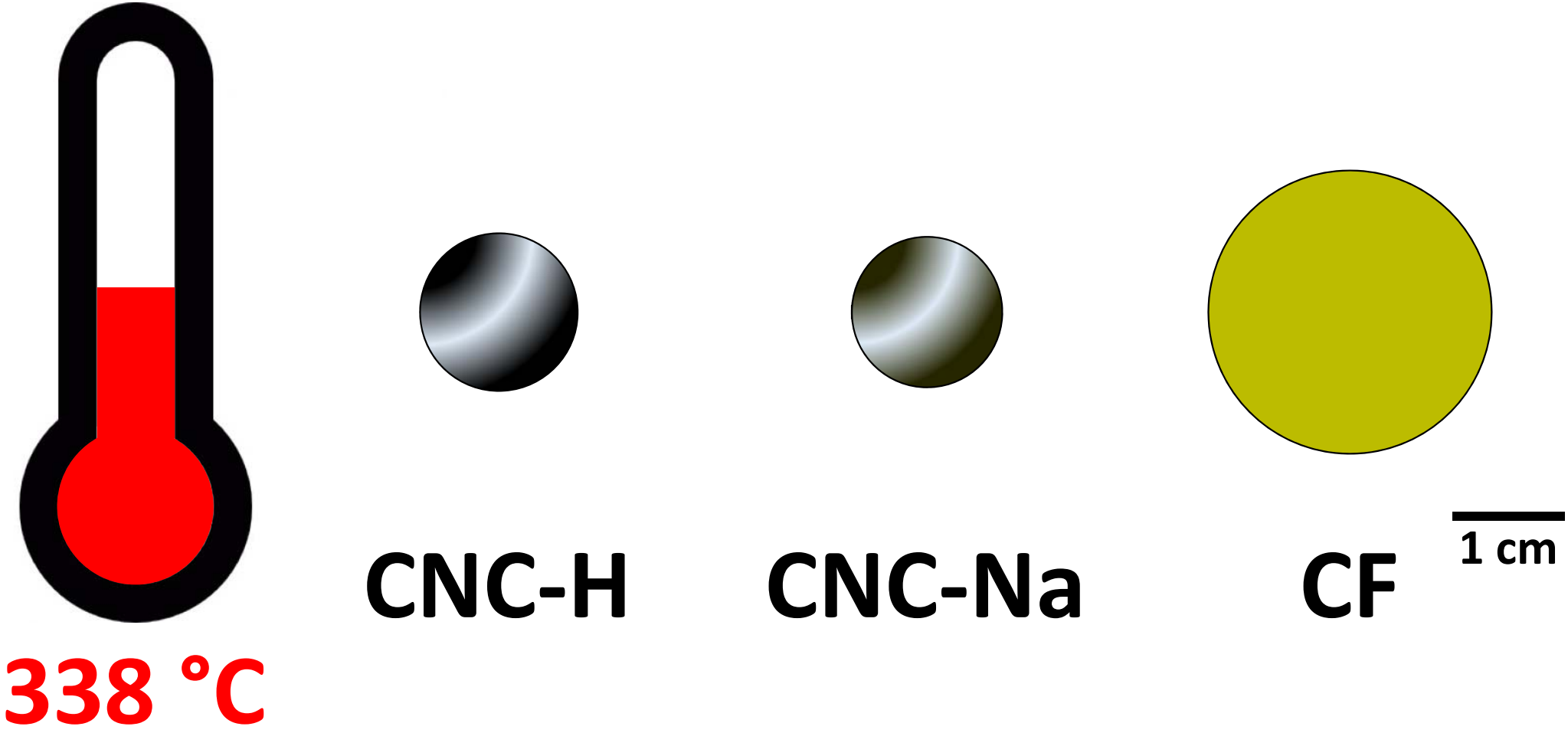

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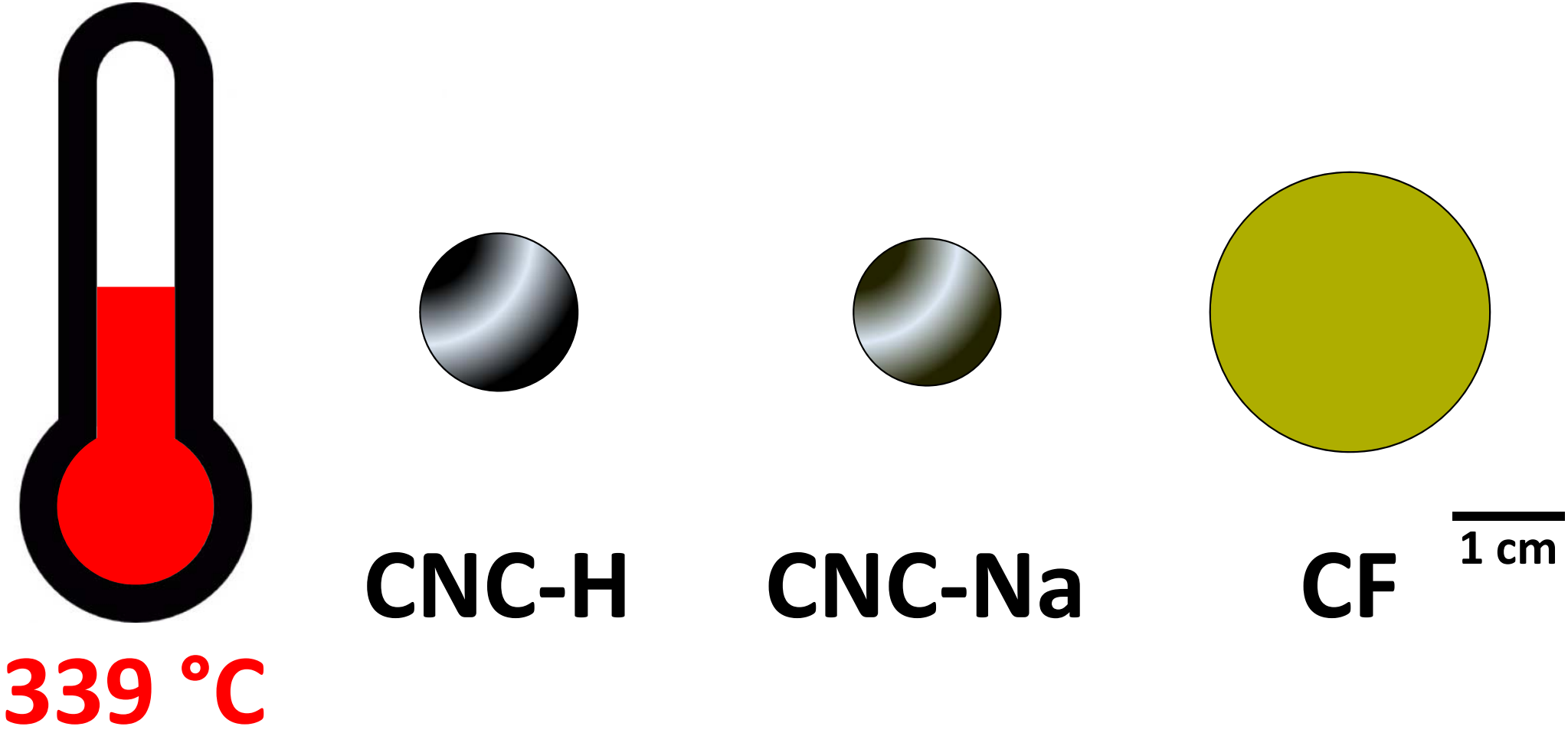

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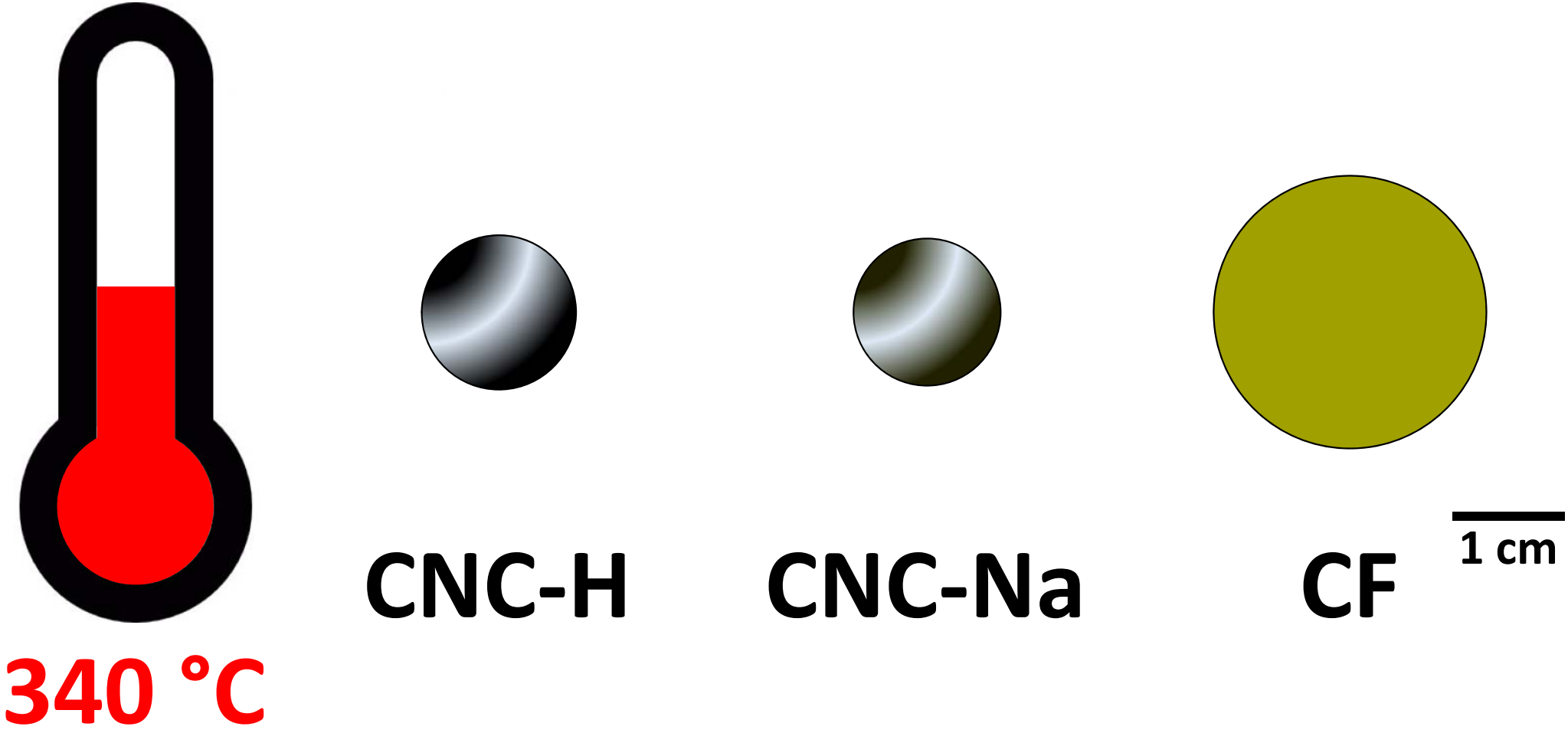

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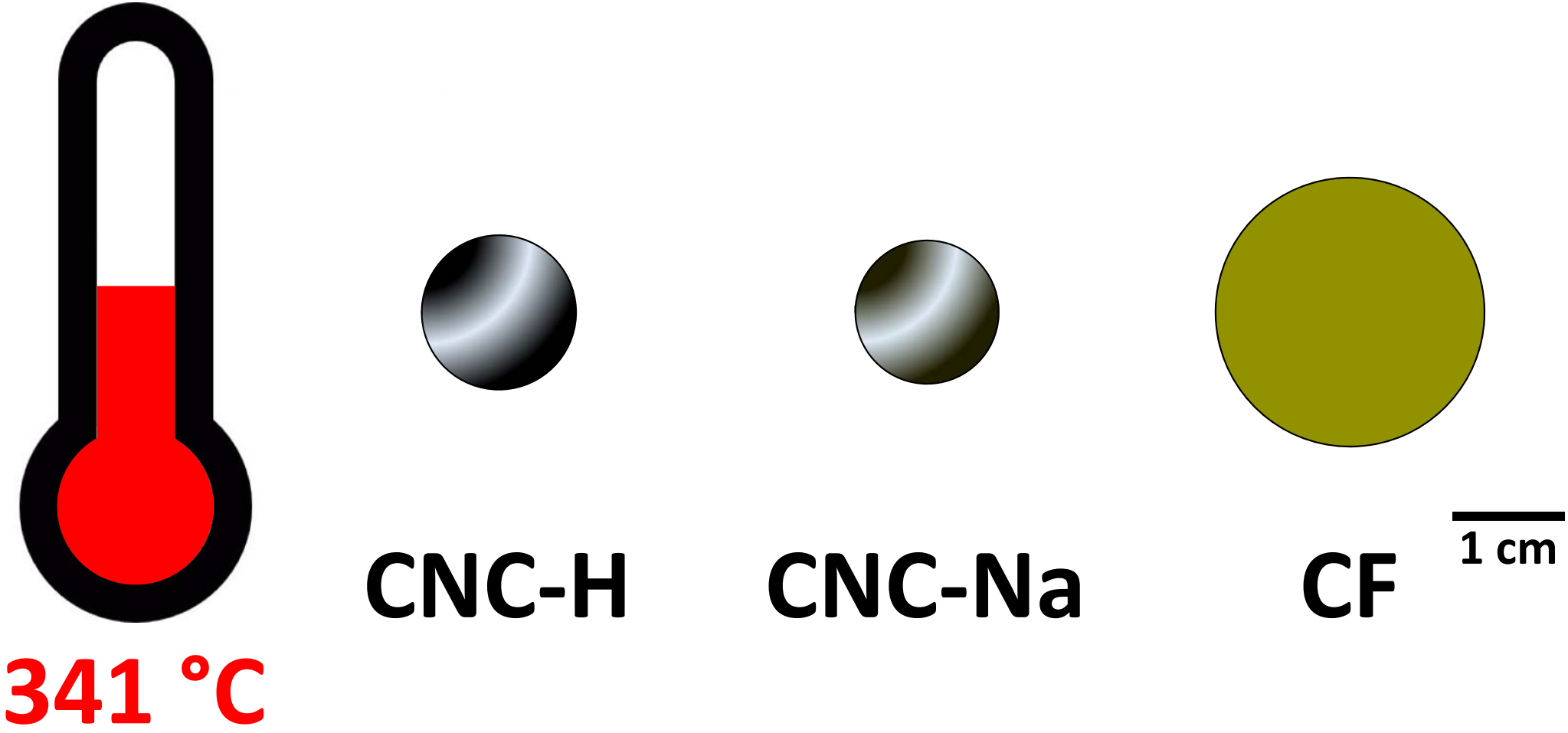

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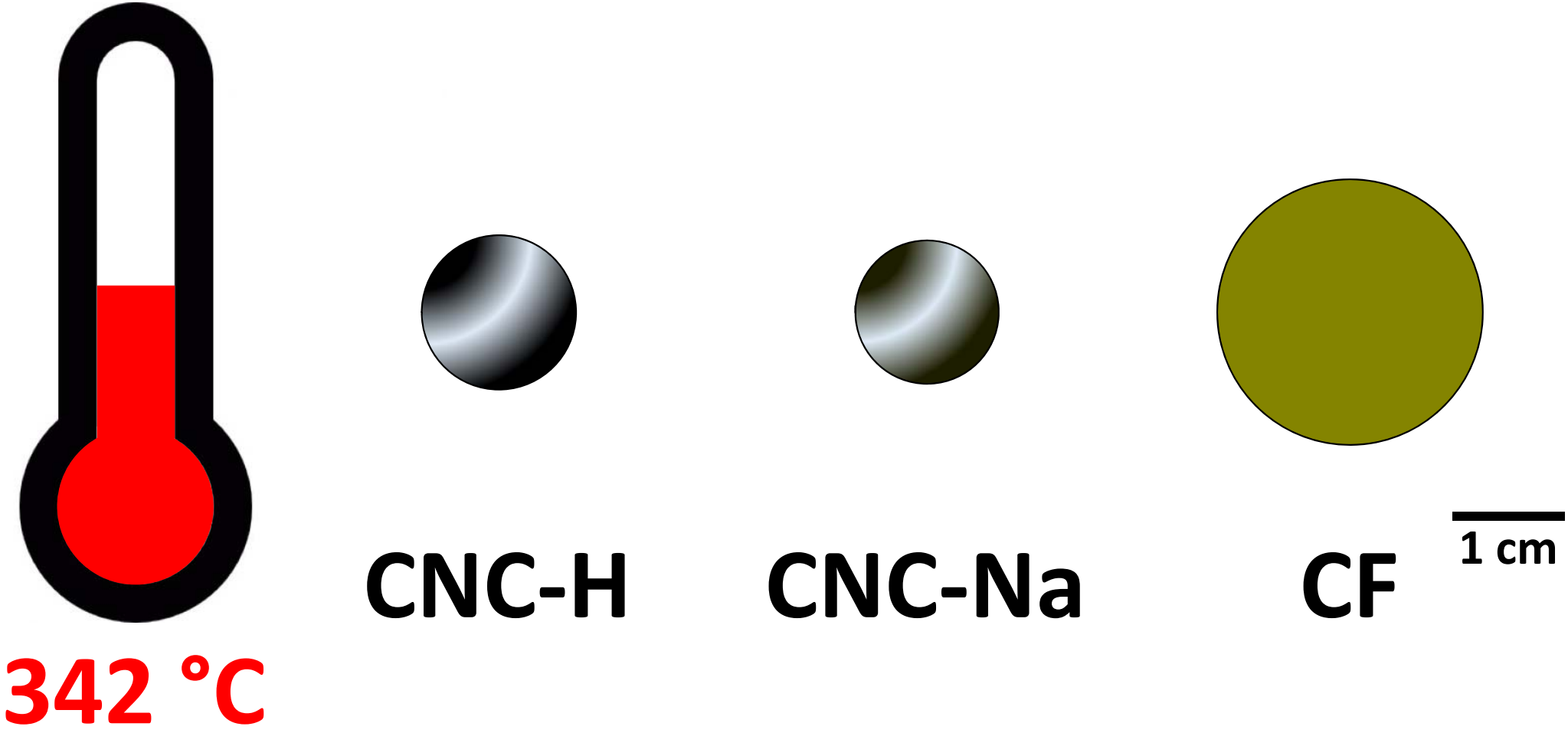

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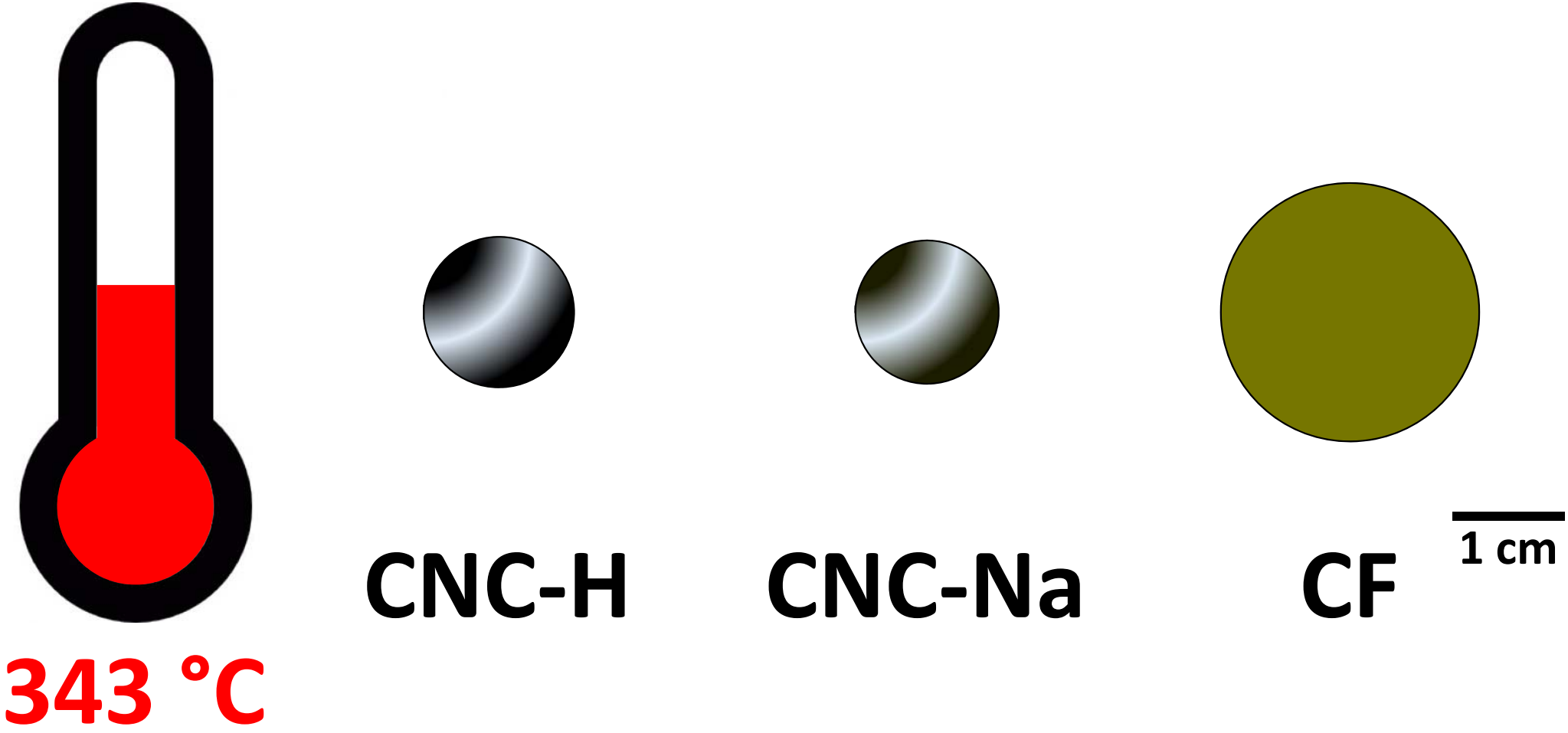

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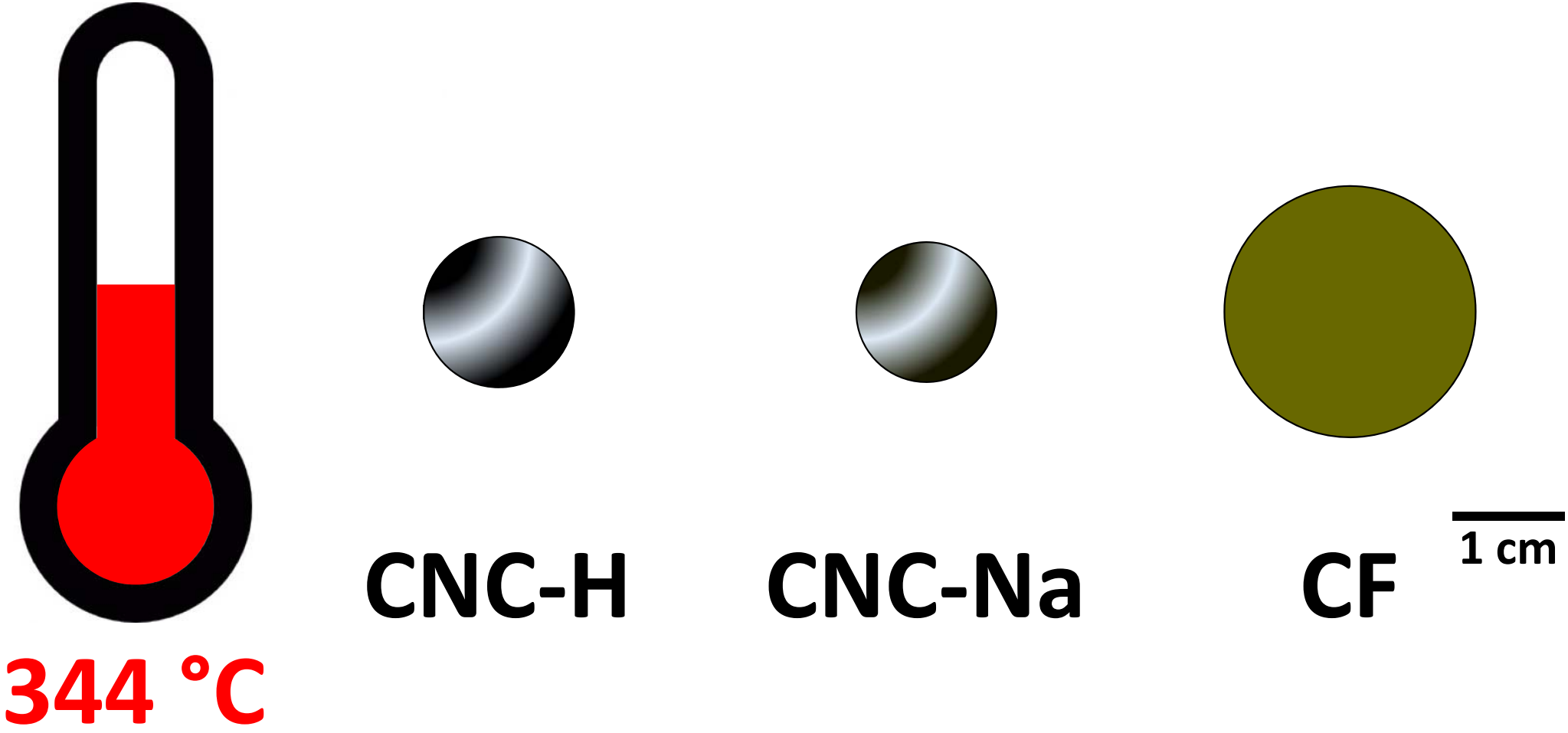

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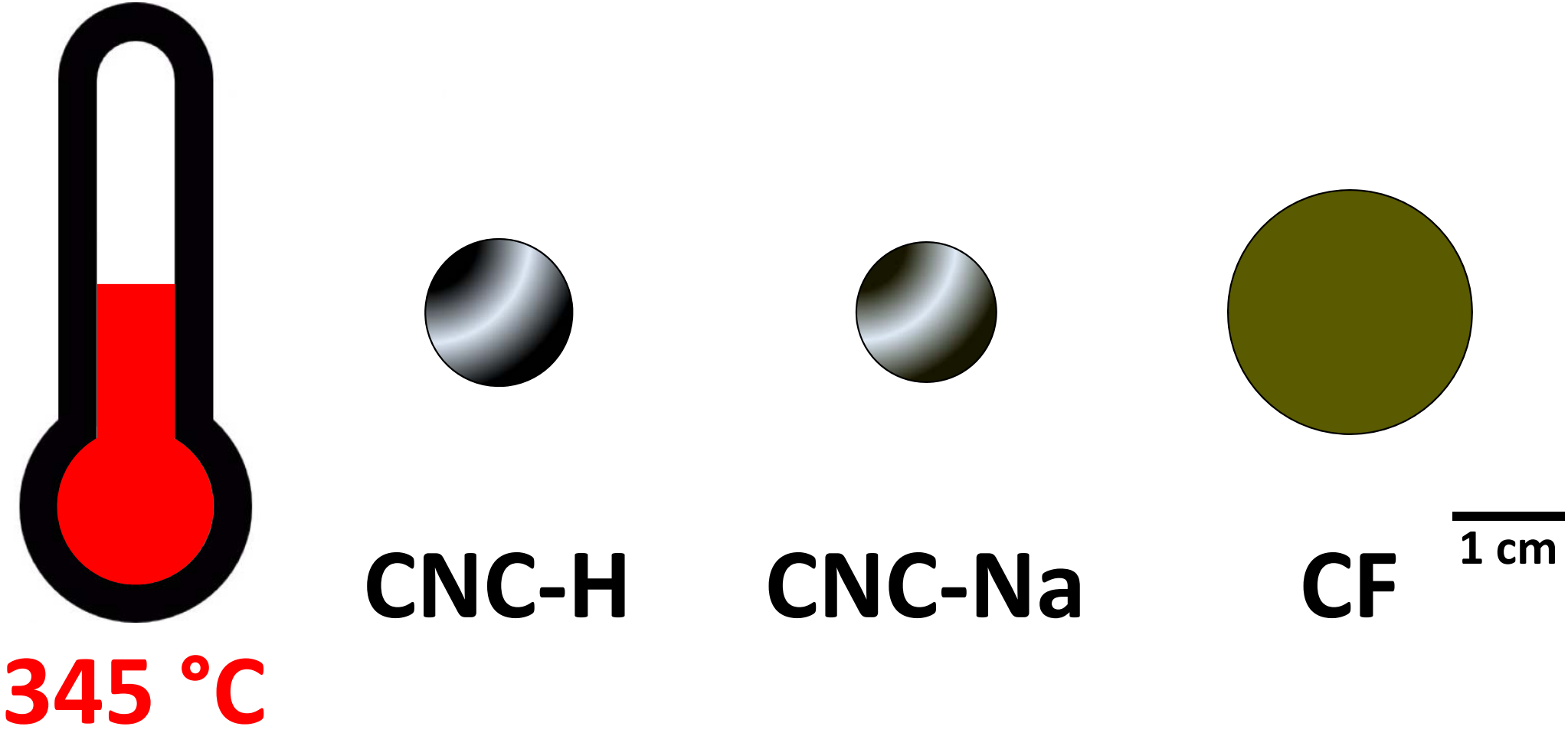

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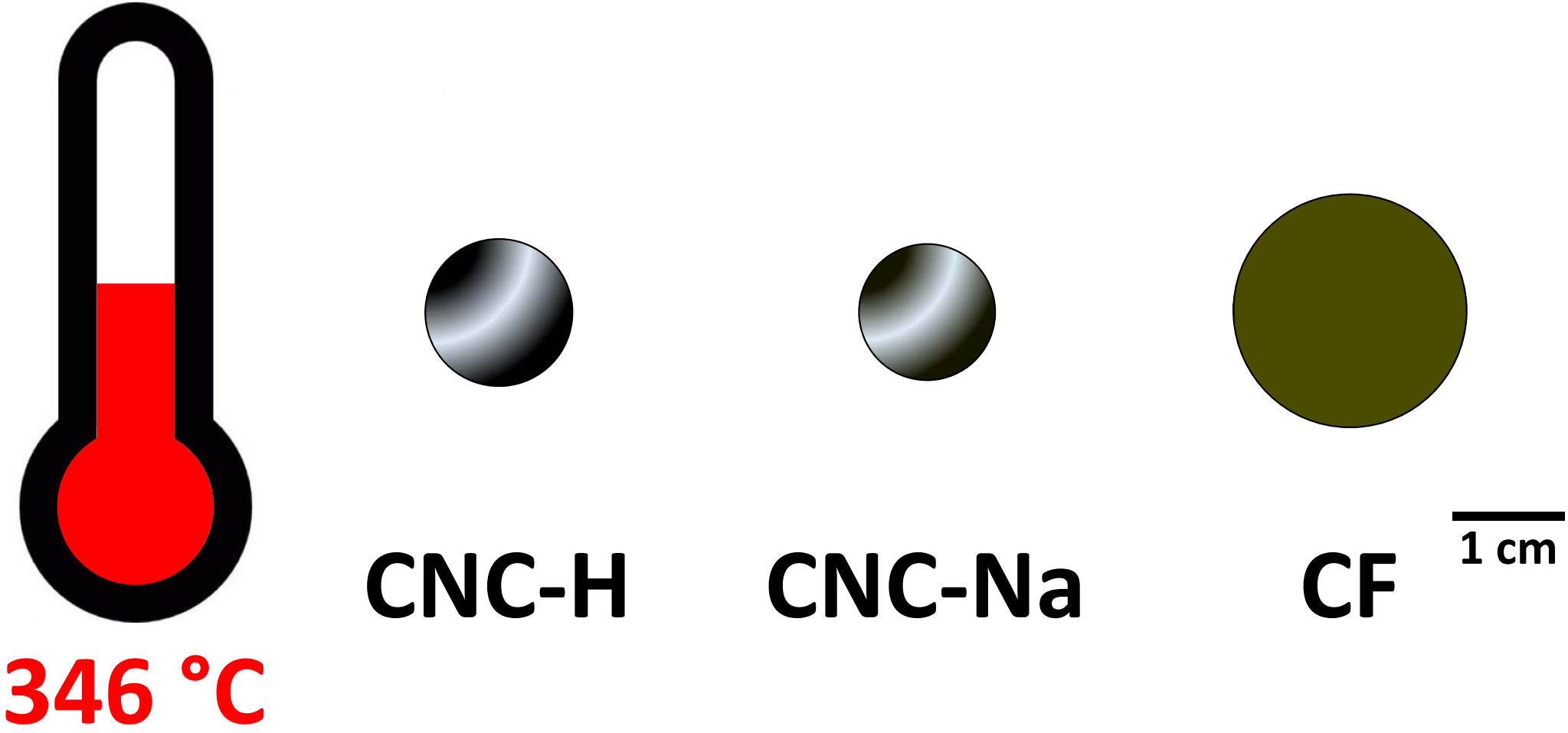

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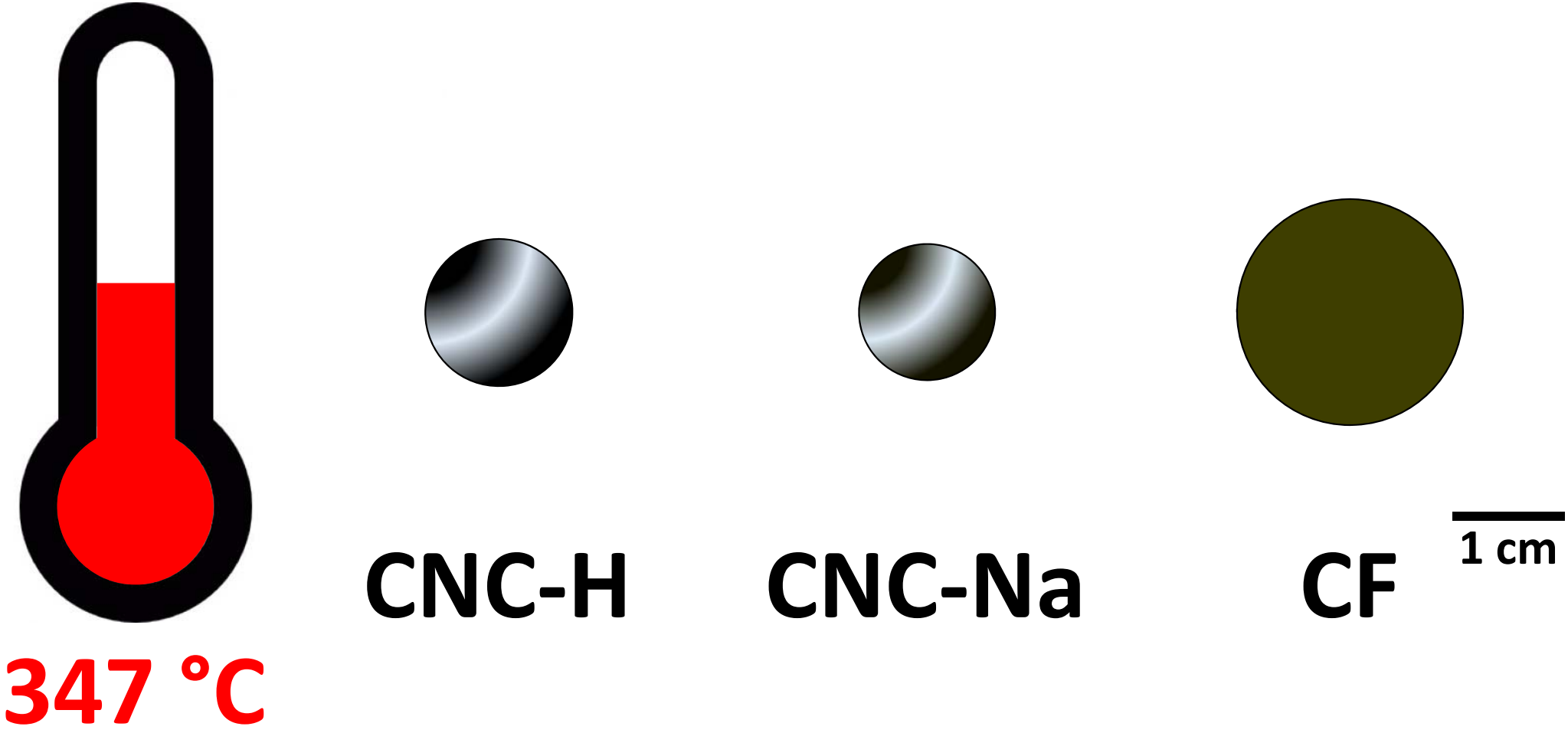

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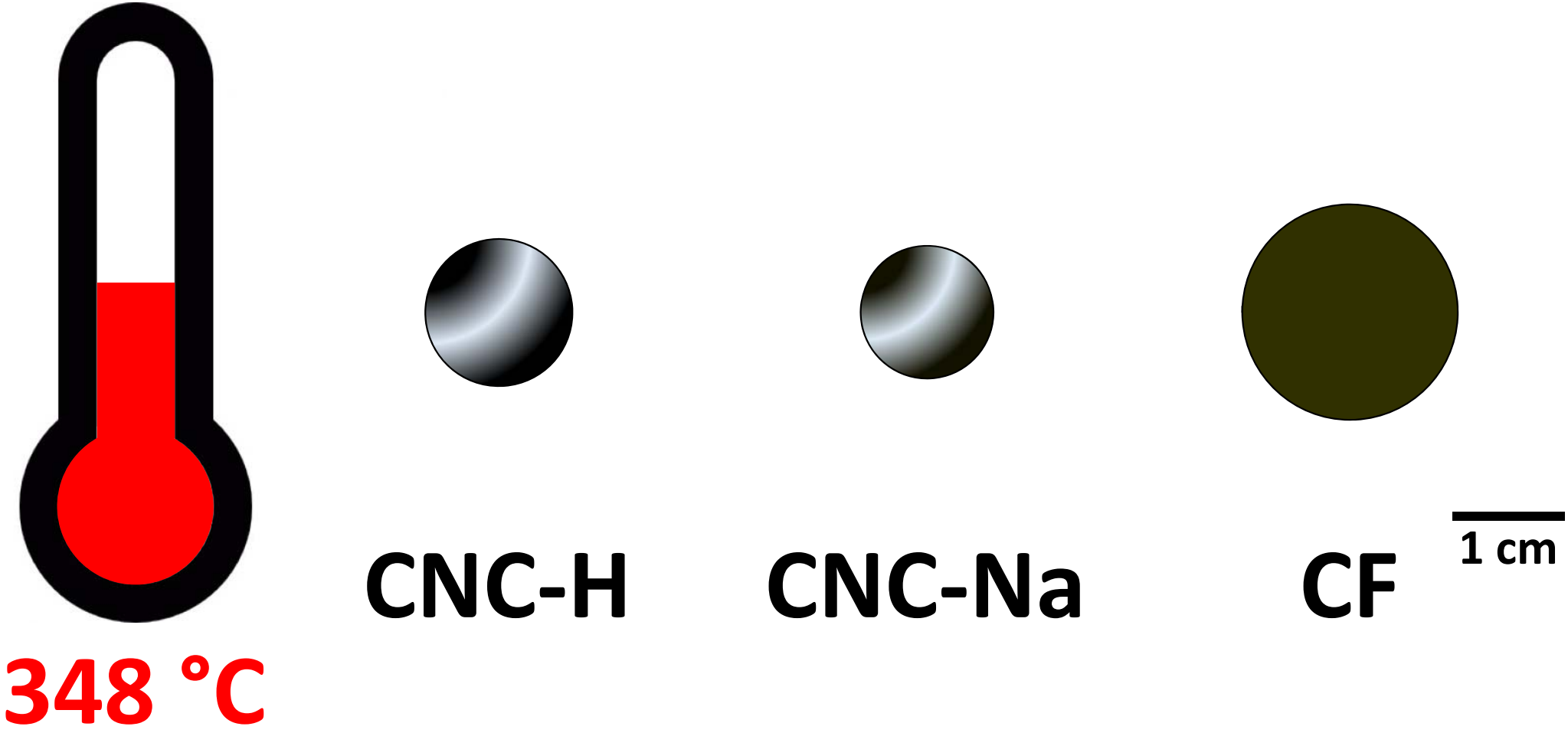

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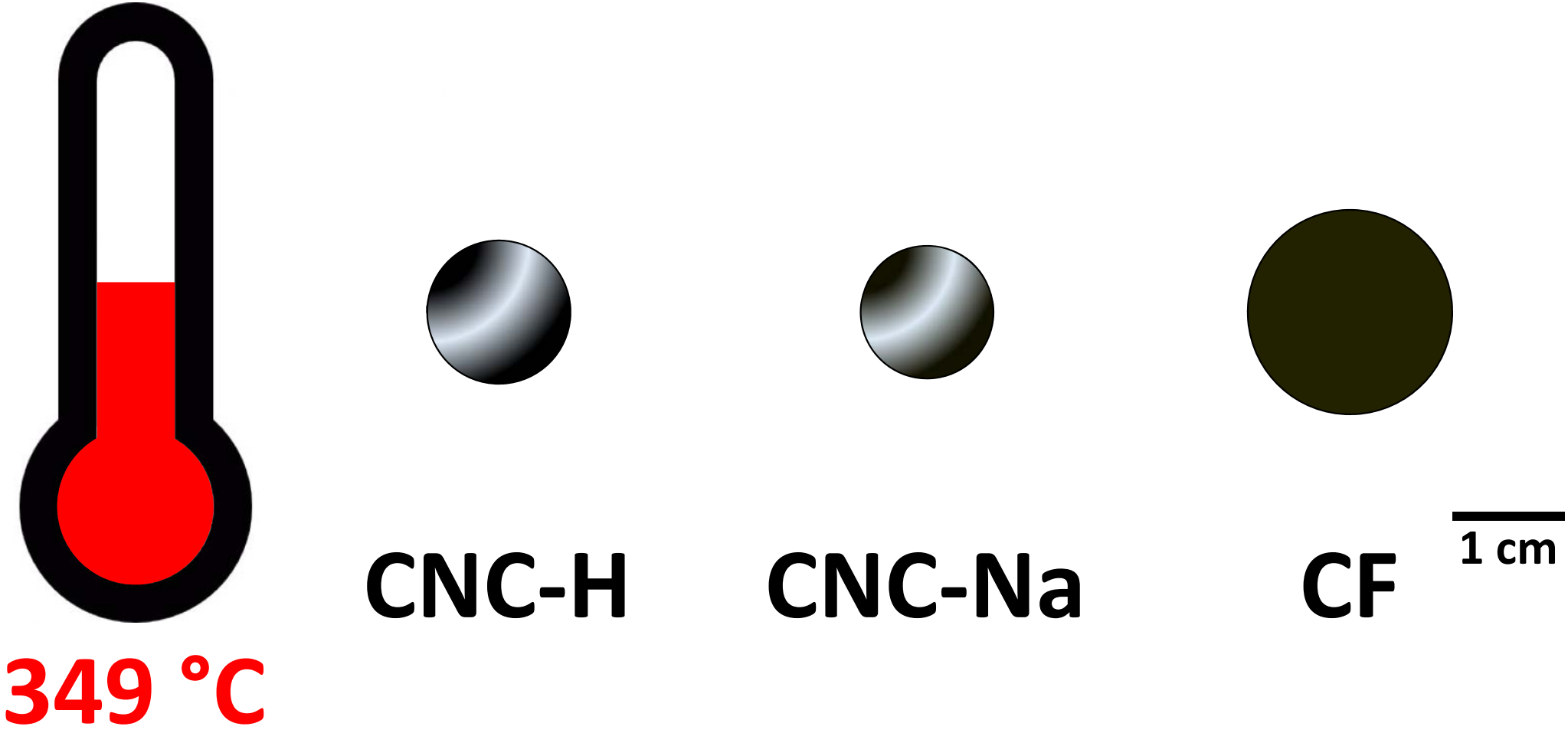

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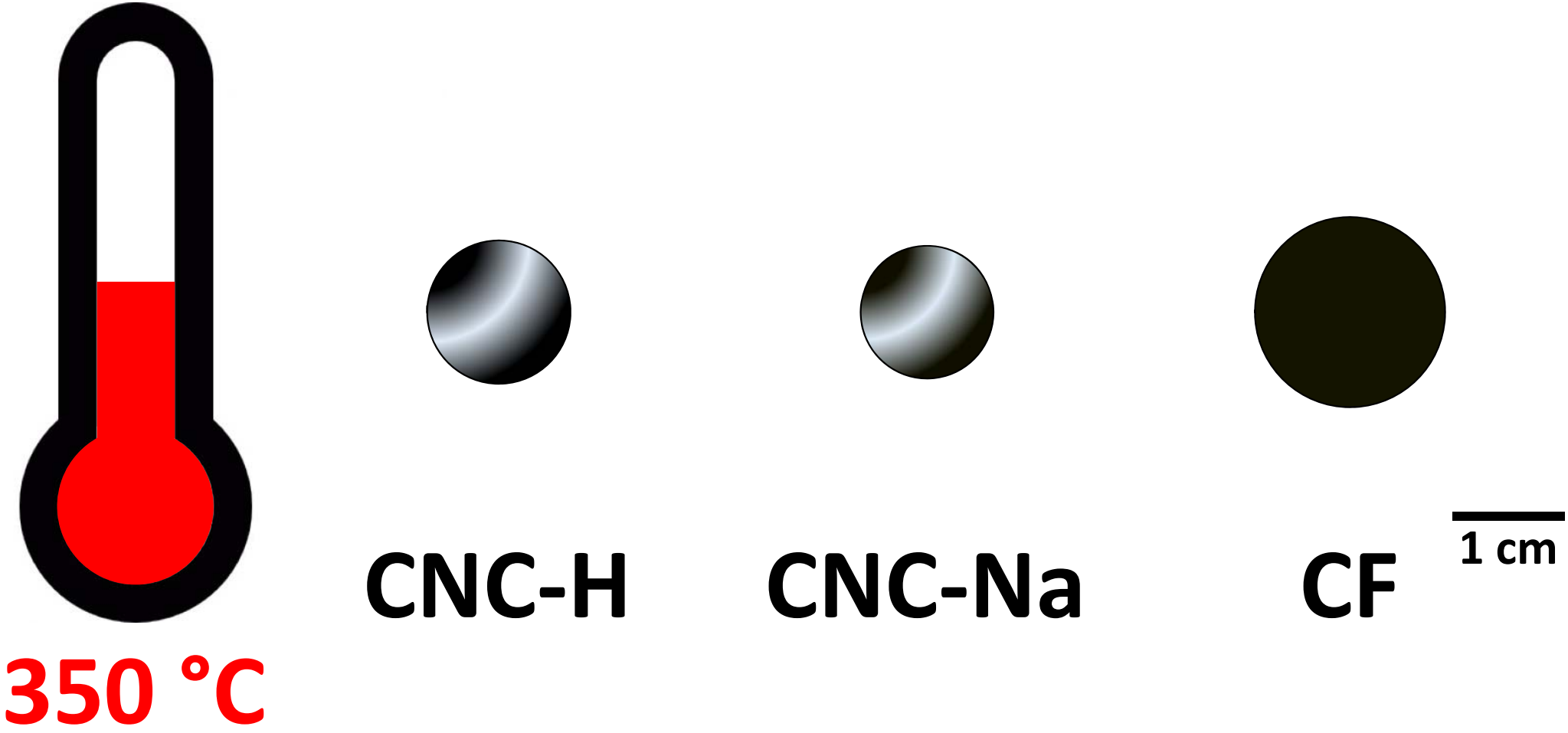

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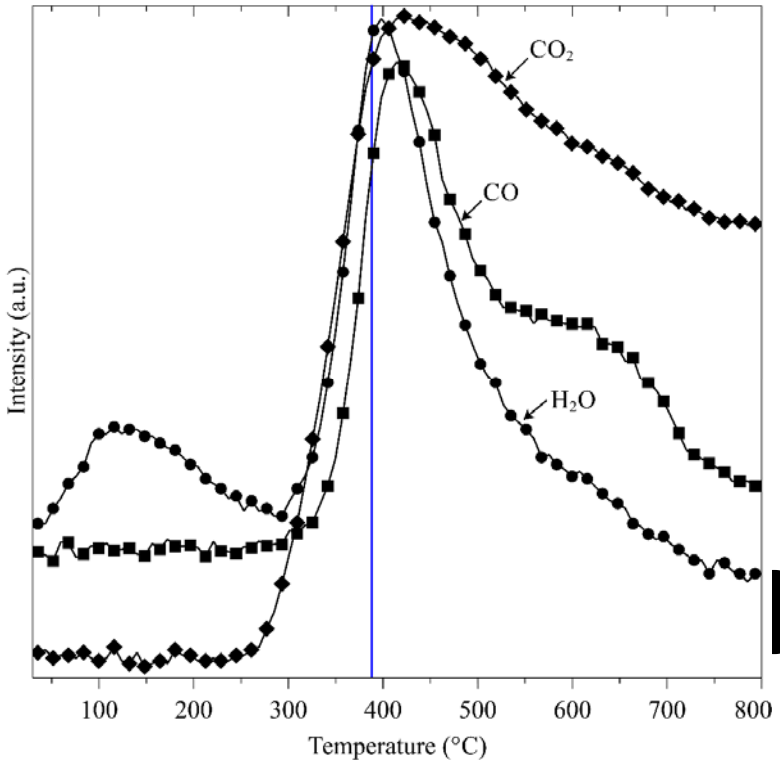

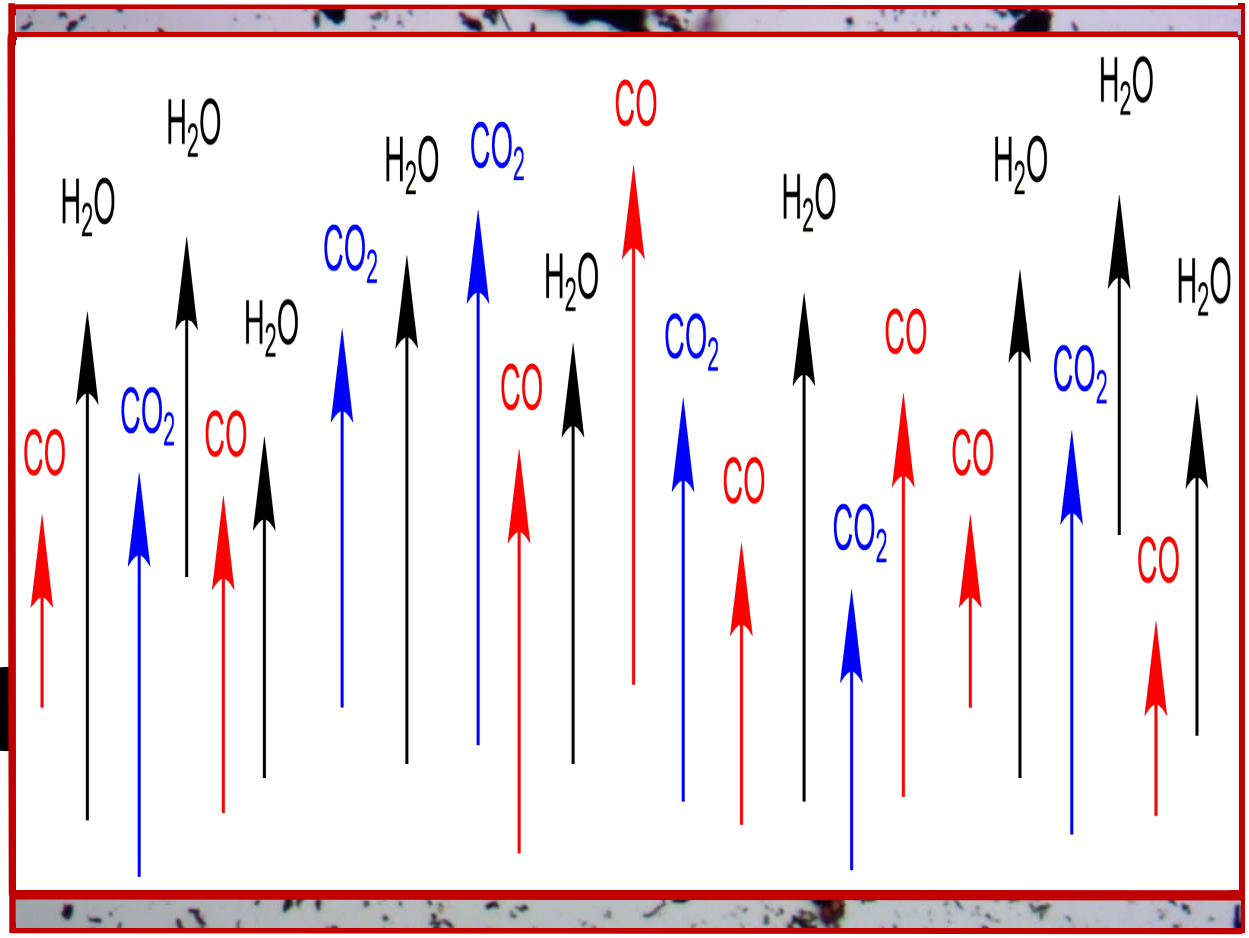

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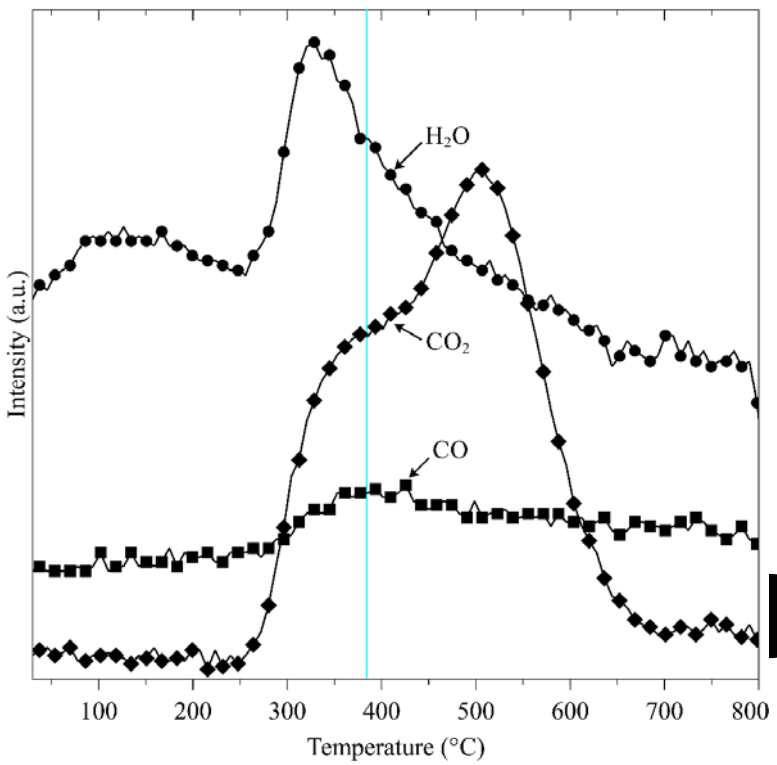
H₂O
CO₂
CO
Intensity (a.u.)
100
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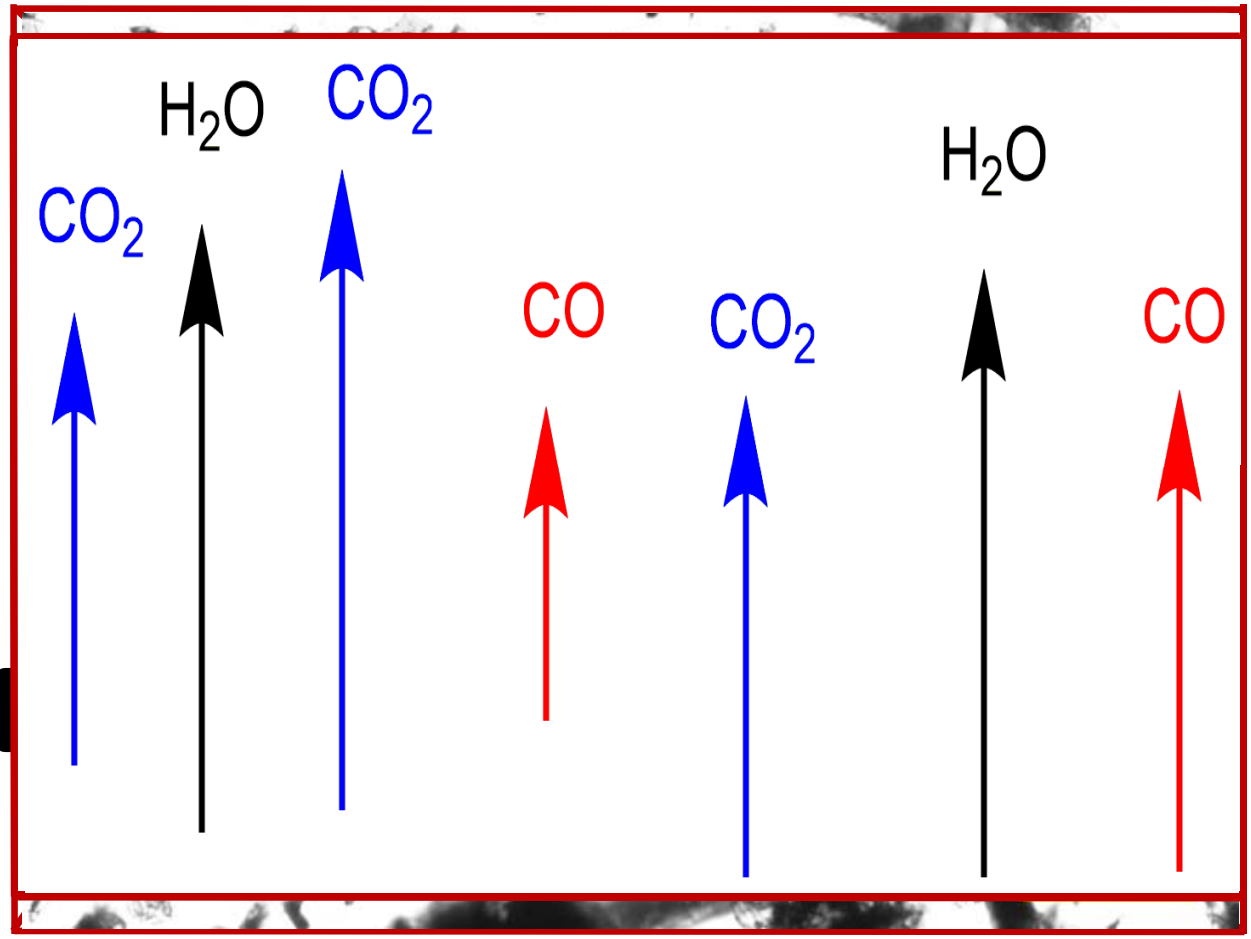
Temperature (°C)


CO2
H2O
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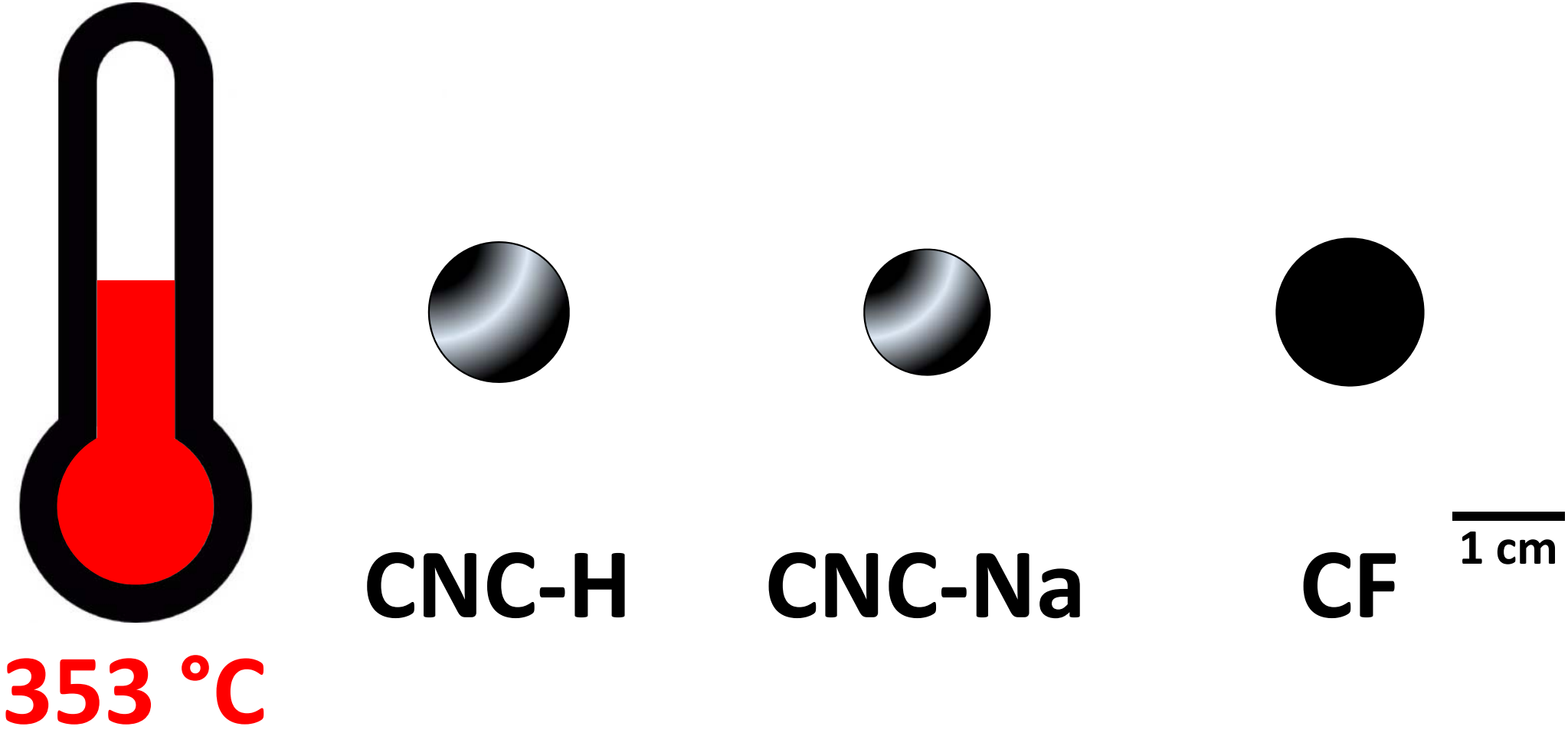
CO
CO2
H2O
CO

Results



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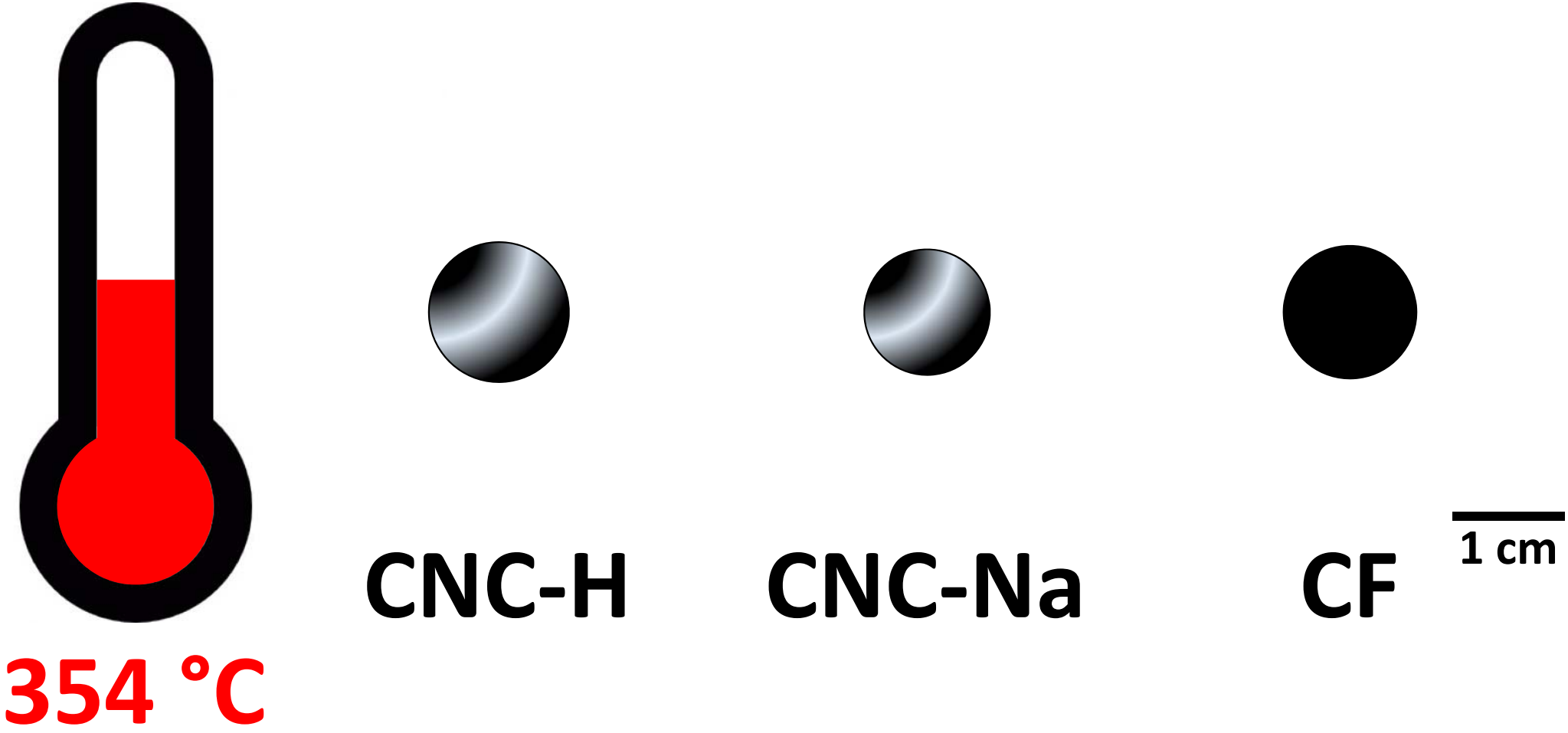

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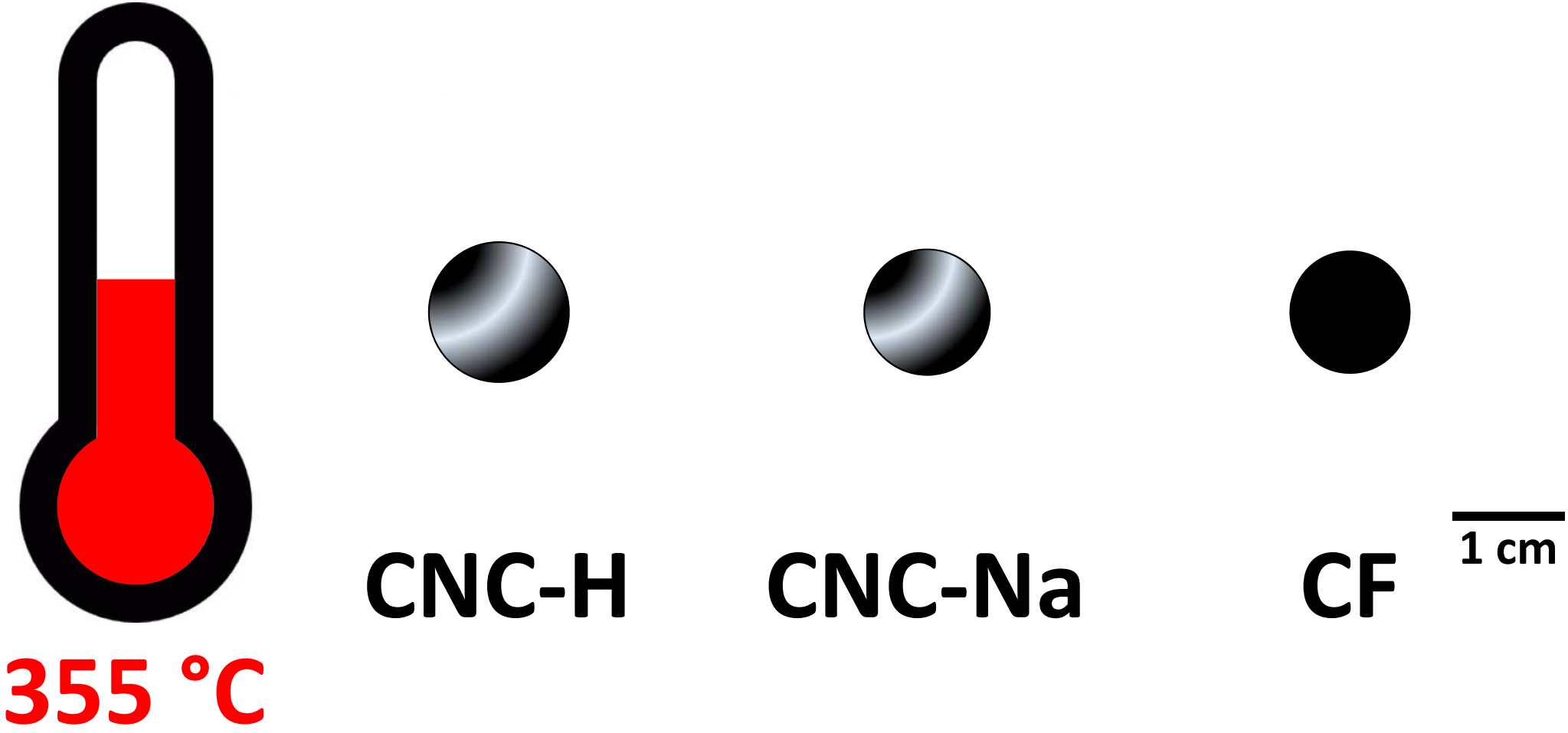

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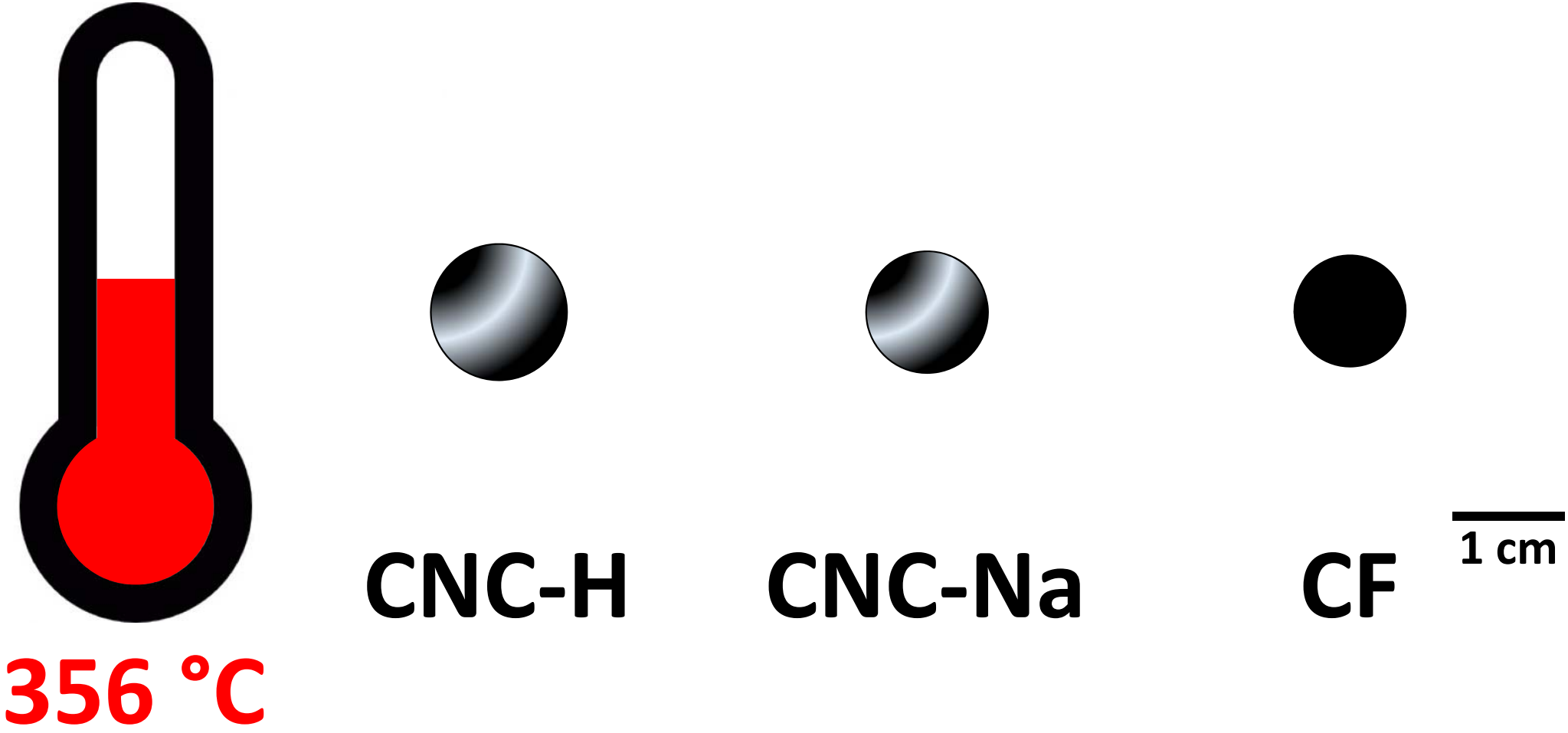

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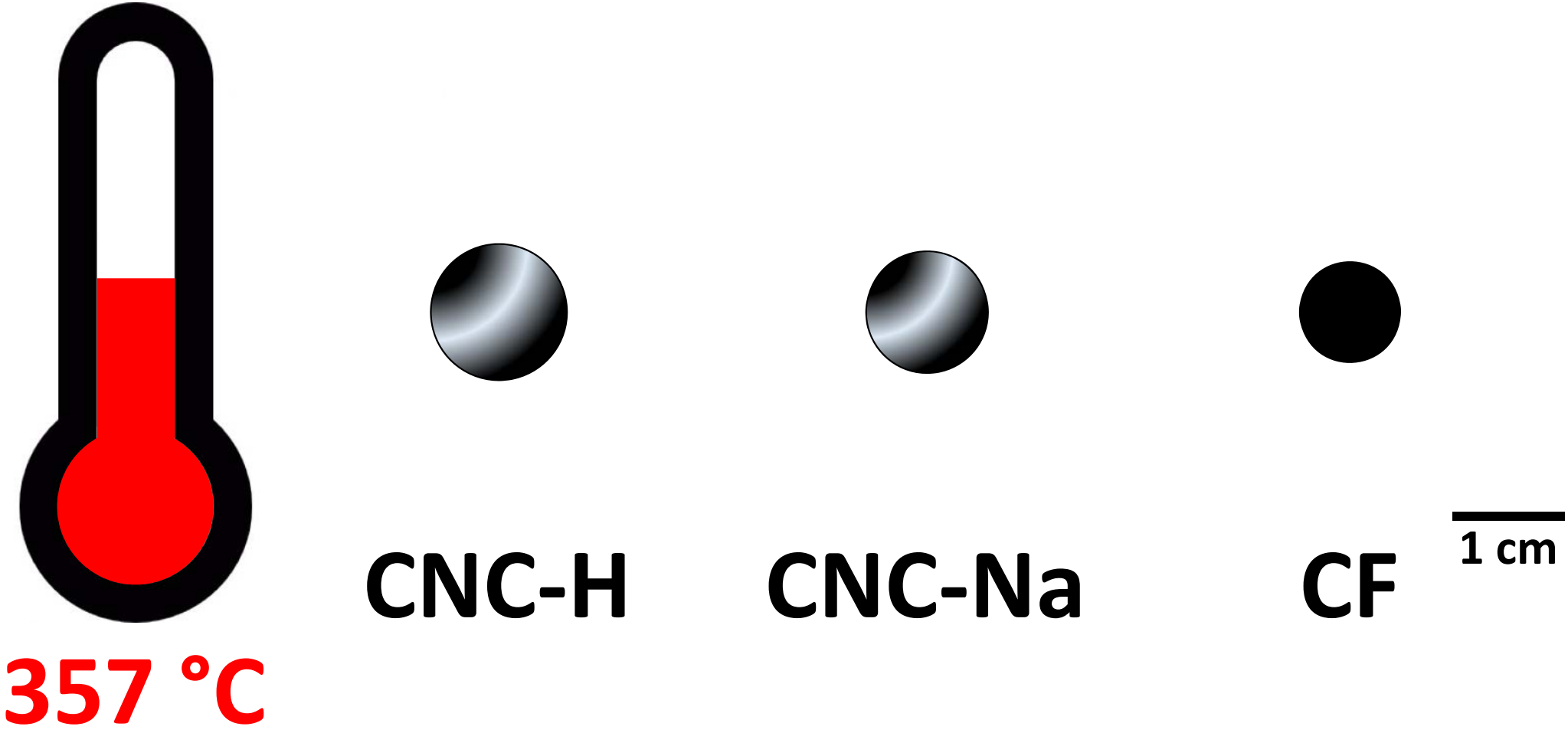

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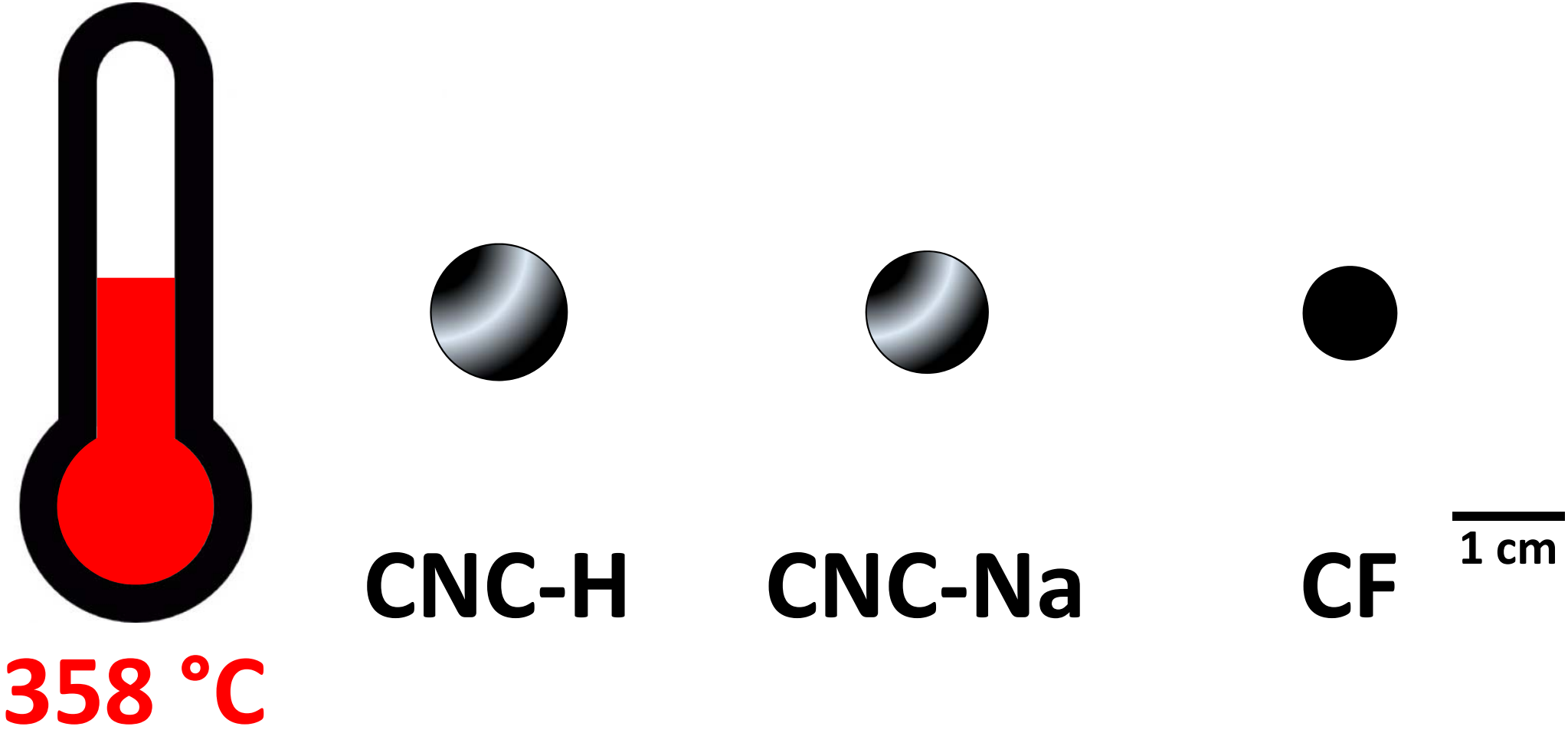

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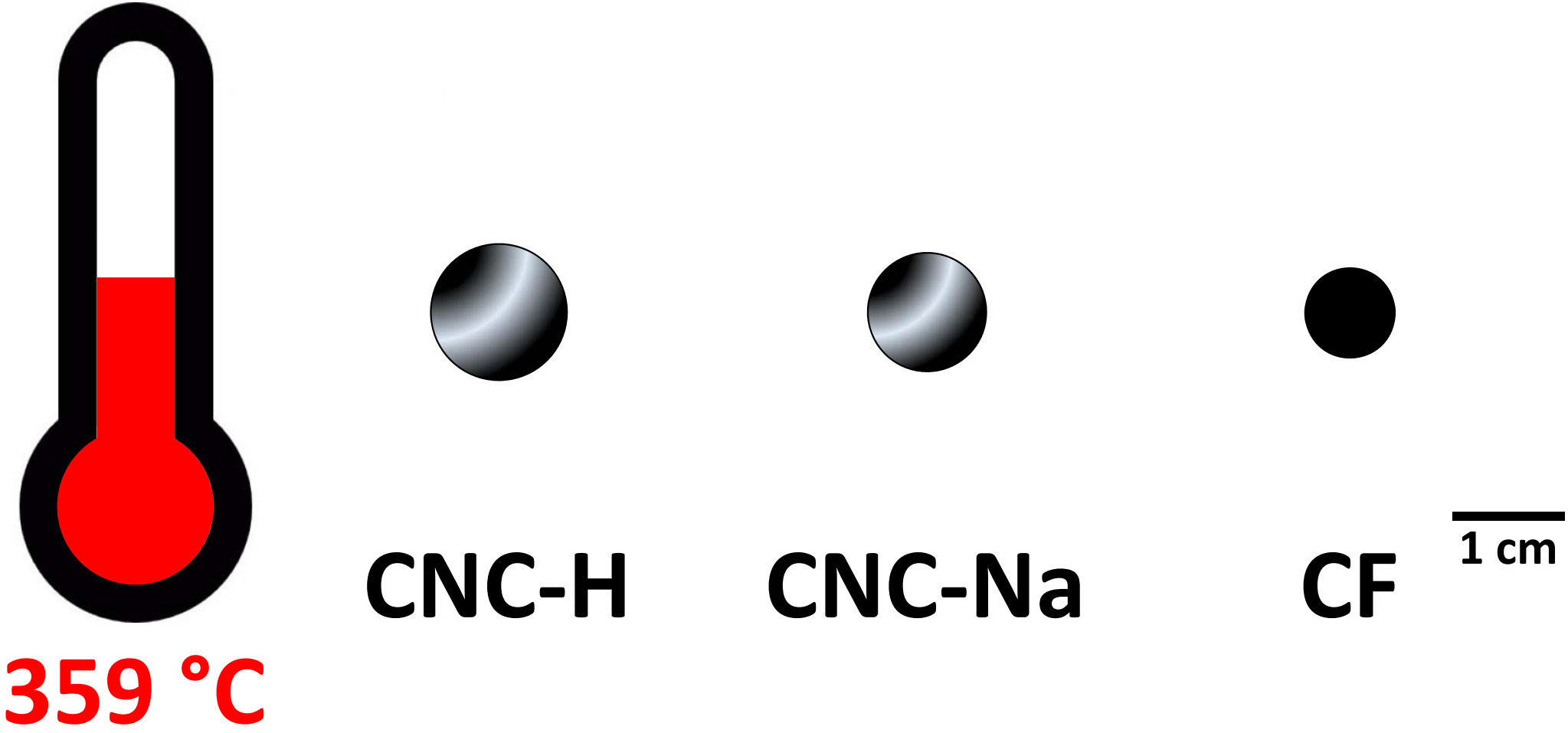

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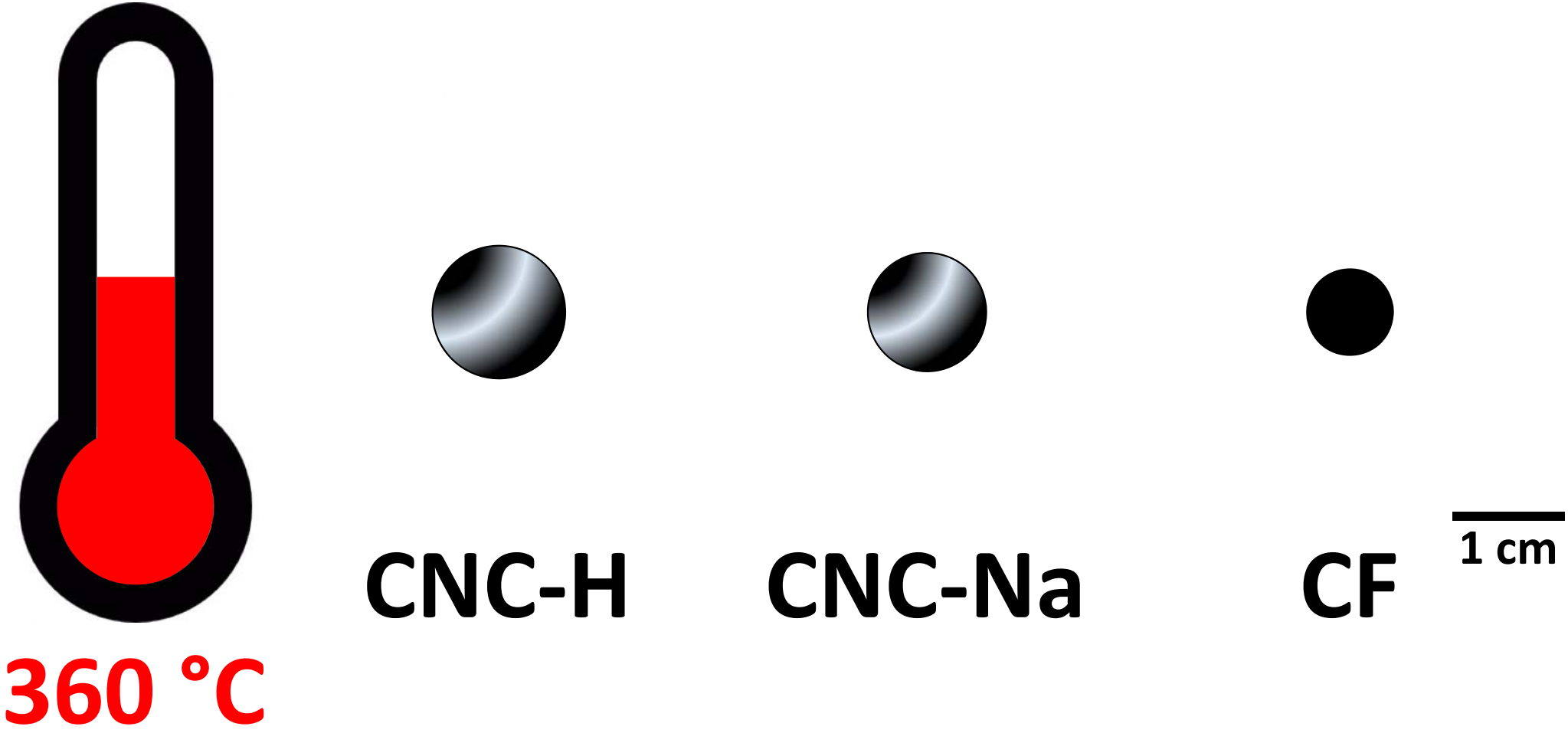

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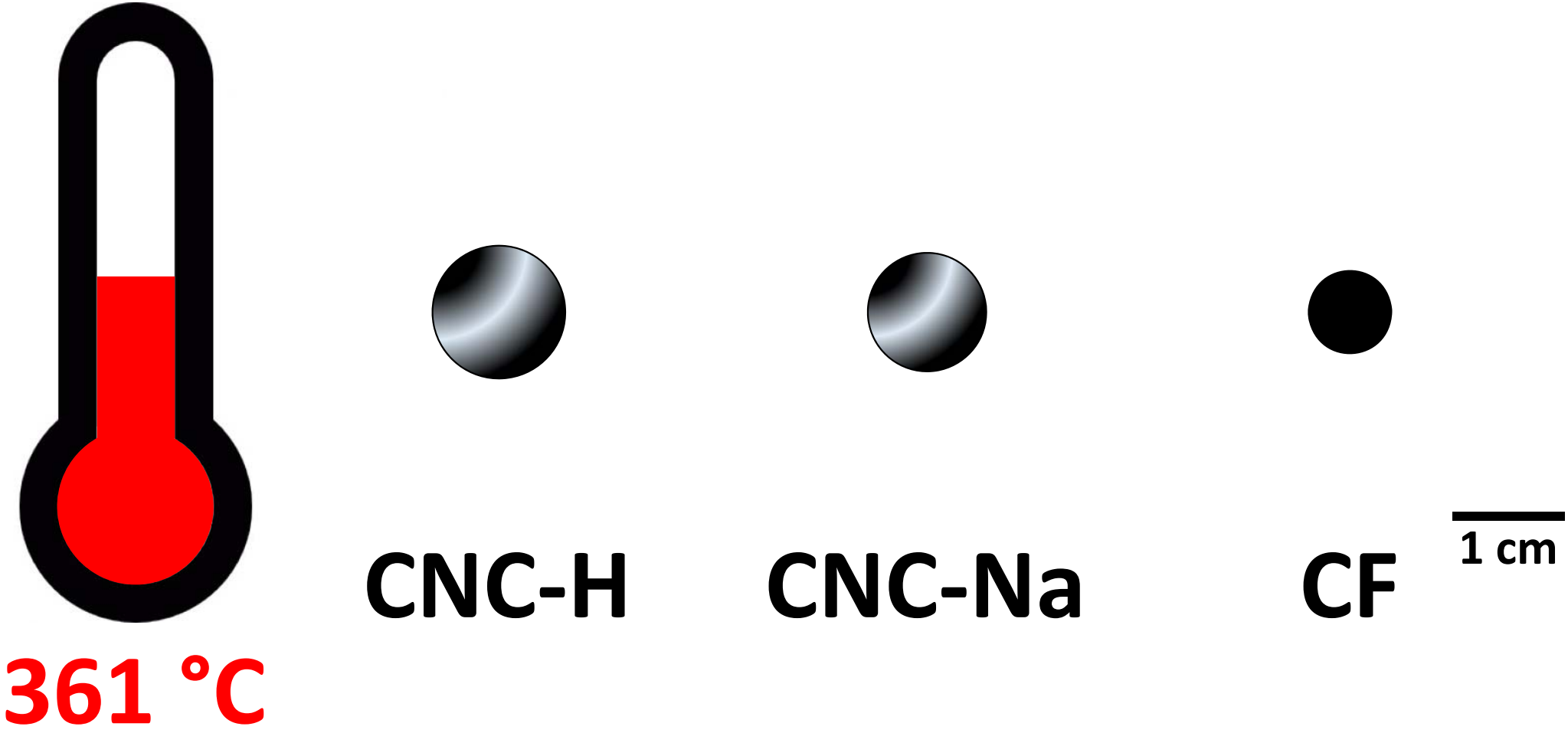

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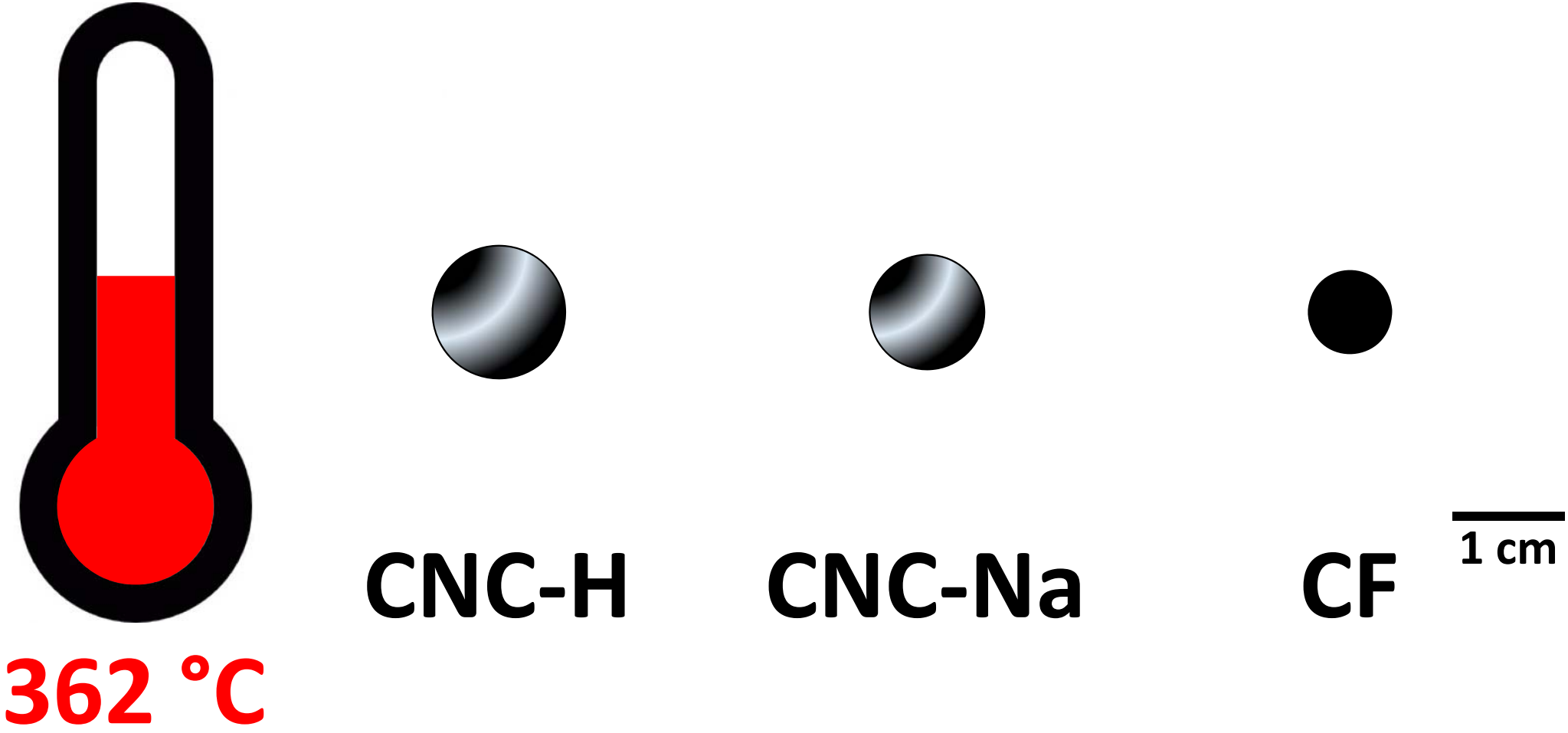
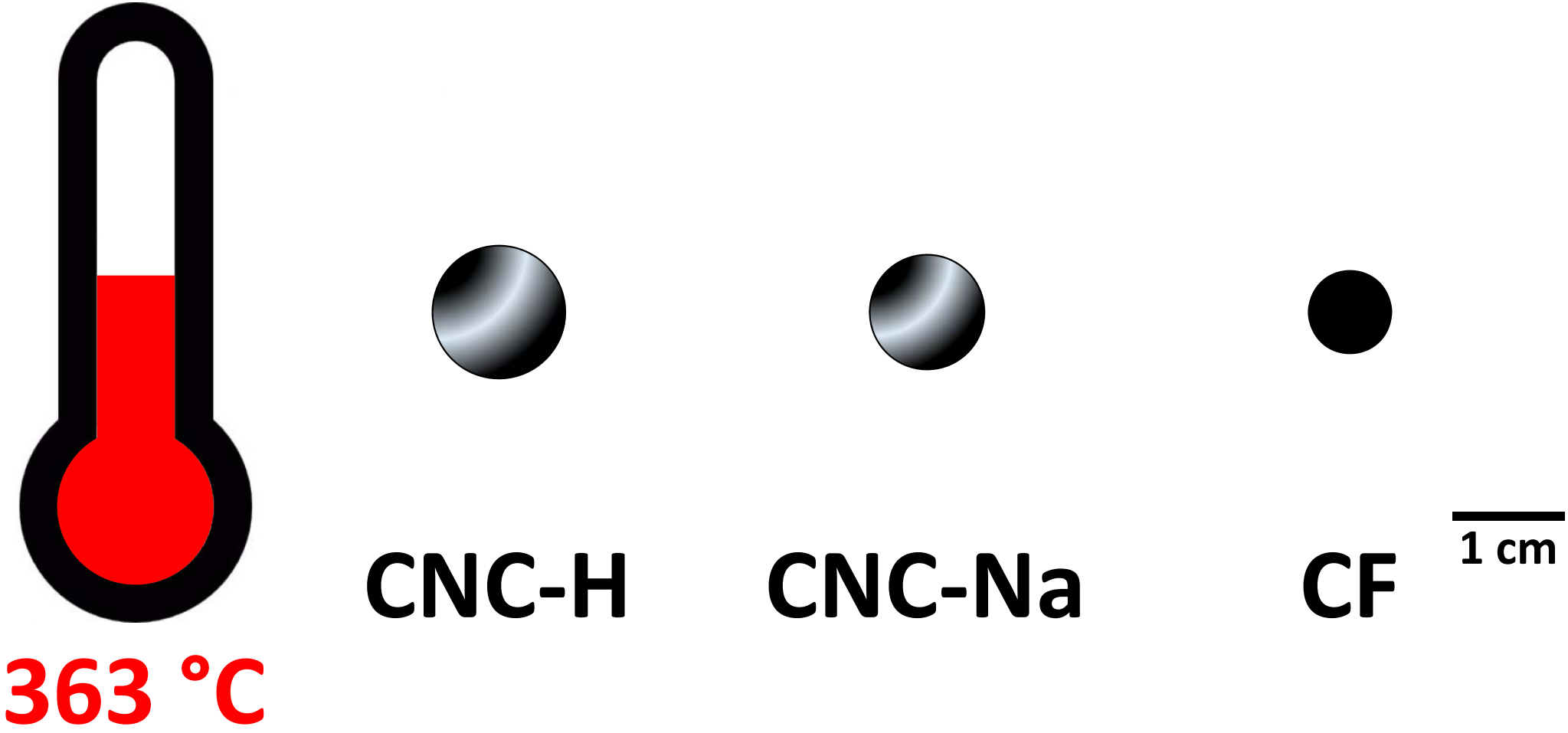


Results



Results

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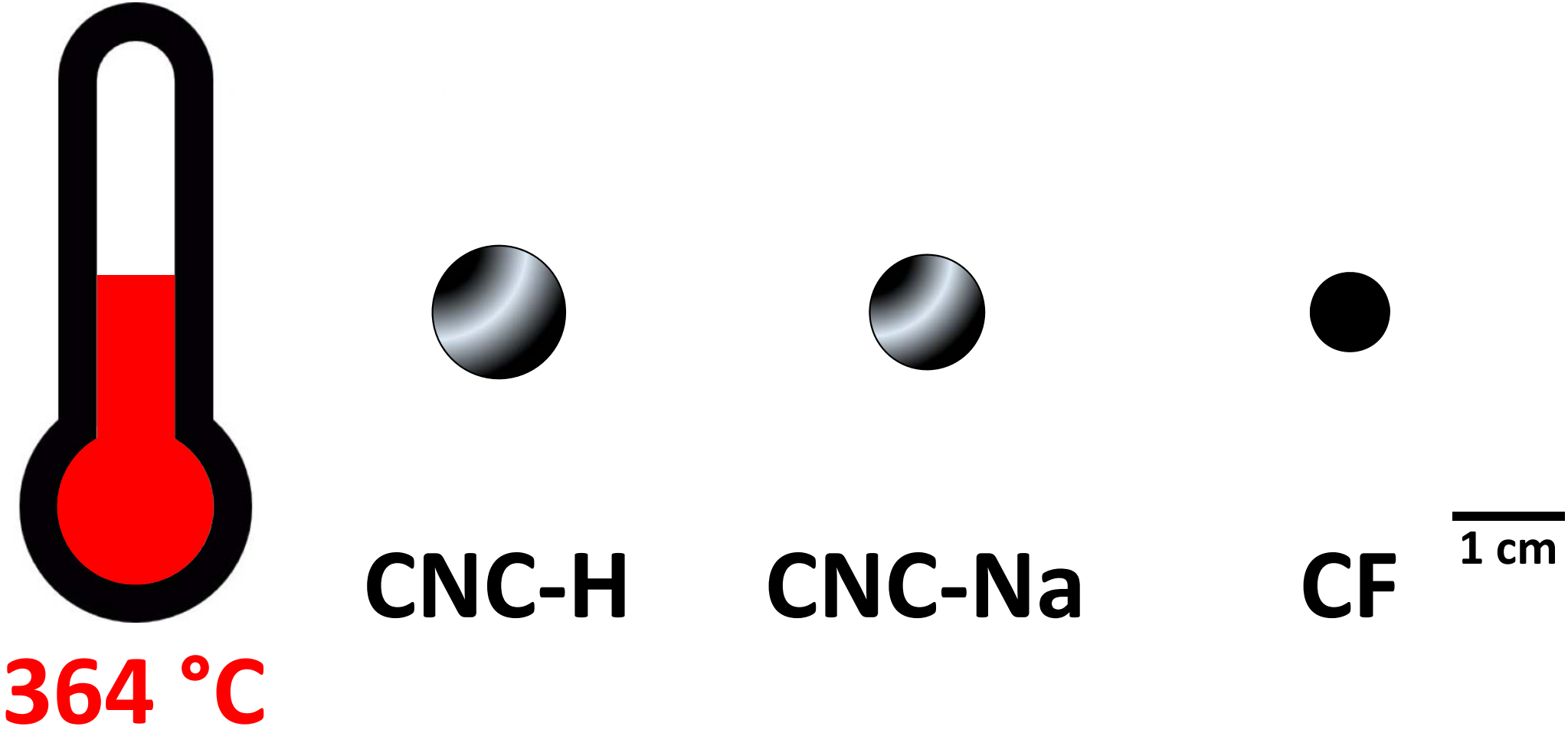

Results

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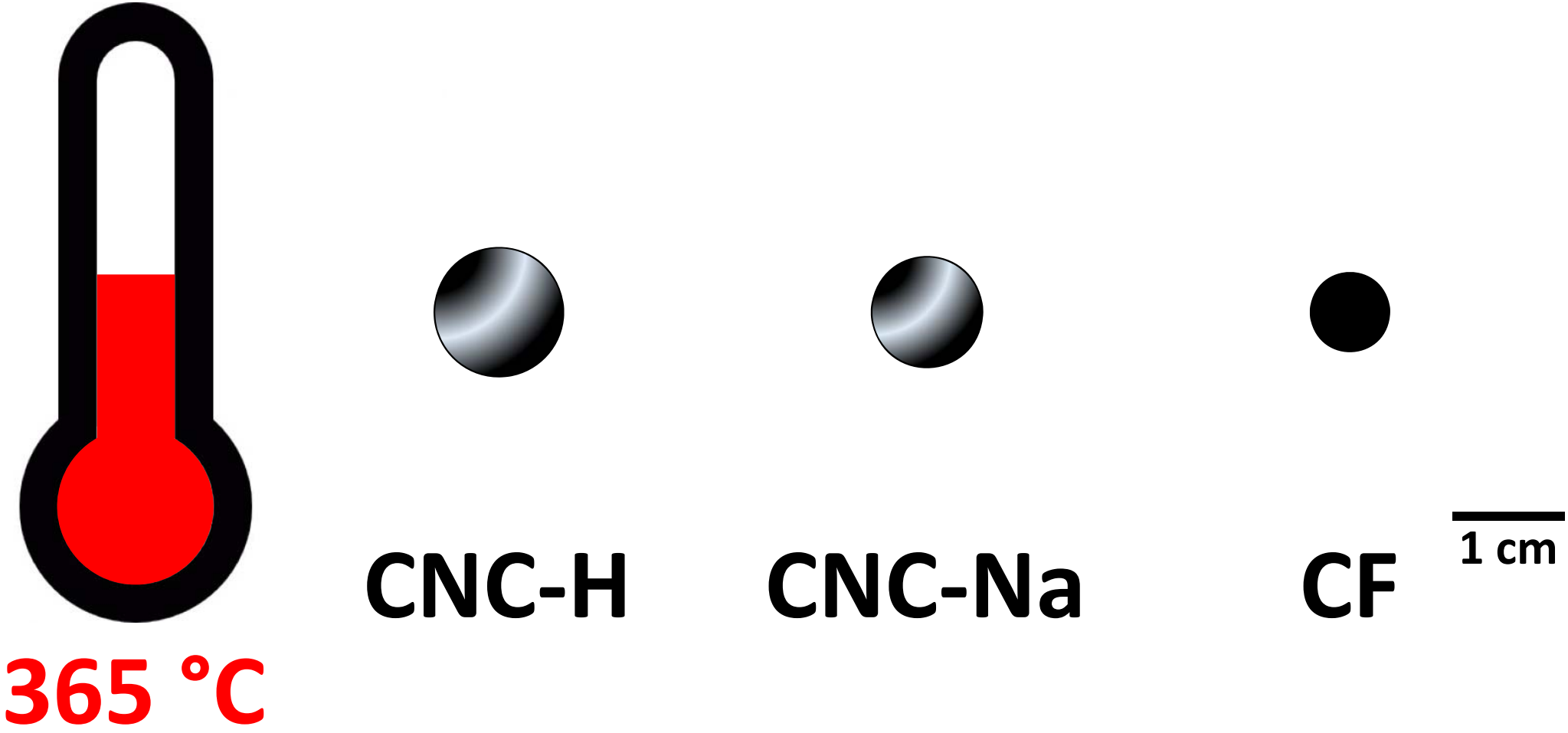

Results

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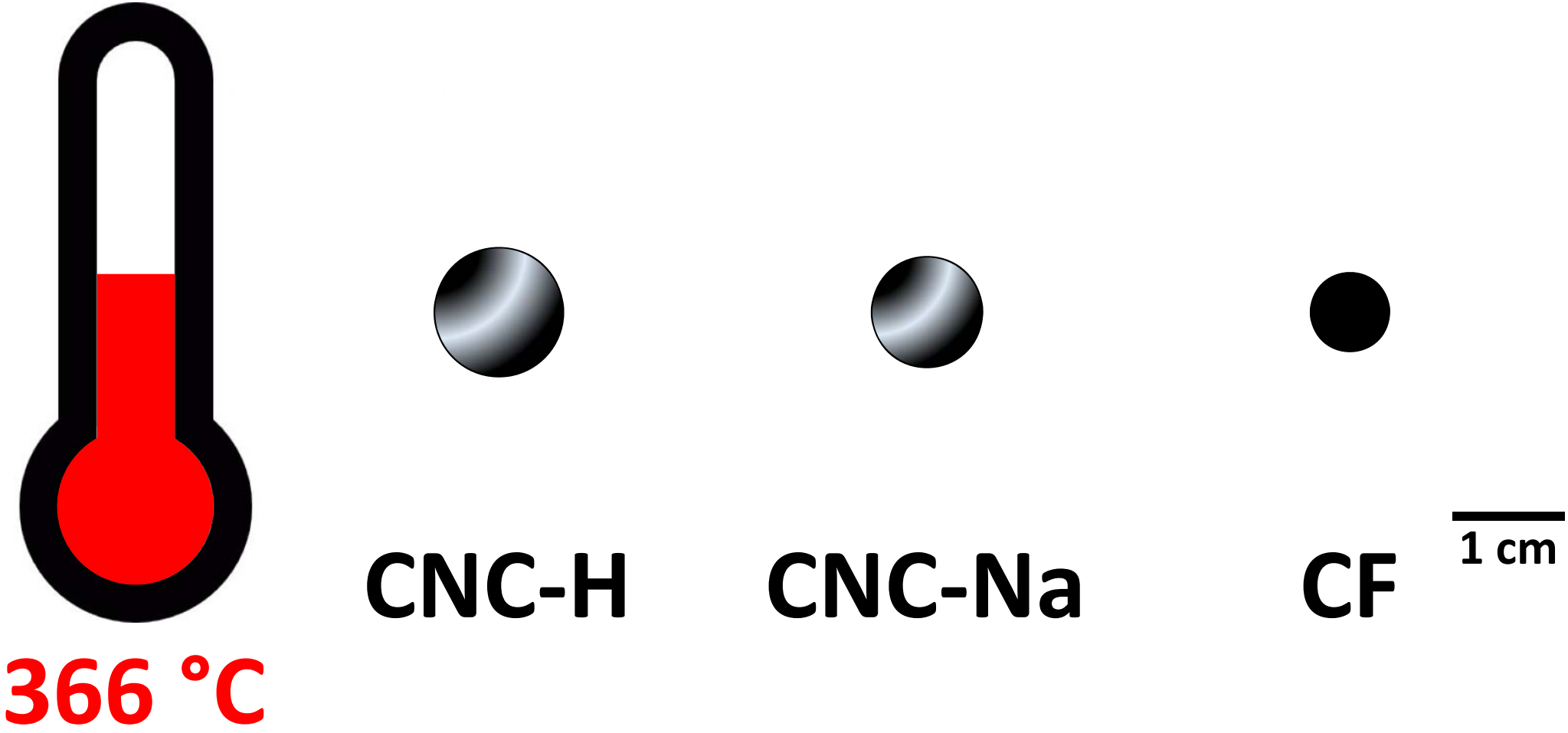

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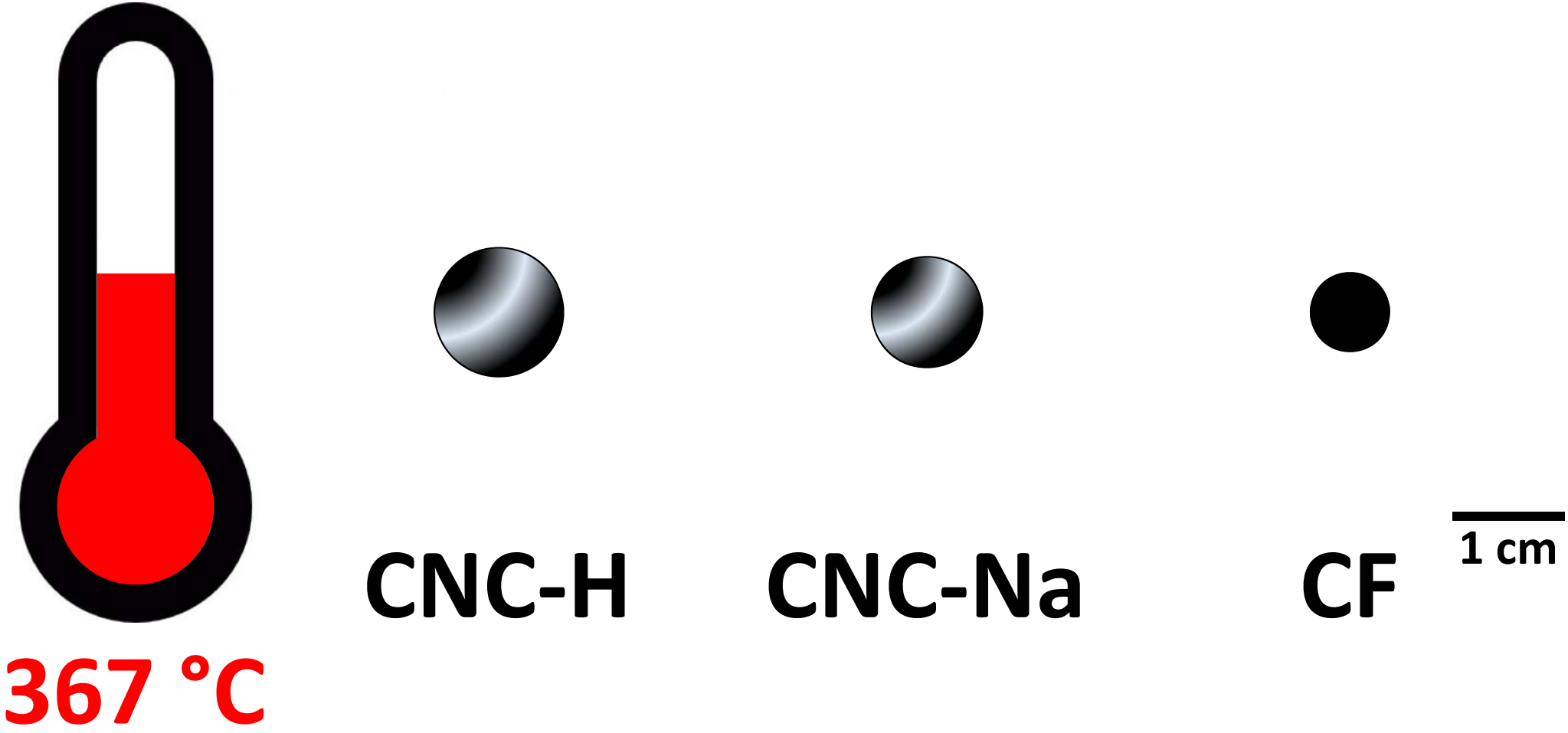

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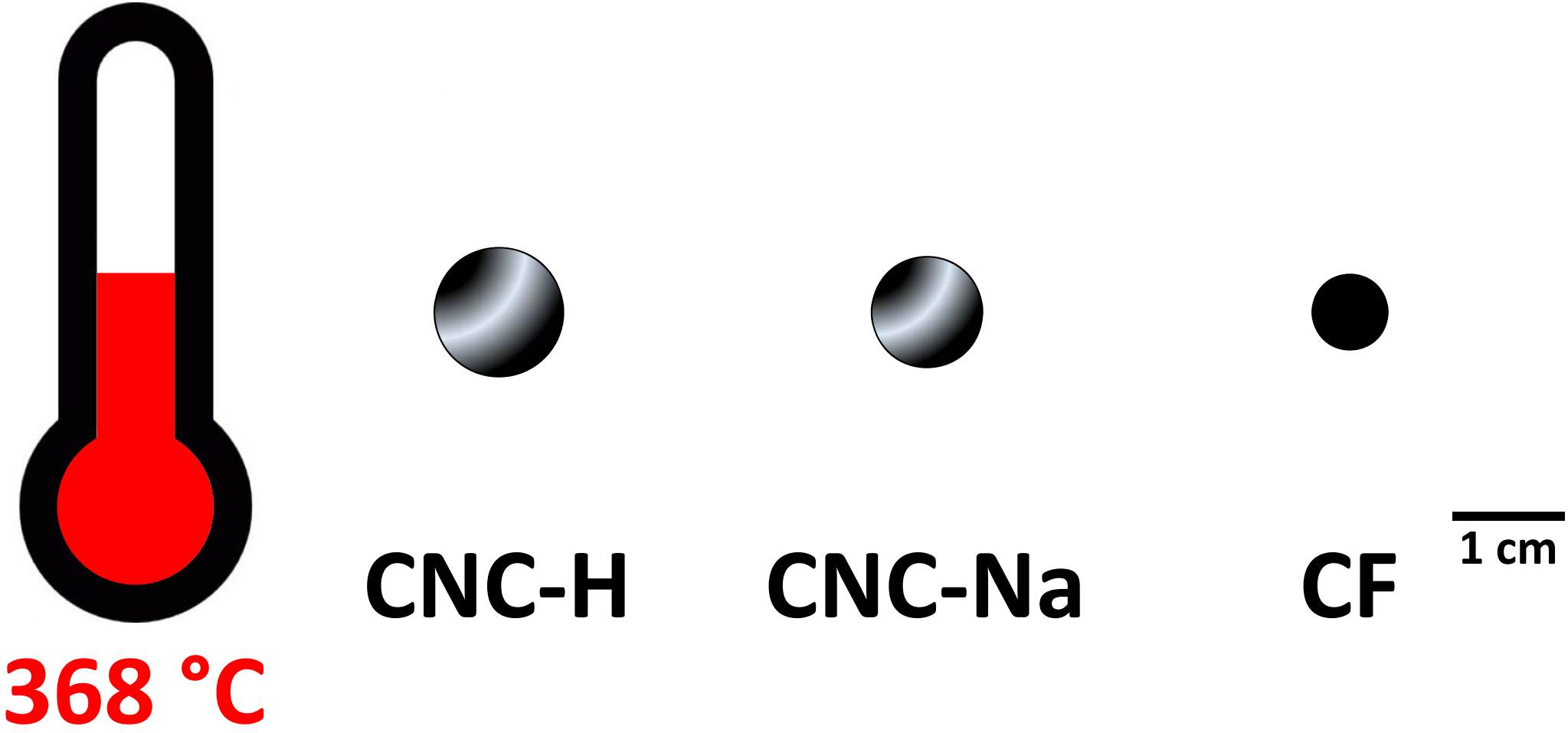

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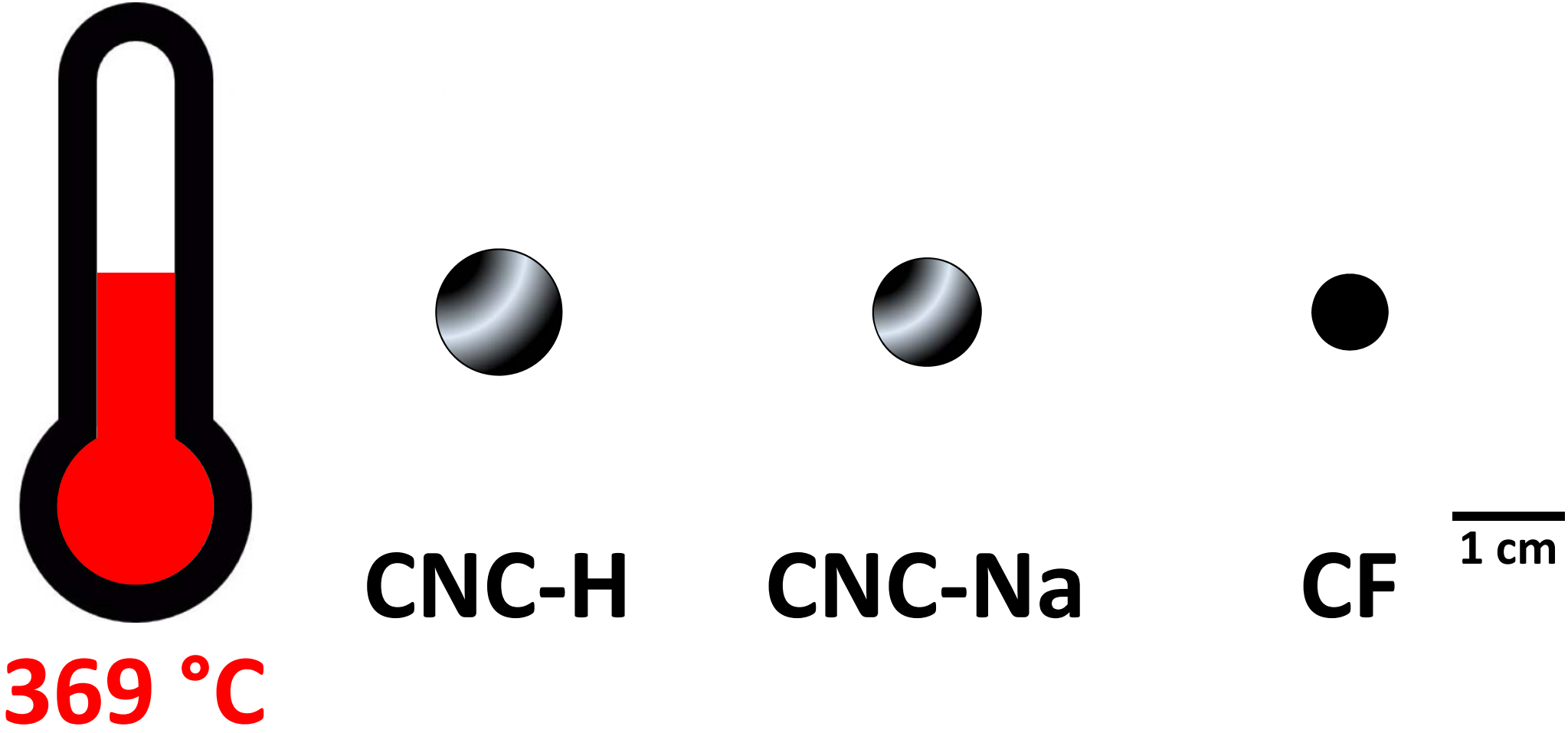

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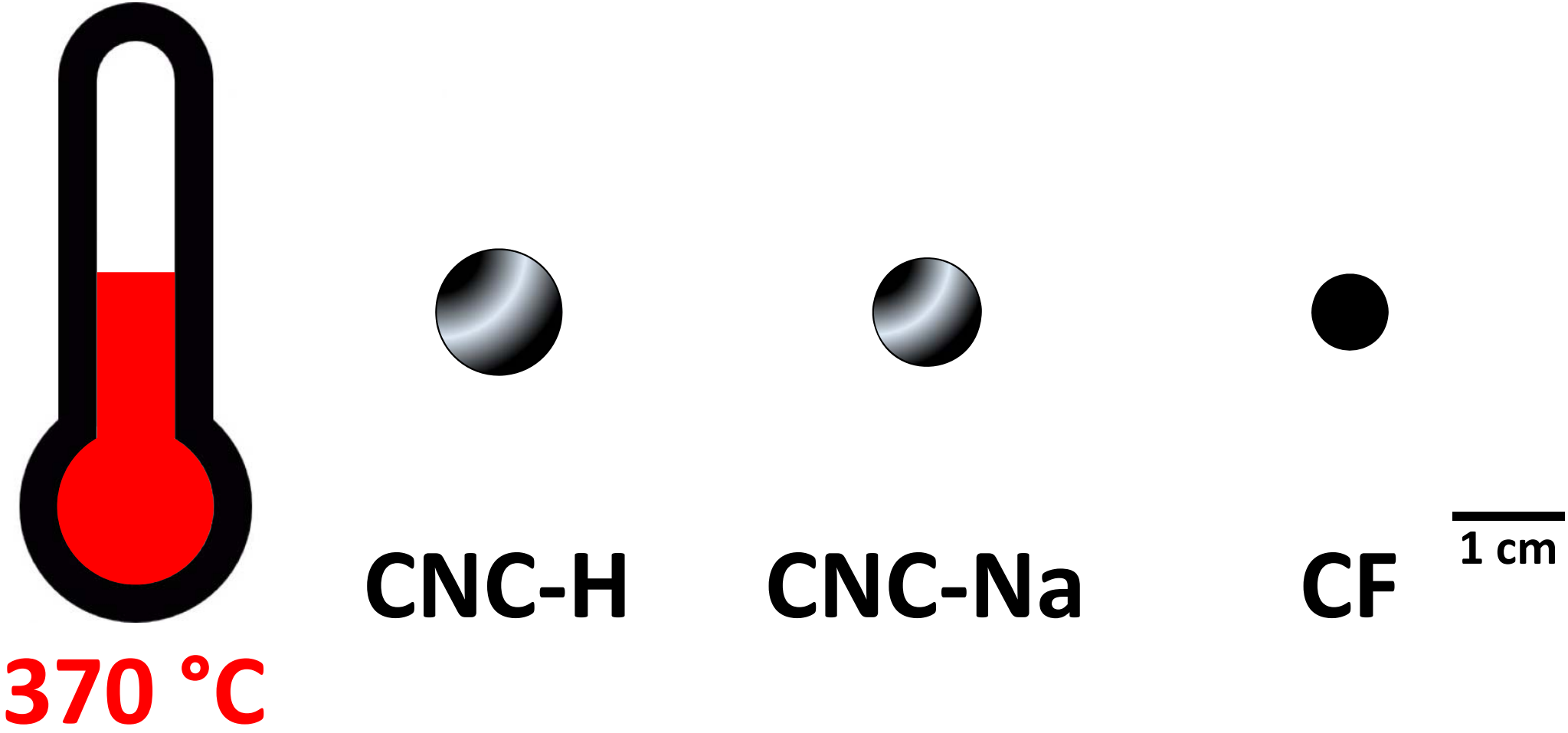

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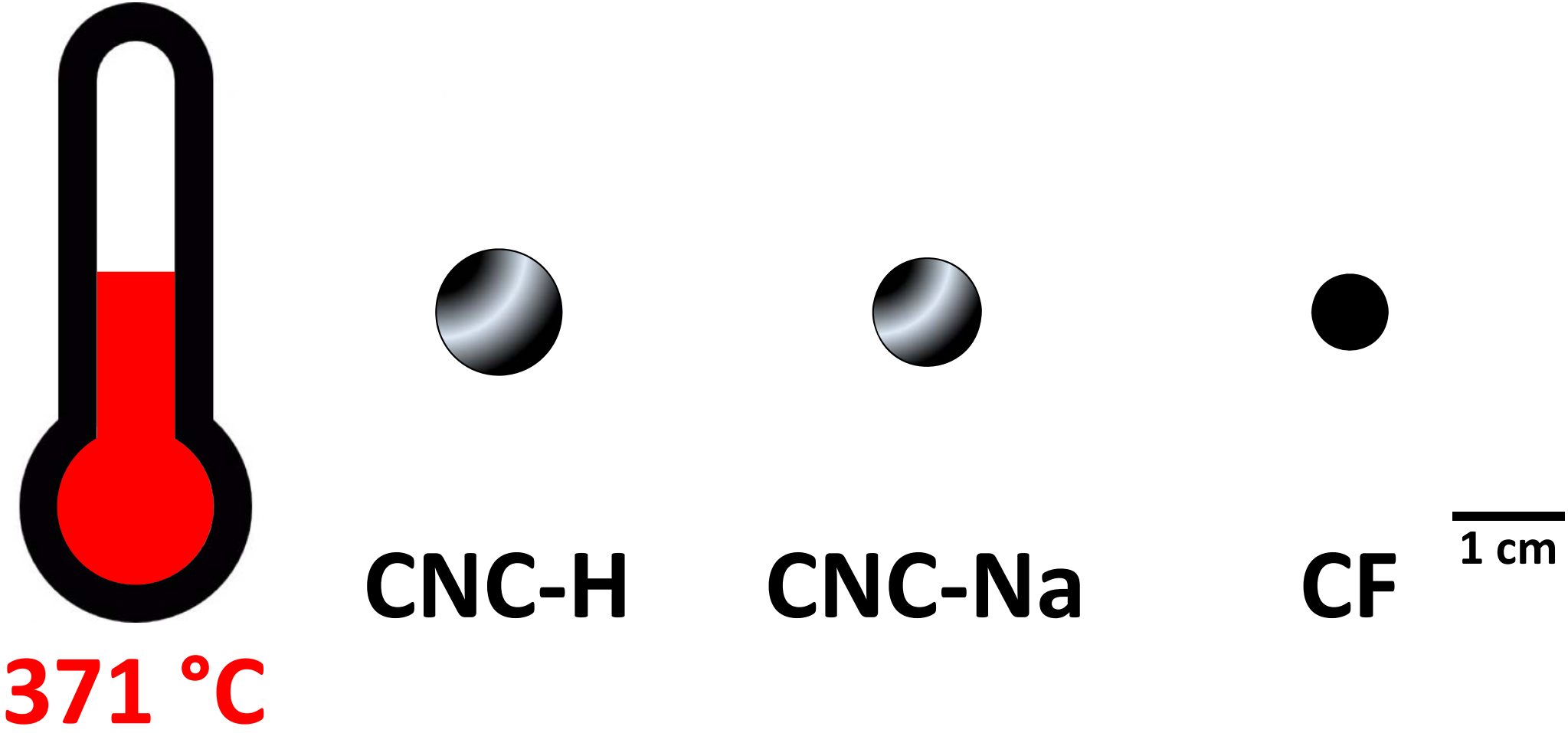

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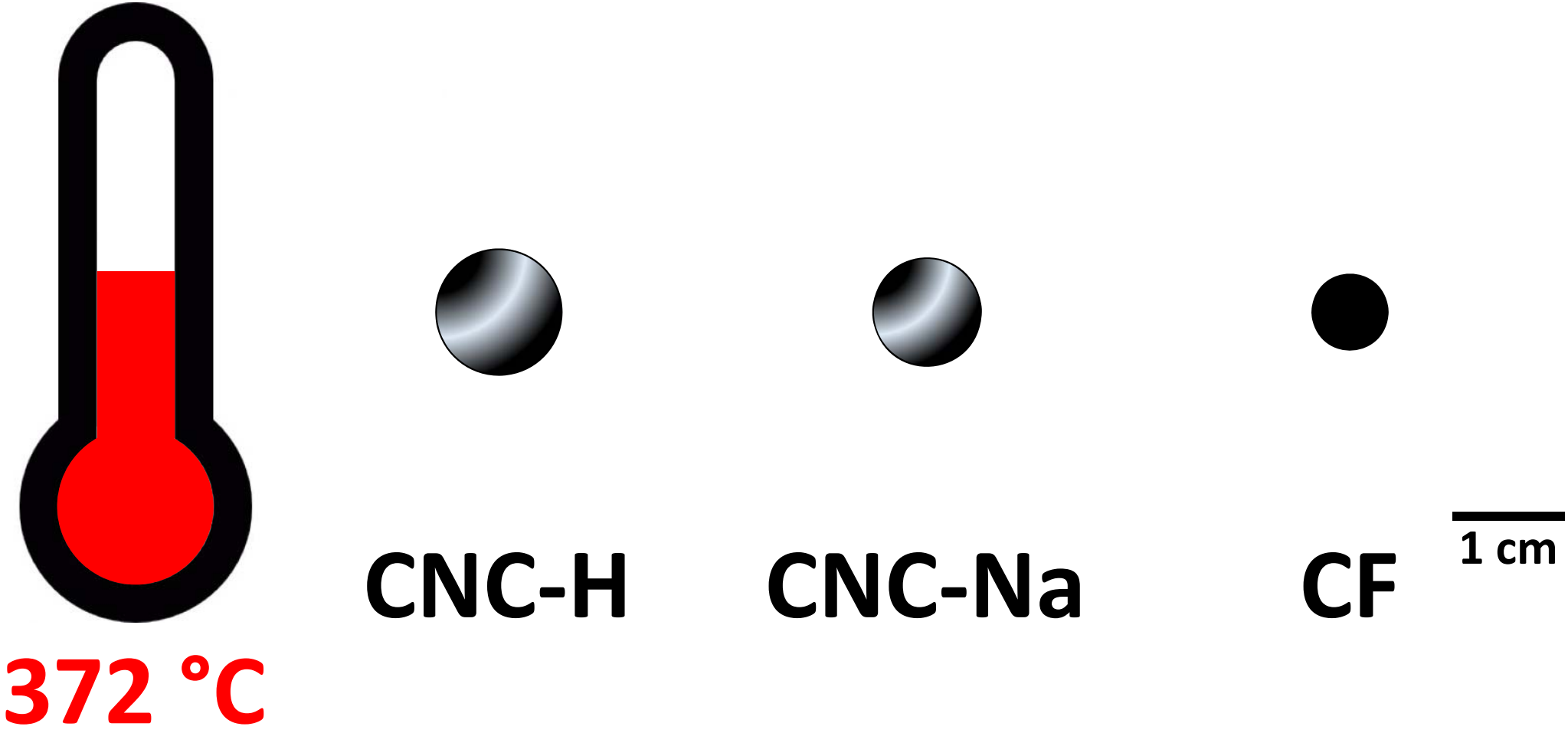

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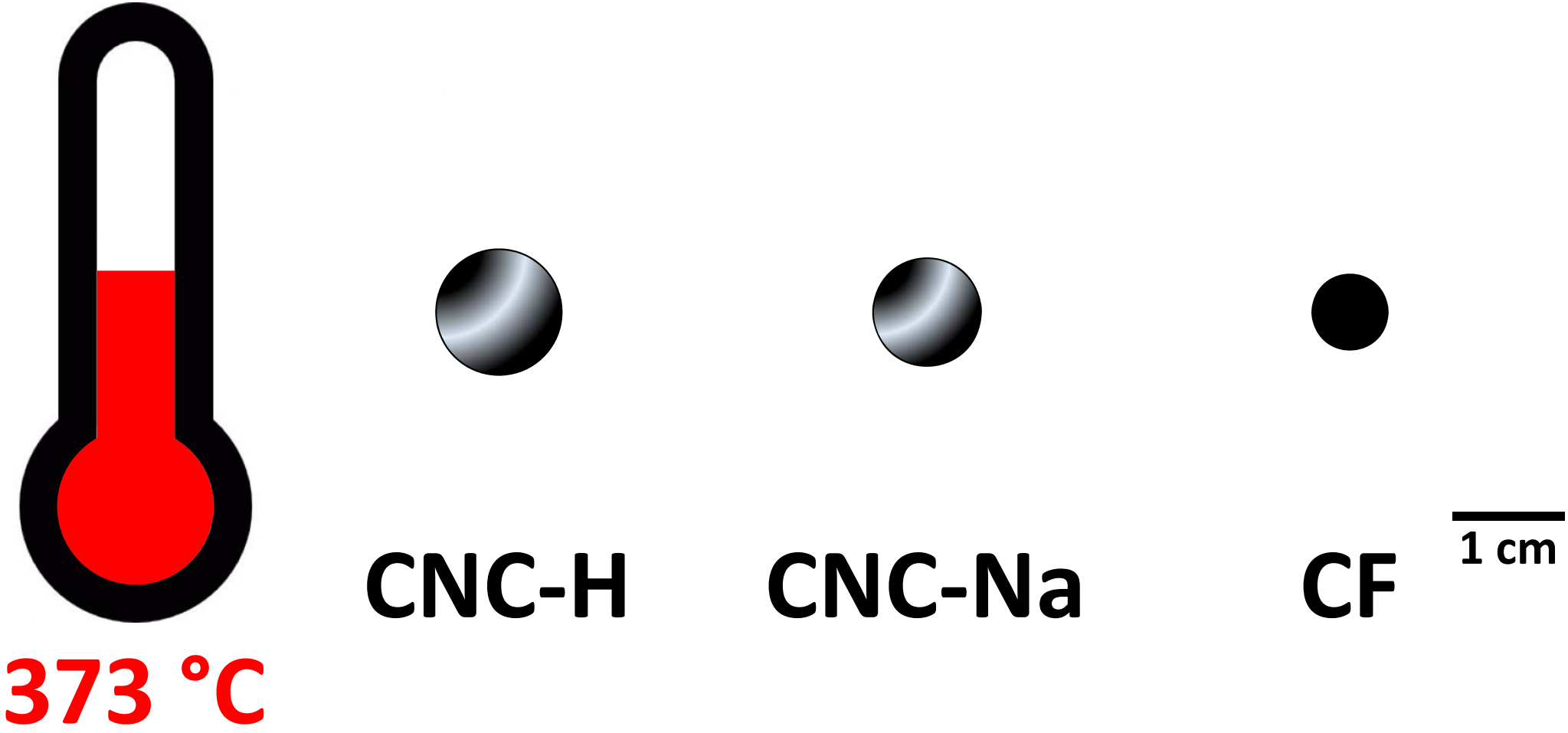

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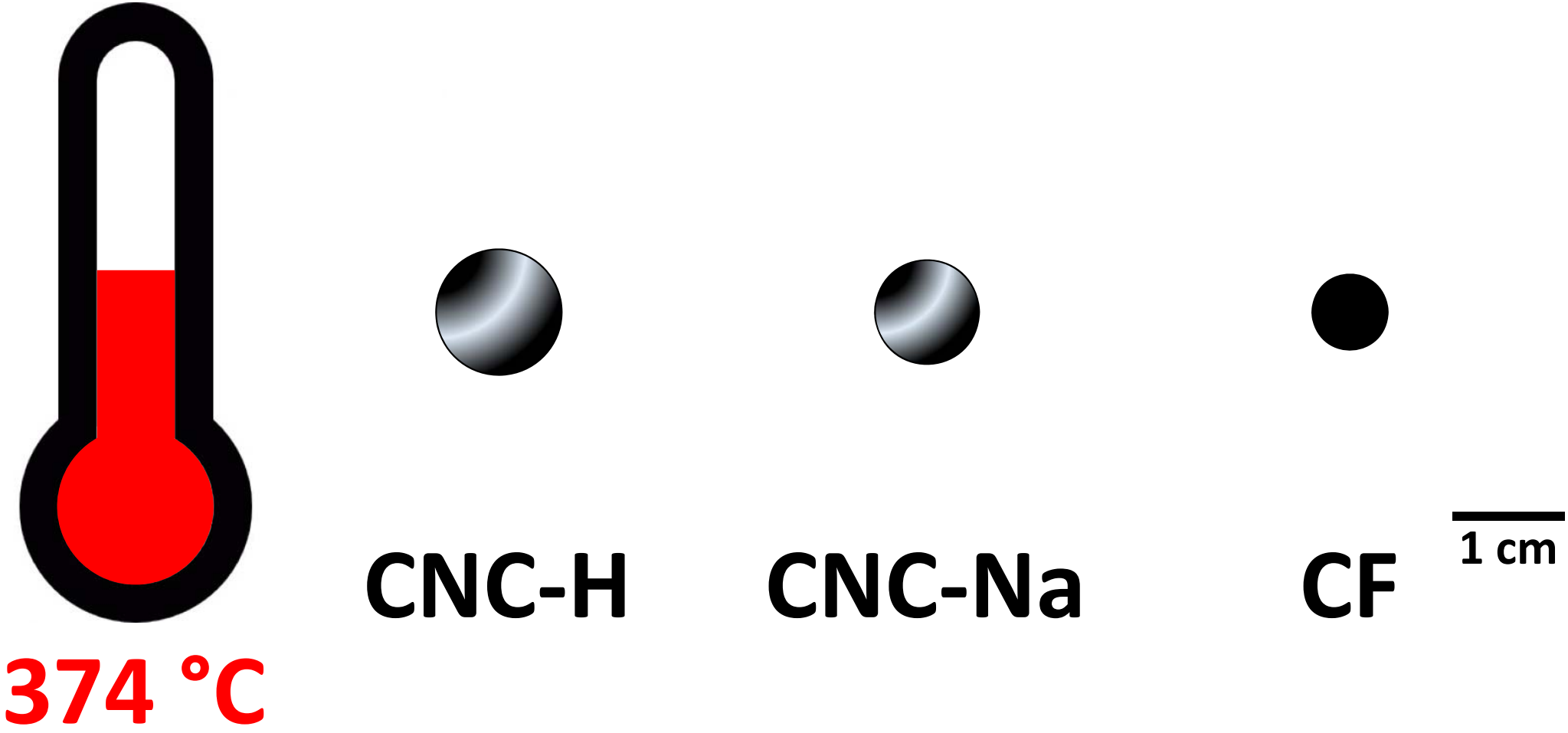

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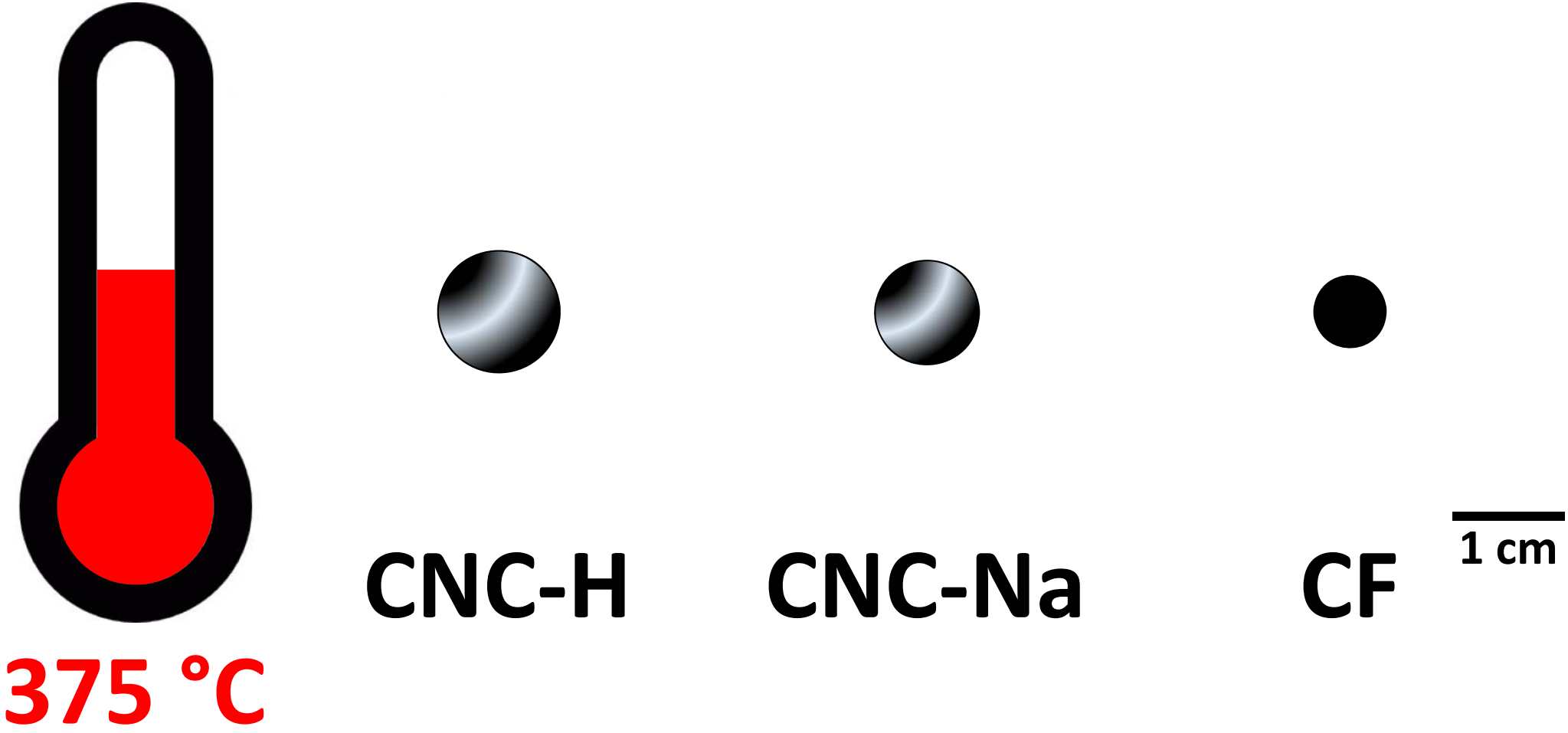

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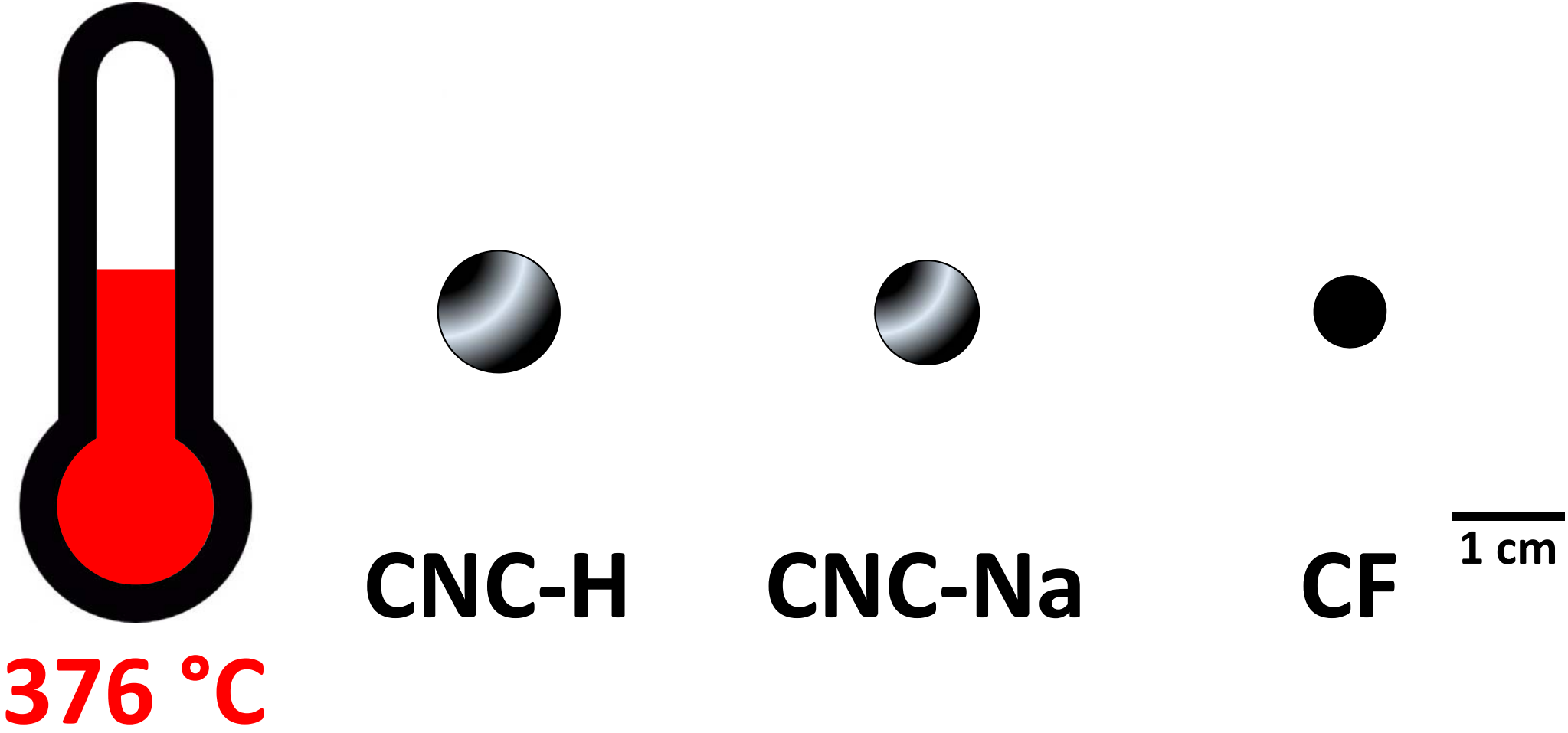

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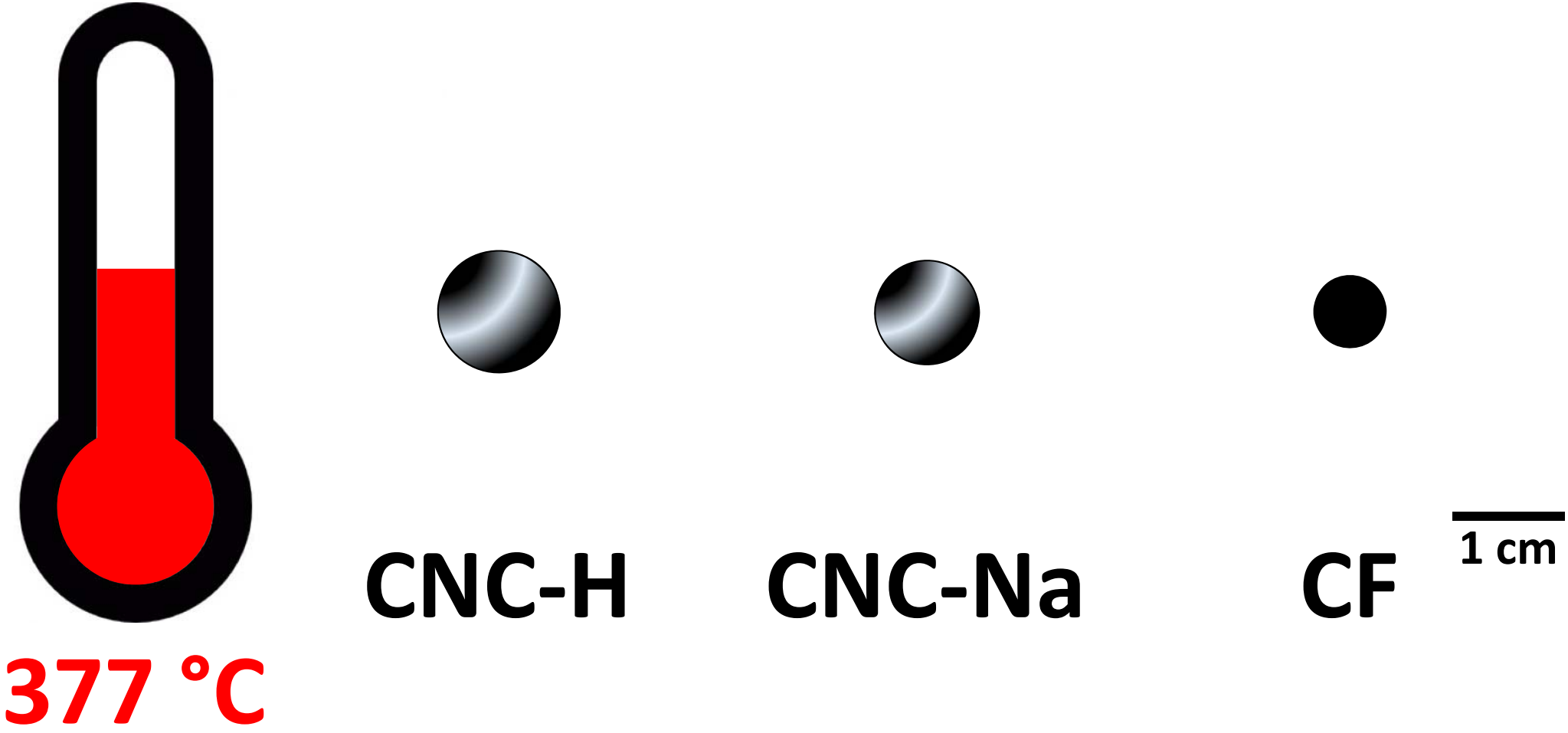

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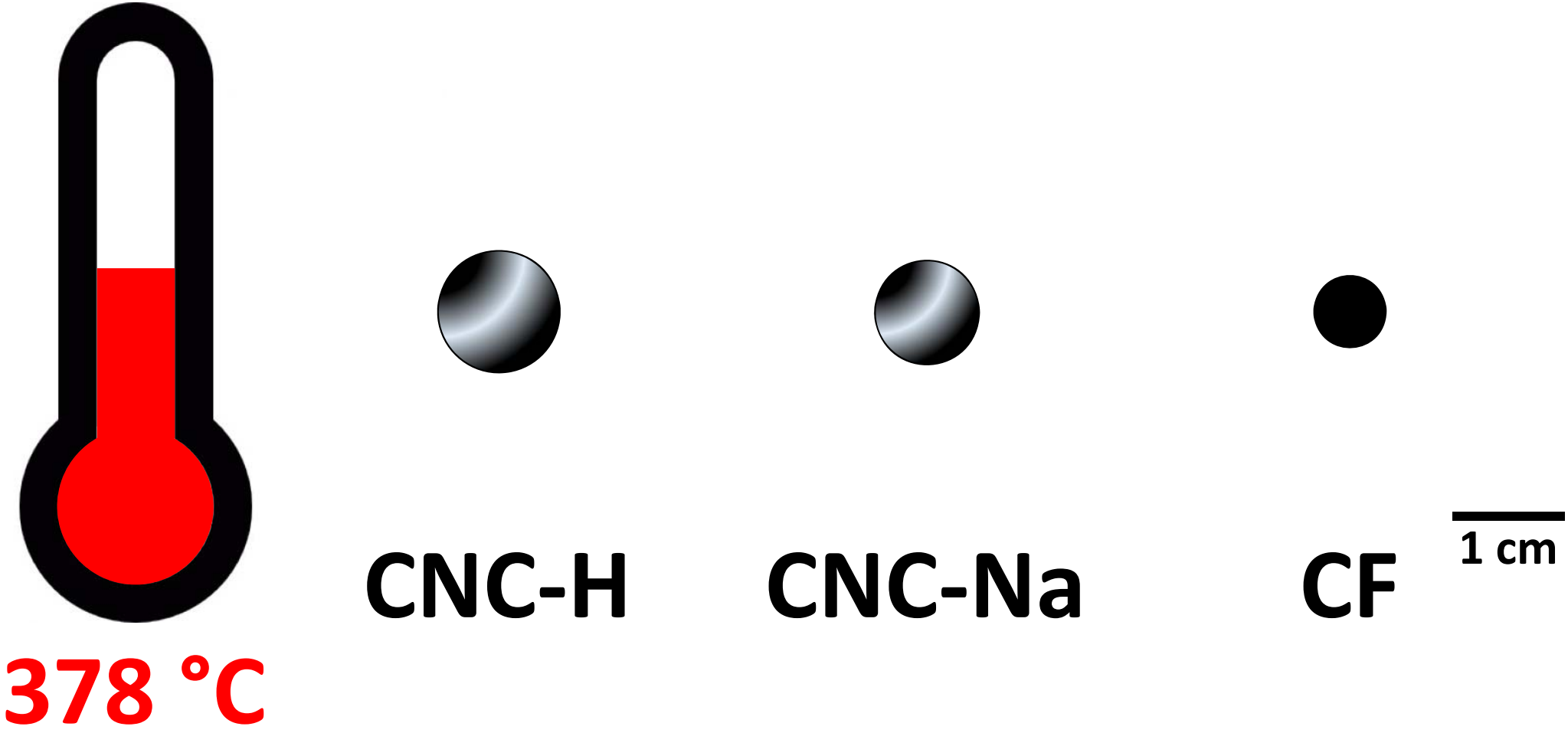

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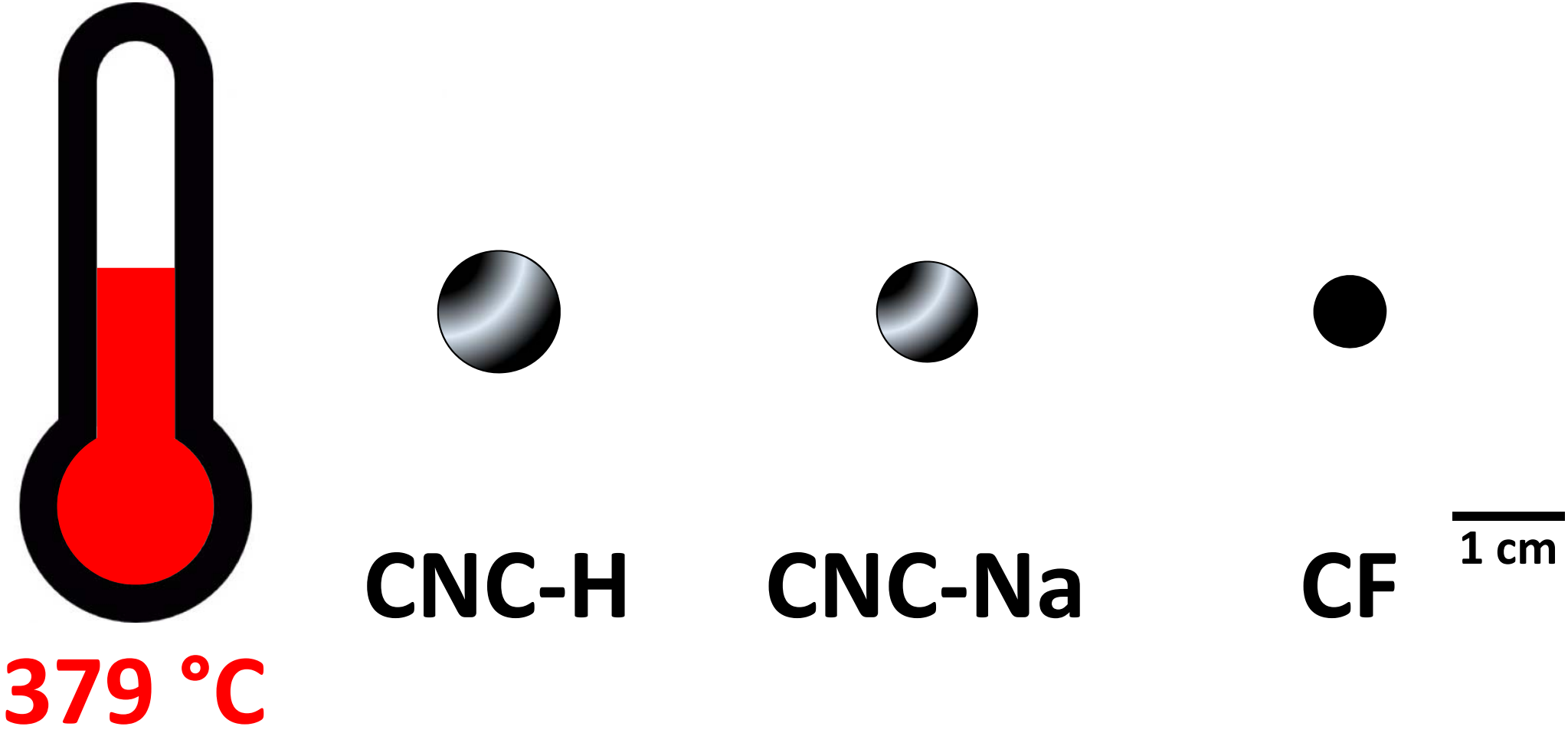

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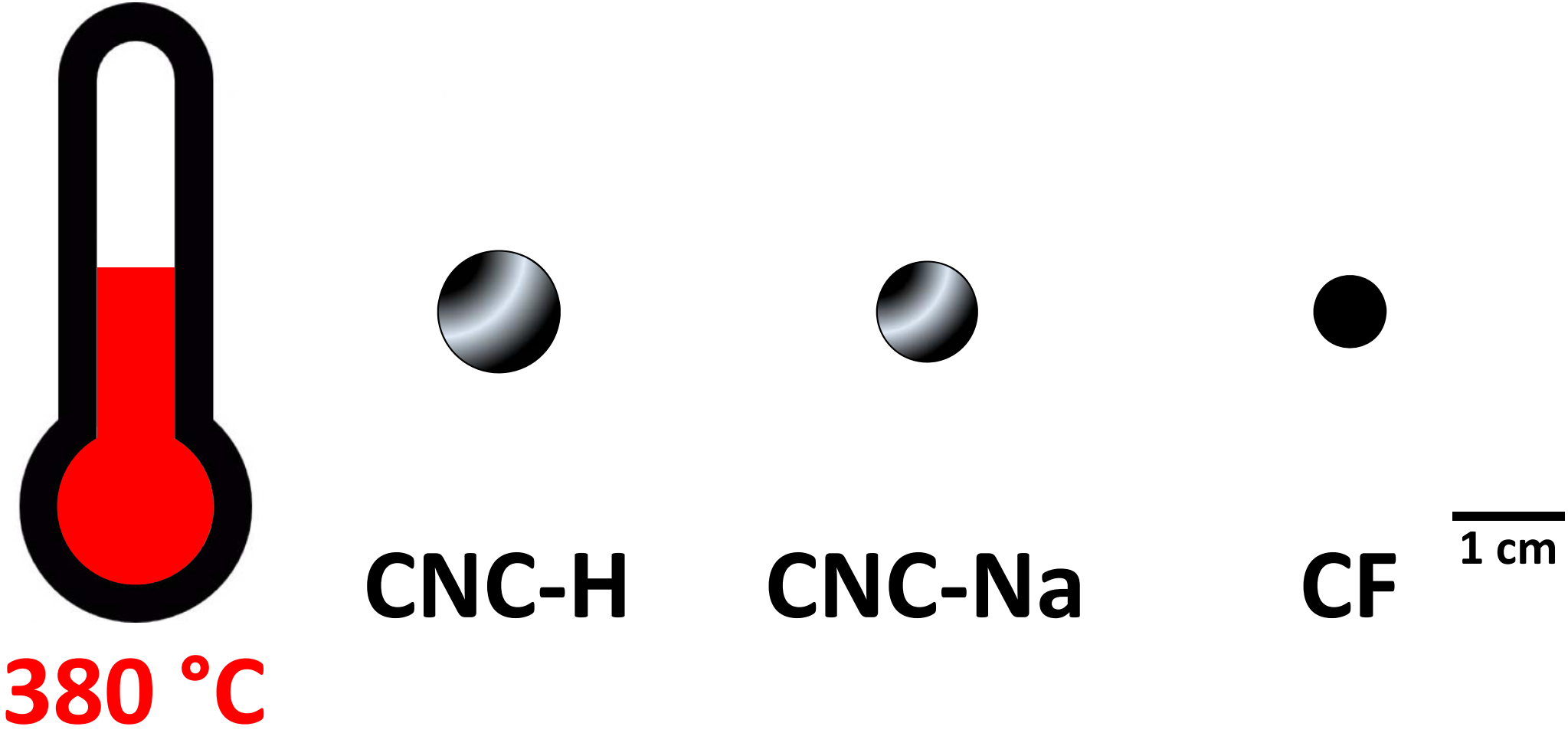

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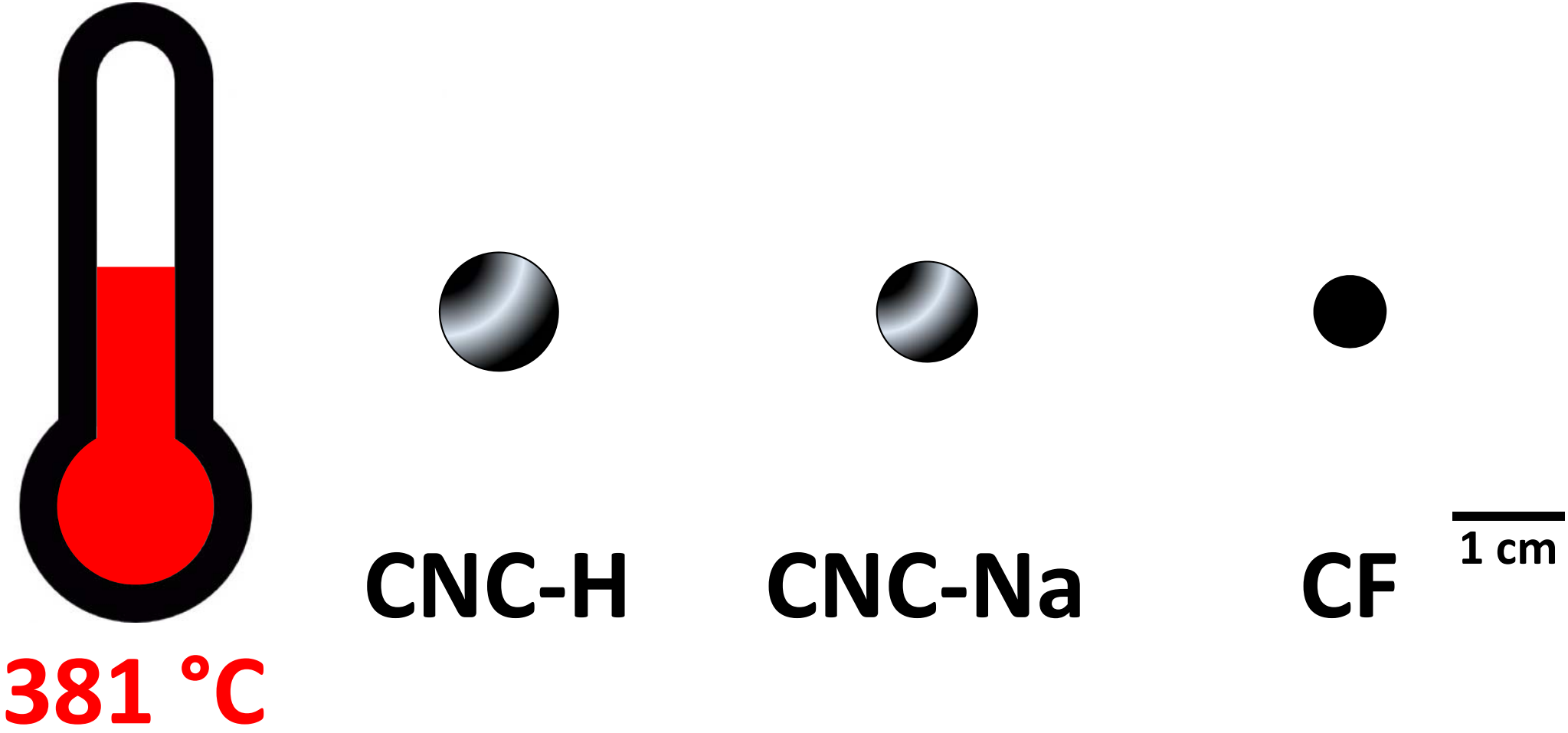

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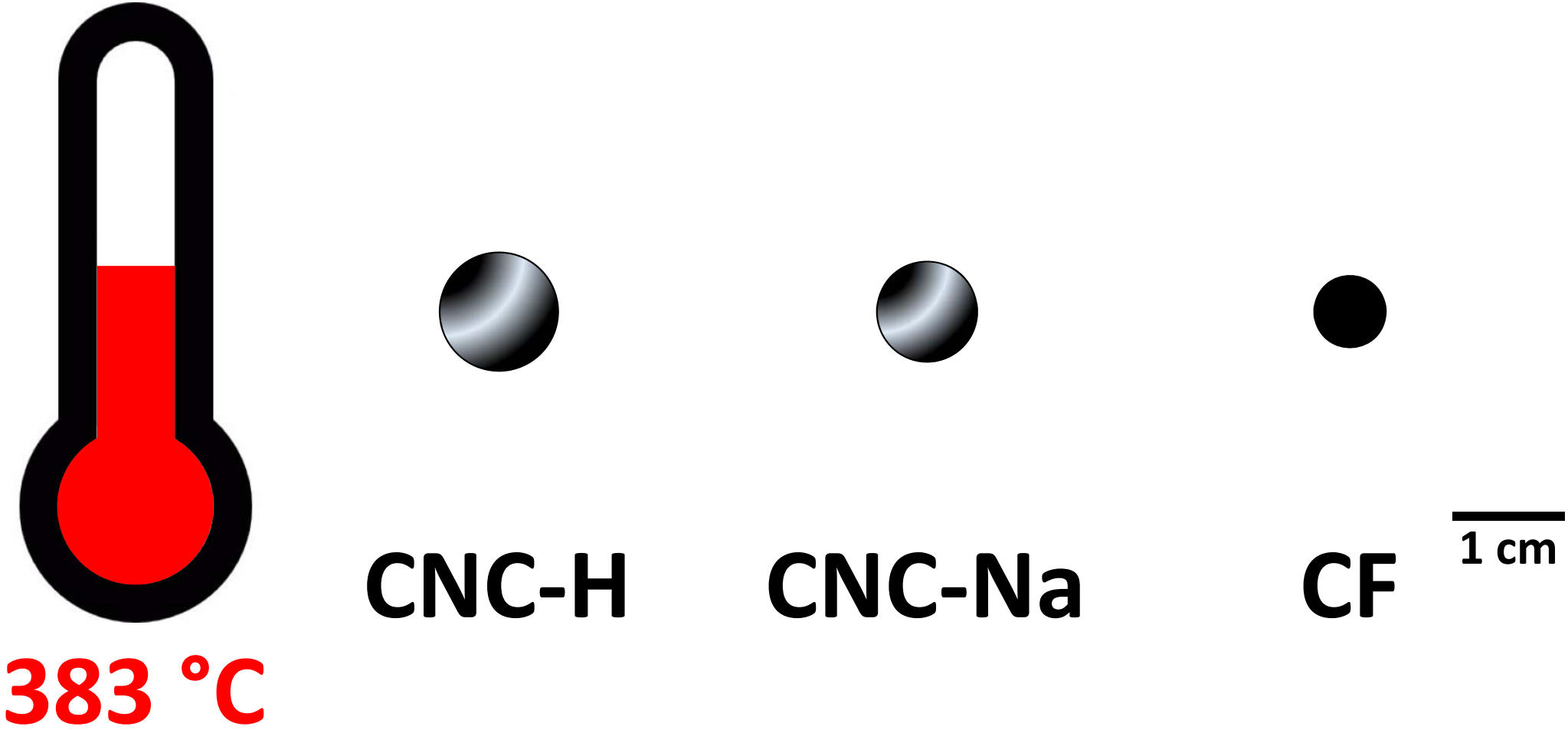

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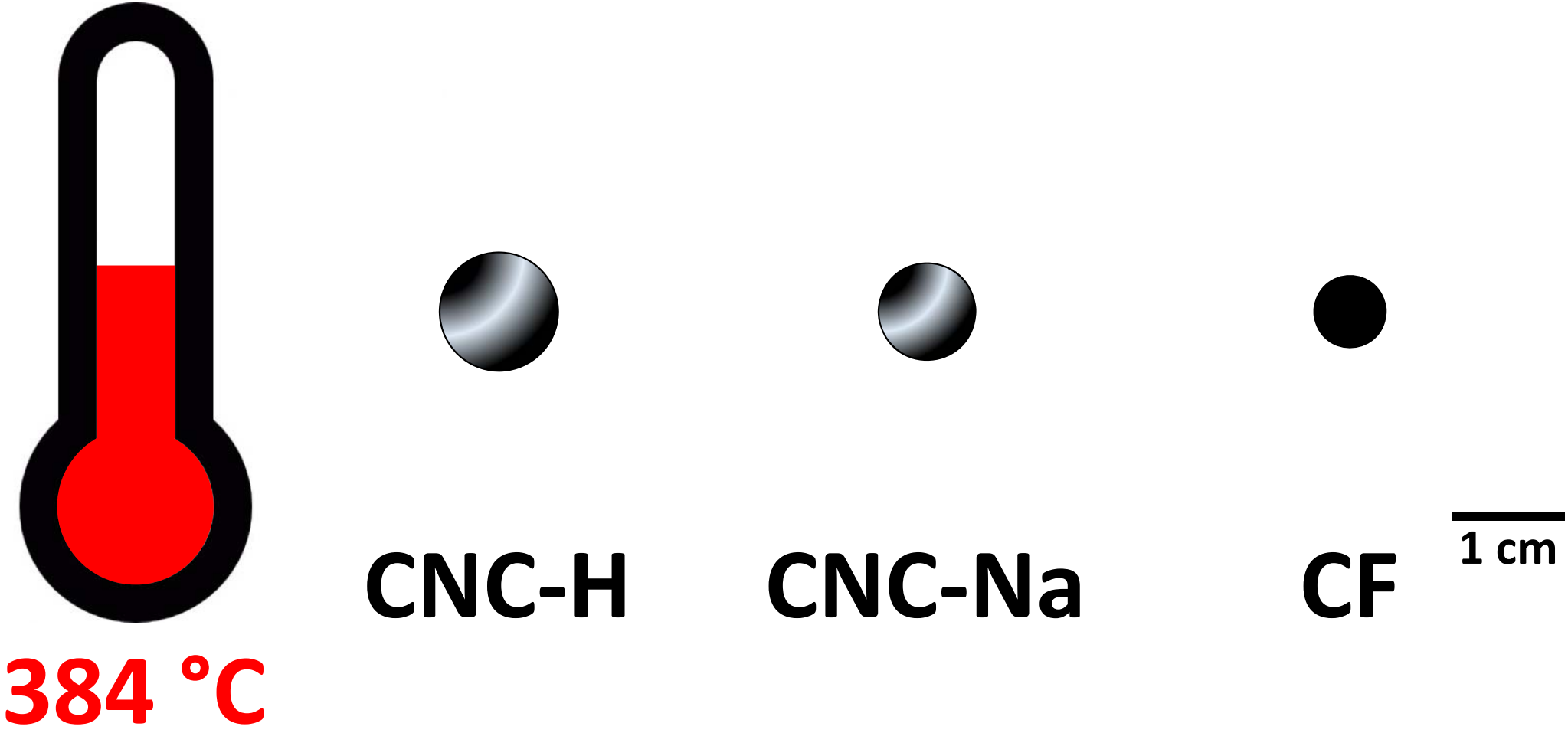

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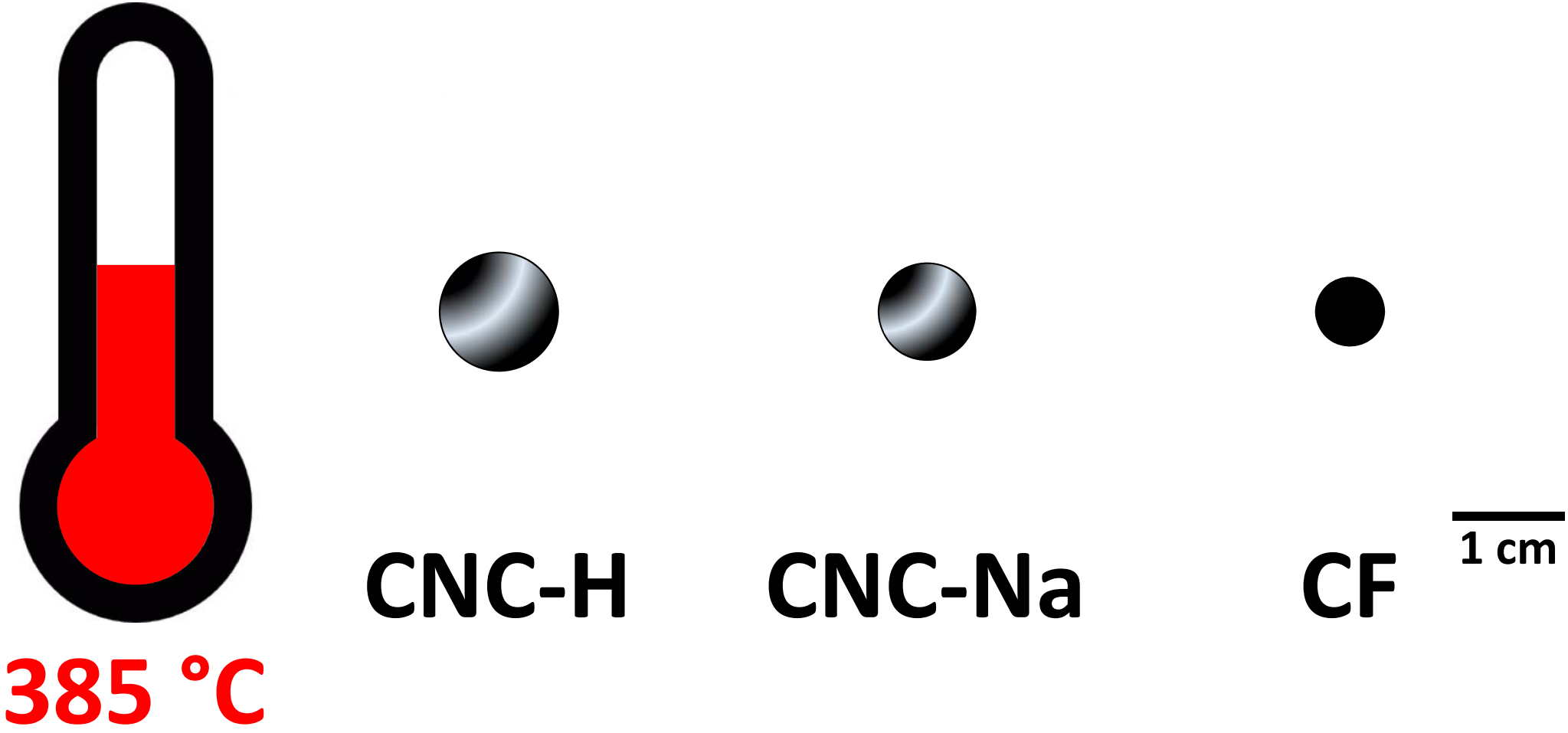

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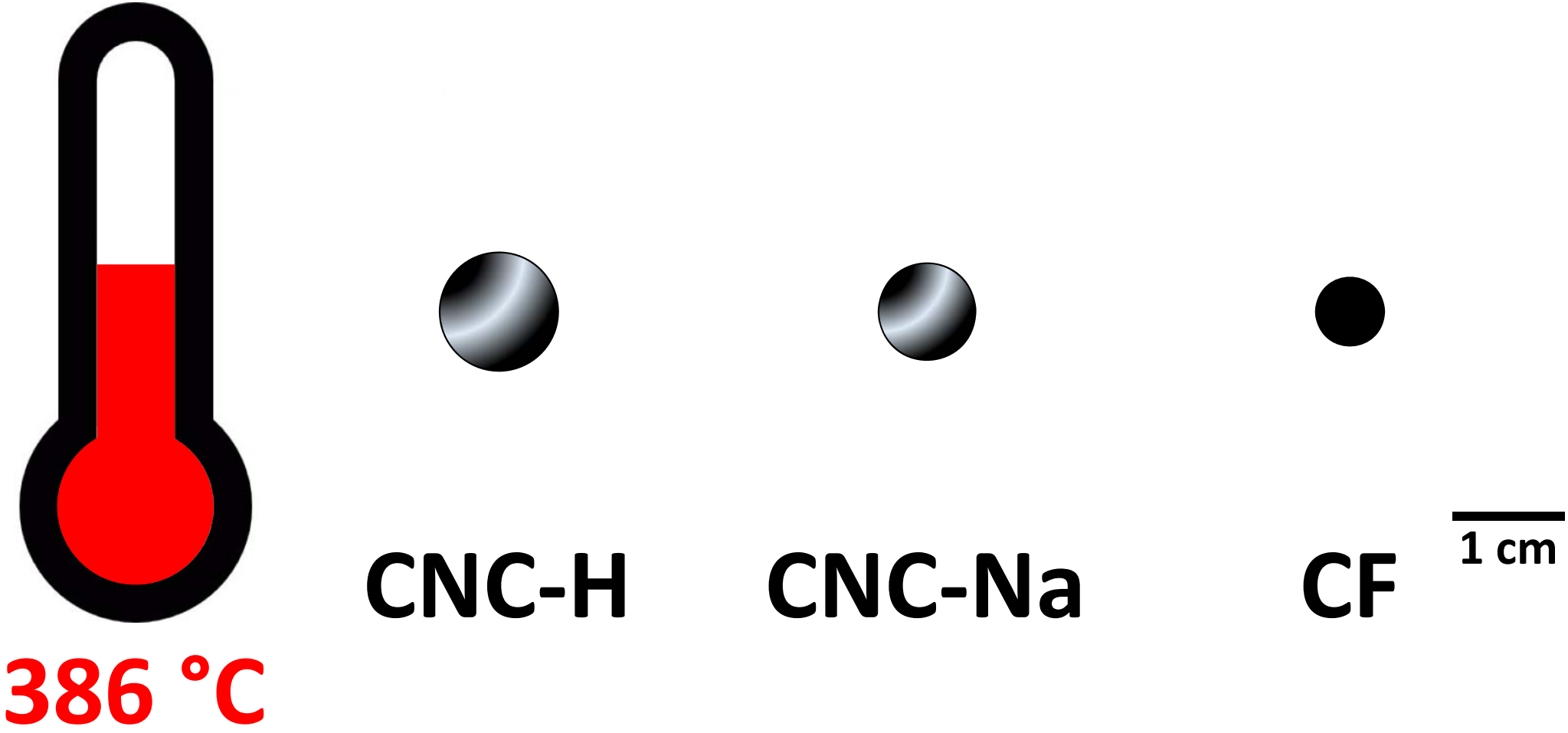

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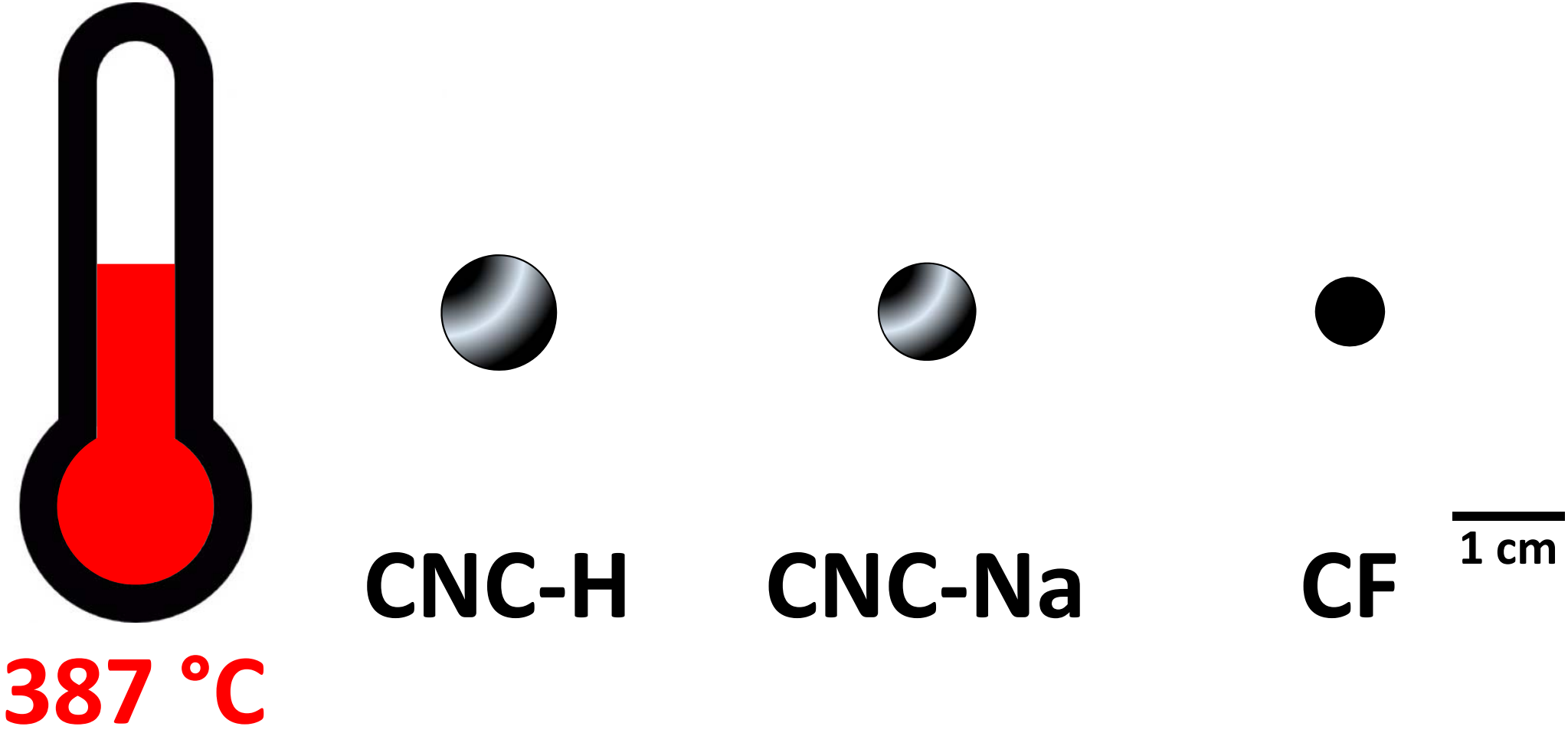

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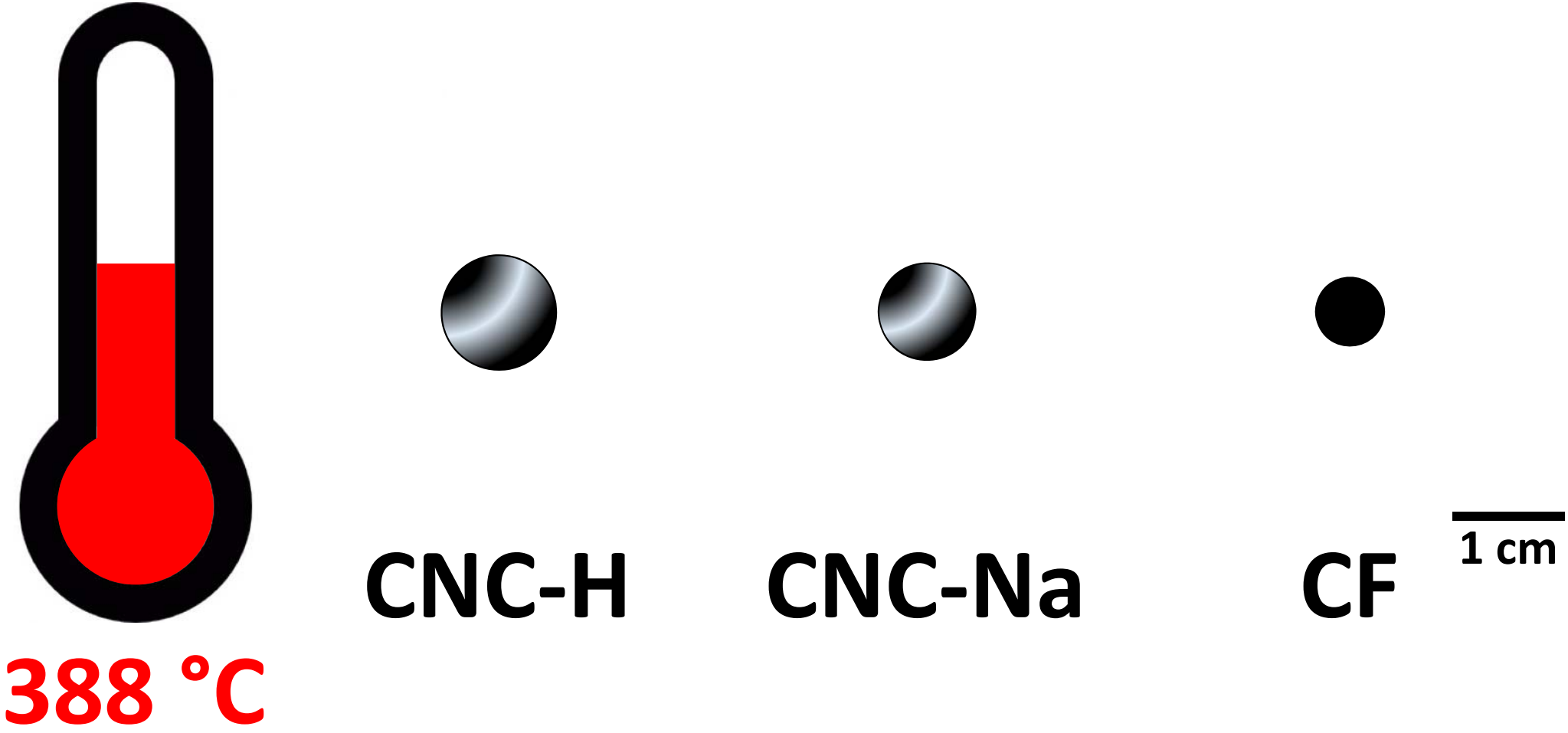

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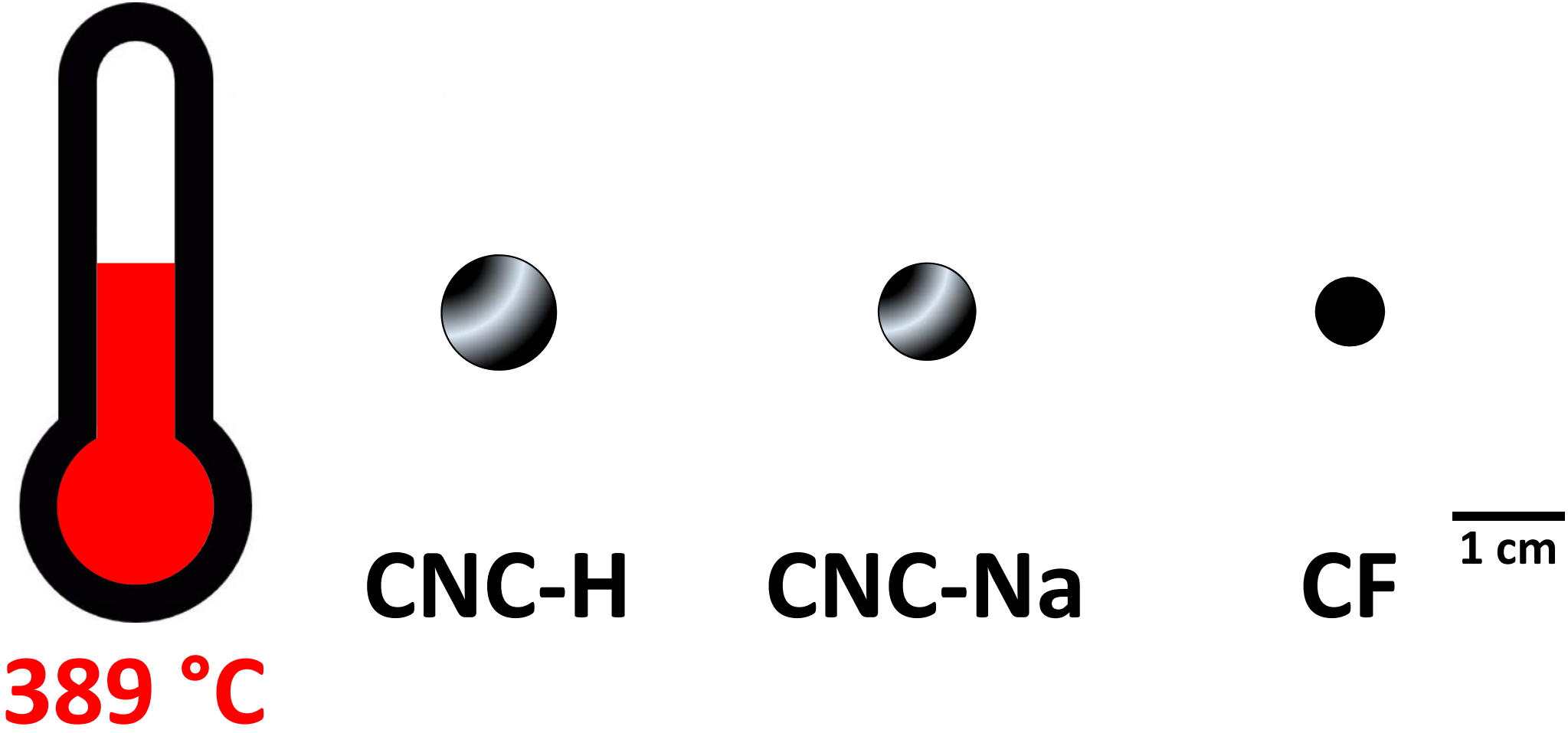

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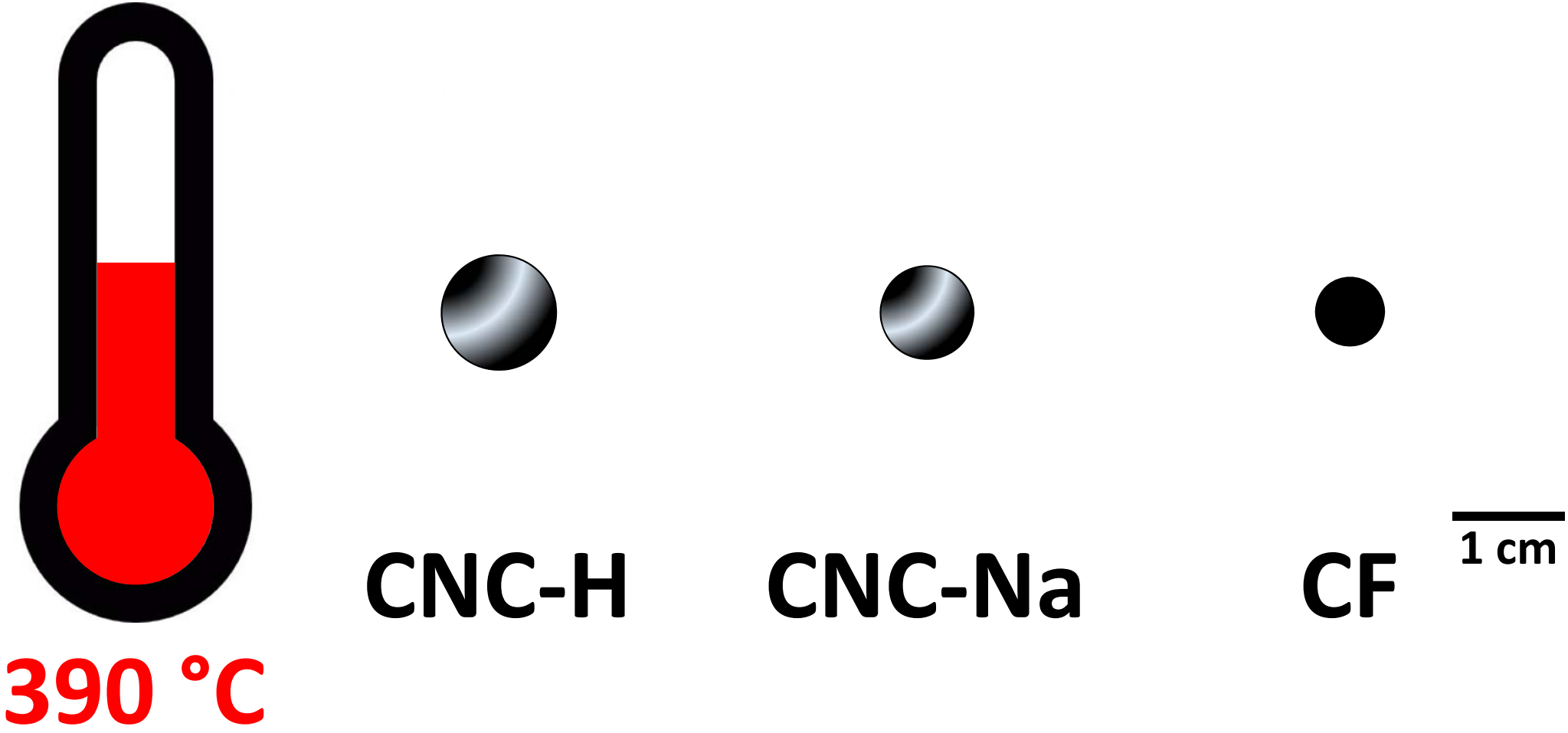

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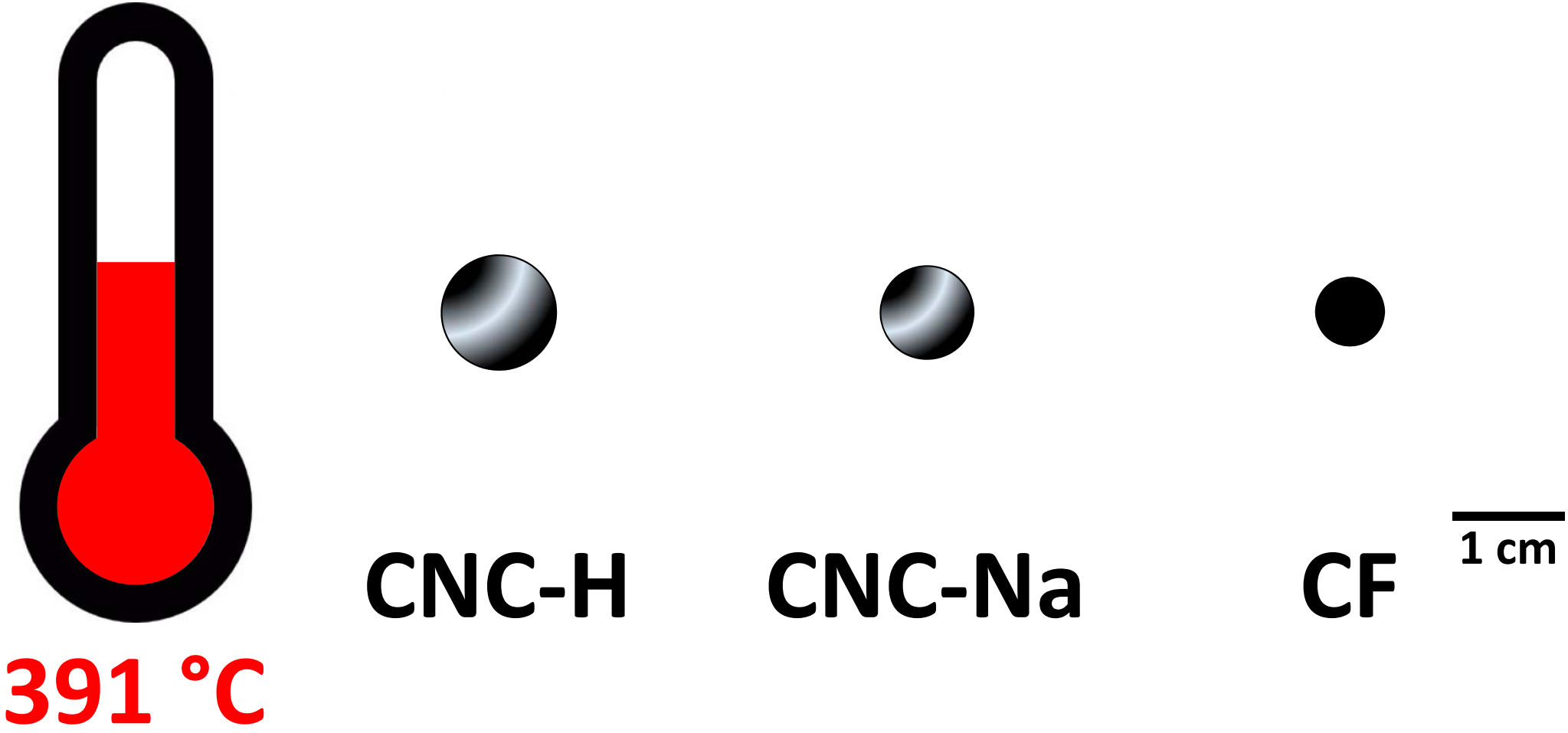

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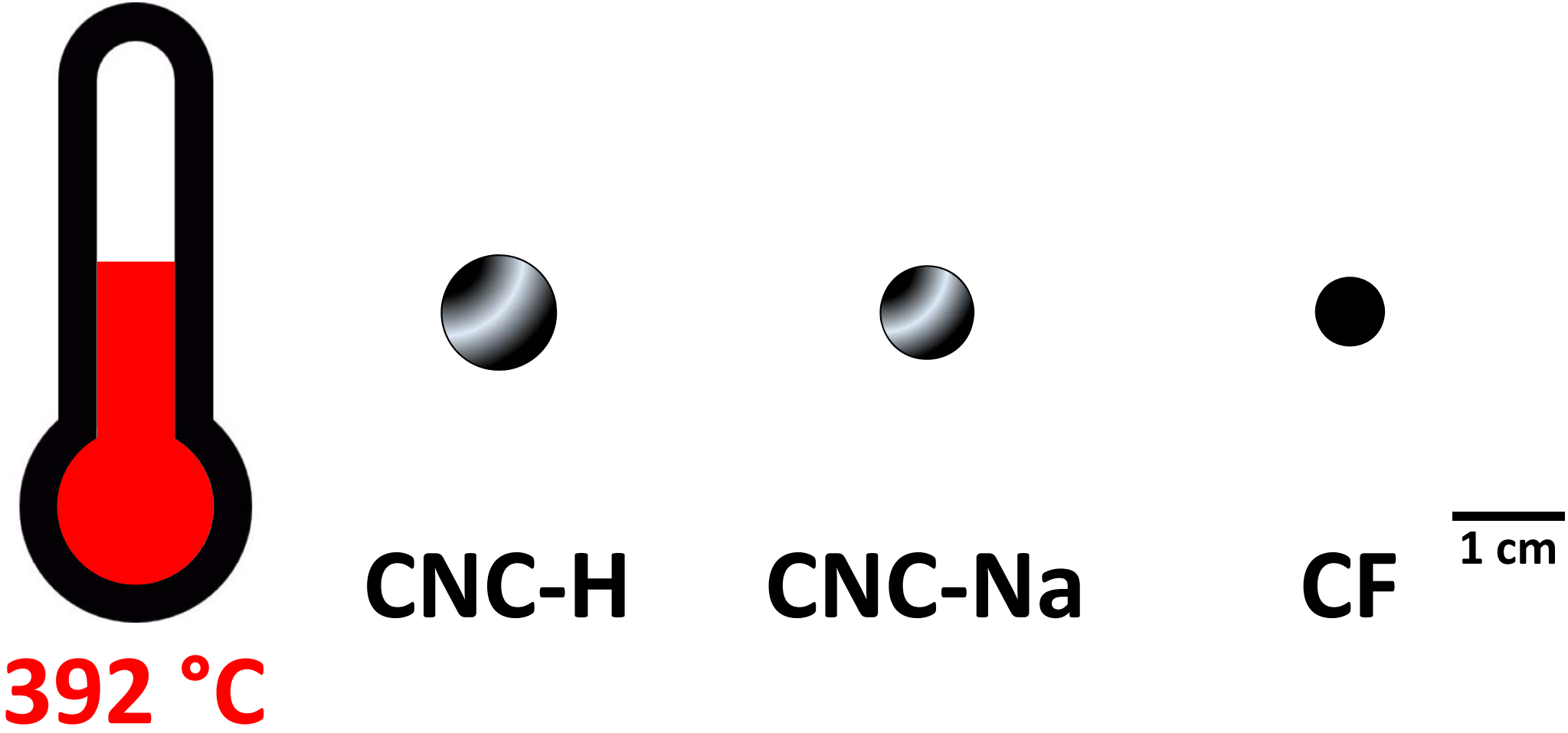

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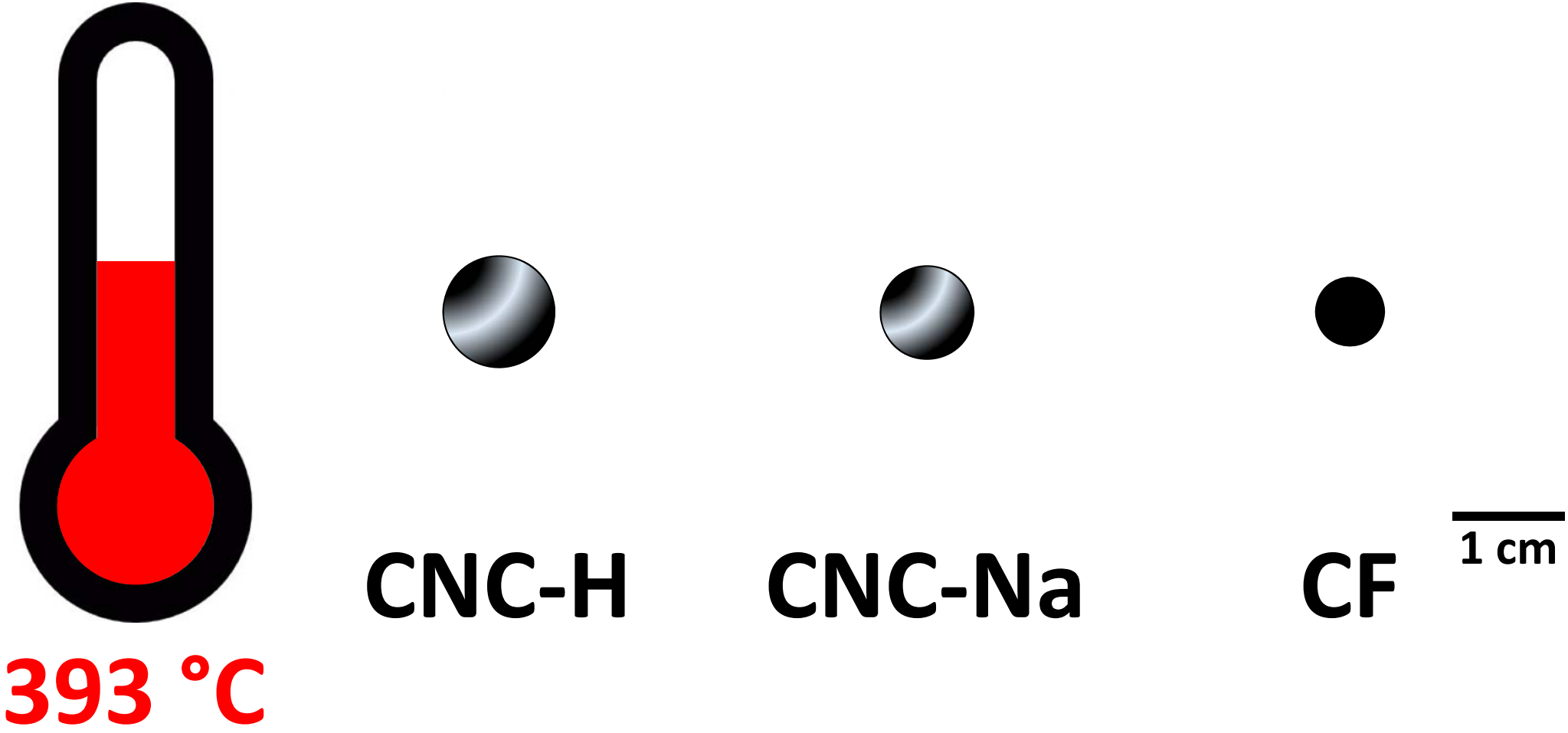

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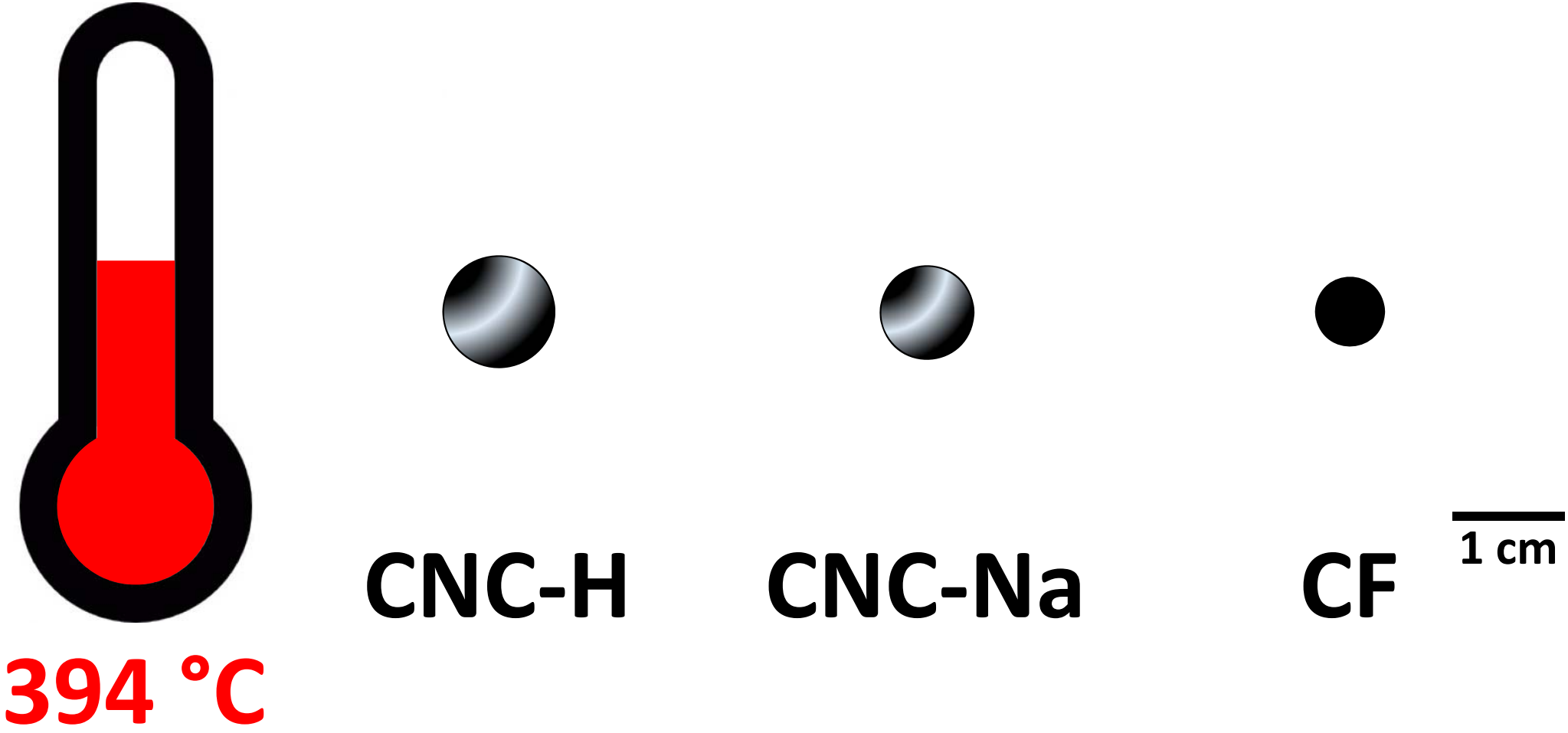

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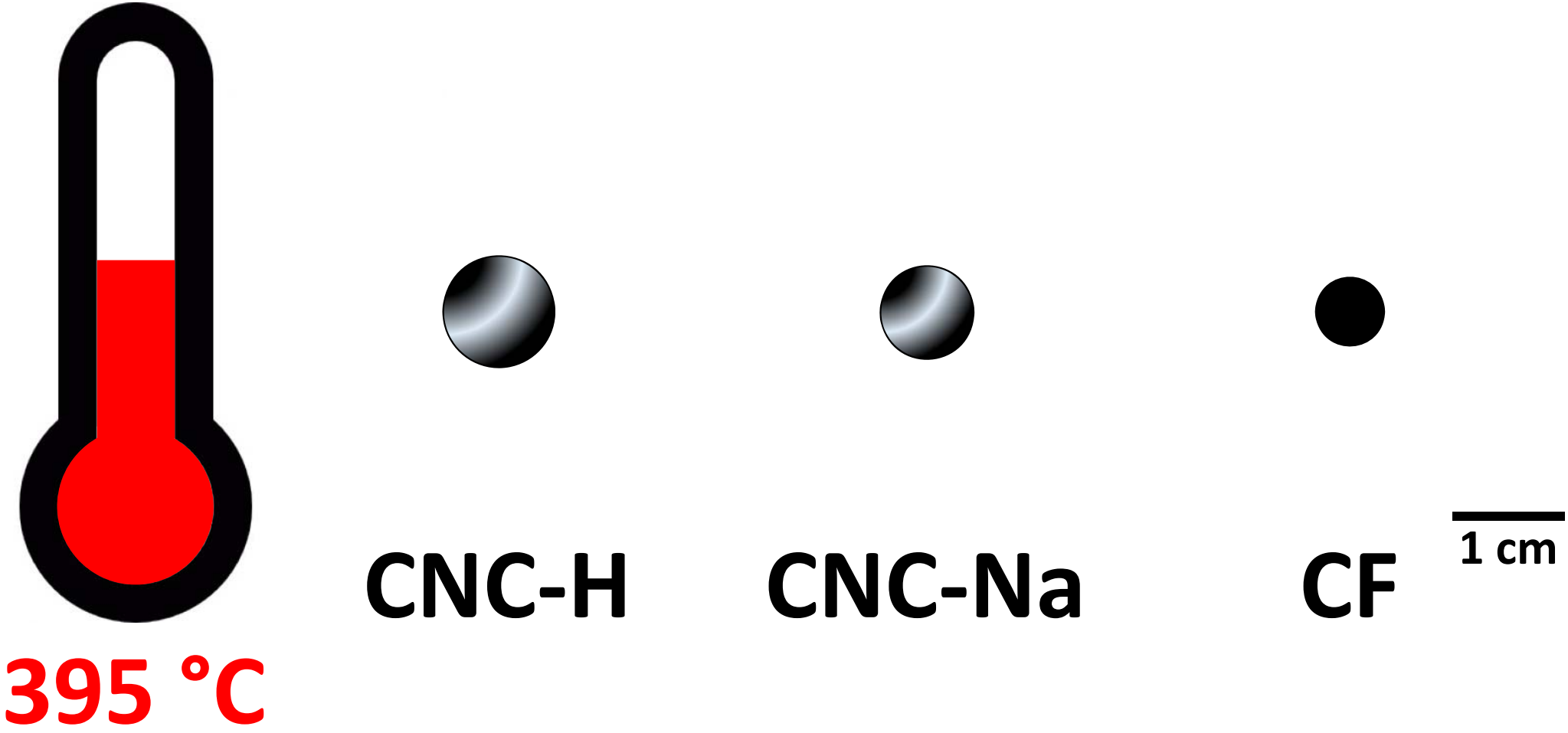

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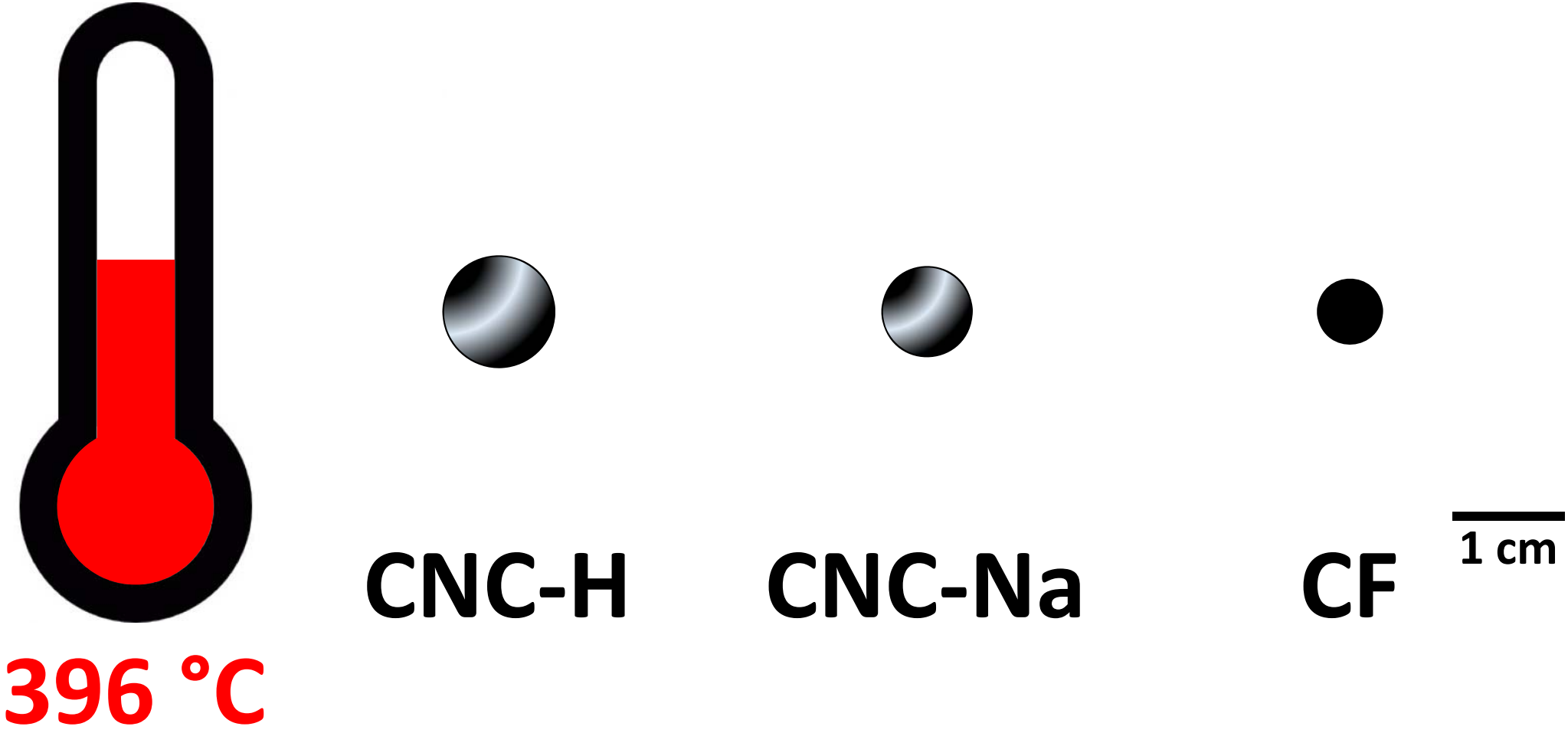

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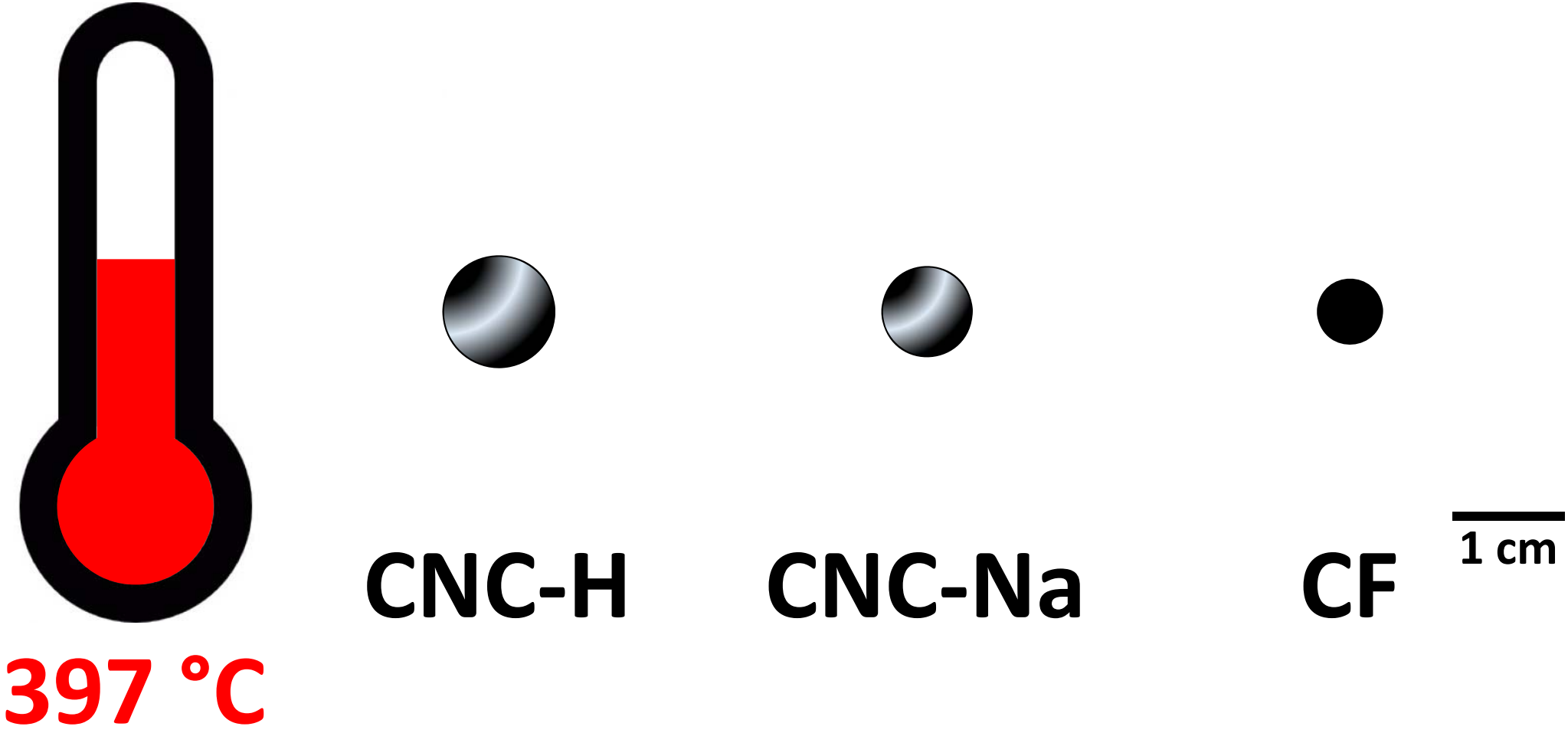

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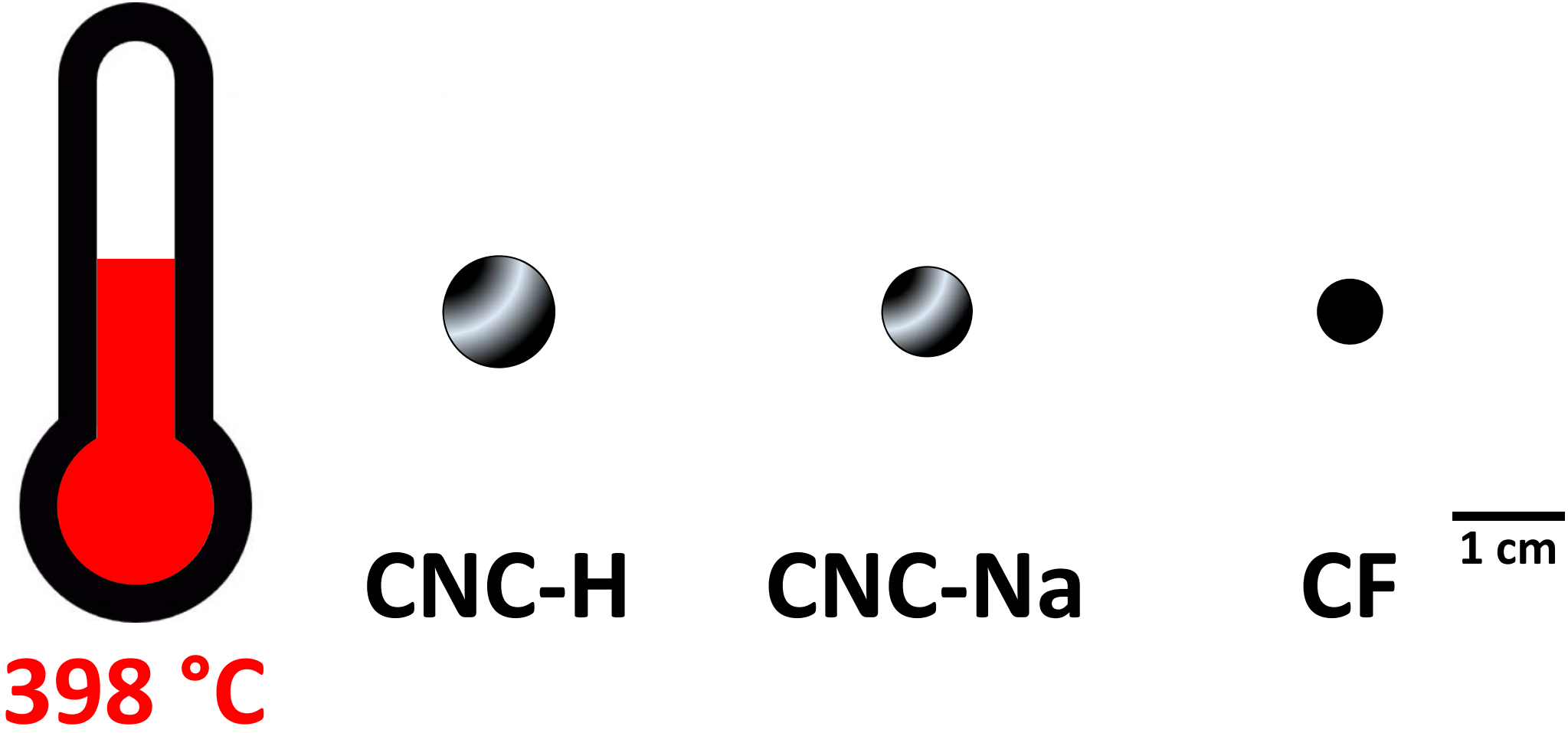

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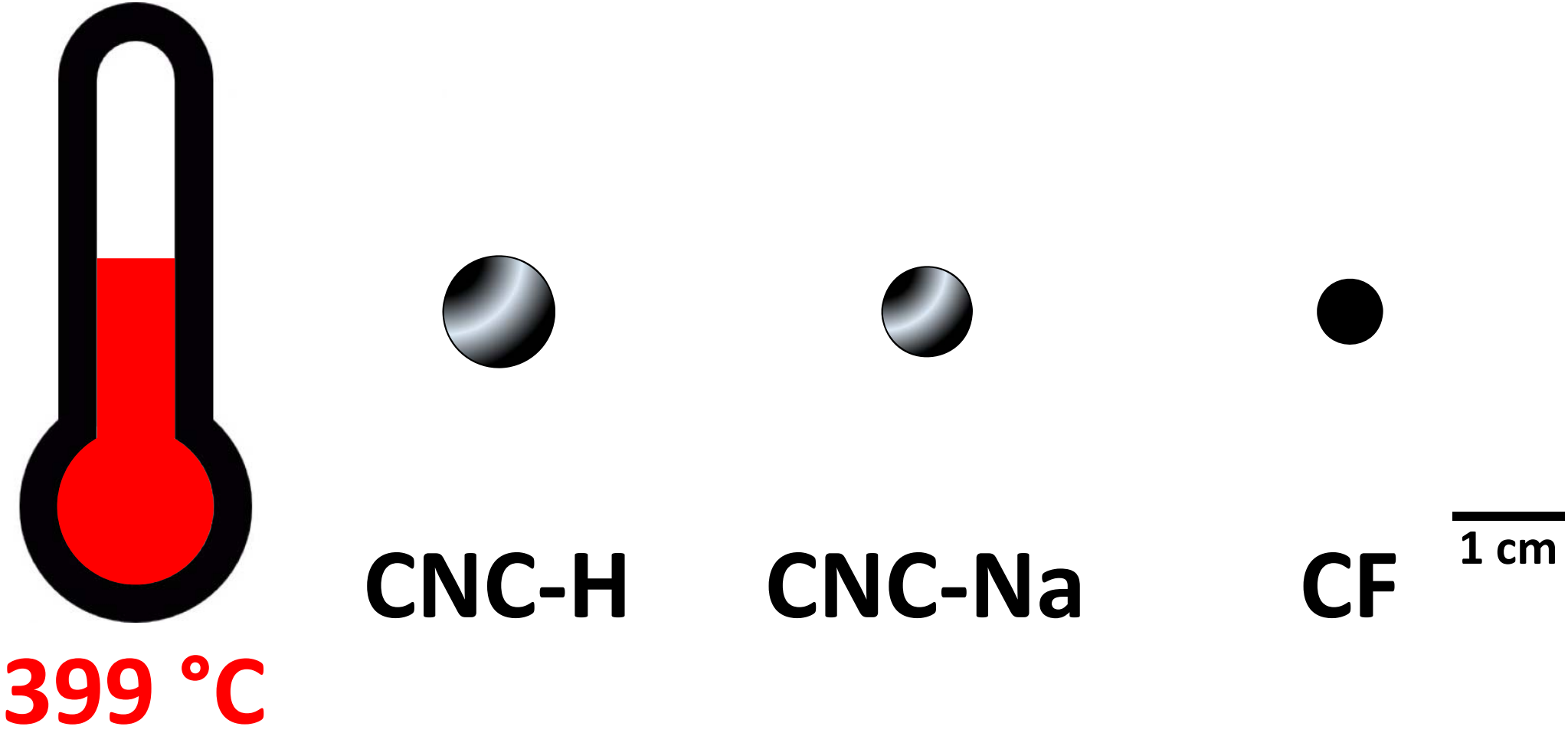

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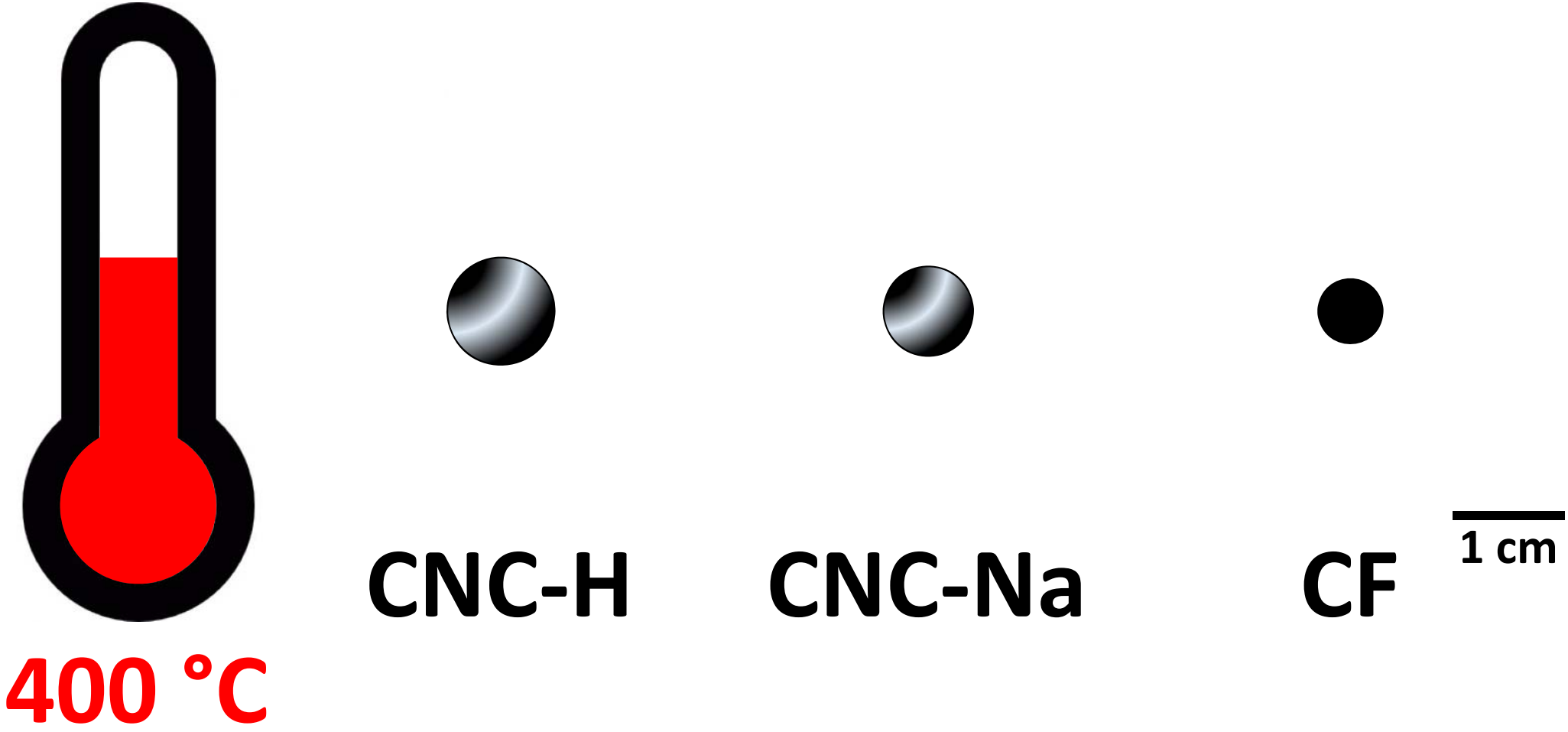

Conclusions

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- Thermal degradation dictated by **surface area** and **surface chemistry**
- *Surface area*: **larger** for CNCs → fast **heat transfer** → **extensive** degradation (low thermal stability, loss of crystallinity and birefringence, etc).
- *Surface chemistry*: residual **hydrolysis by-products** as **Lewis** acids → thermal degradation **catalyzed** for CNCs + formation of gaseous $\mathbf{H_2SO_4}$ (in CNC-H) and solid $\mathbf{Na_2S}$.
- CFs and **thermal-stable** CNCs → great potential for many **applications** (composites, foams, etc)

Improvement

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Mechanical methods (e.g., sonication, compression, …)

Physical methods (e.g., adsorption, …)

Chemical methods (e.g., click chemistry, …)

Thank you

PRESENTED BY

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