Adsorption of sulfur on the surface of silver nanoparticles stabilized with sago starch

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Biopolymer Nanocomposites

- Polymer nanocomposites combine advantageous properties of polymers with size-tunable optical, electronic, catalytic and other properties of metal and semiconductor nanoparticles.

- Polymers can not solely be regarded as good host materials; they can also be used to modify the surface and/or to control the growth of nanoparticles.

- Most of the methods for the preparation of high quality nanostructured metals and semiconductors produce nanoparticles that are non-polar and insoluble in aqueous solvents, thus, incompatible with biological systems.

- To address this problem, besides well known silanization method, several other methods have been suggested, such as modification of particle surfaces by using bifunctionalized ligands and amphiphilic polymers.

- Recently, biopolymers, such as chitosan, alginate and starch, have been introduced as capping agents and/or matrices for semiconductor, metal and semiconductor-semiconductor core shell nanoparticles.
Sago starch-Ag nanocomposite

Sago starch-\( \text{Ag}_2\text{S} \) nanocomposite

The band gap of bulk \( \text{Ag}_2\text{S} \) \( E_g = 1 \text{ eV} \)

Crystal structure of nano \( \text{Ag}_2\text{S} \) monoclinic
Optical properties of sago starch-Ag nanocomposite

<table>
<thead>
<tr>
<th>concentration</th>
<th>peak</th>
<th>(\lambda_c) (nm)</th>
<th>(\Delta\lambda) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_1)</td>
<td>I</td>
<td>380</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>425</td>
<td>80</td>
</tr>
<tr>
<td>(c_2)</td>
<td>I</td>
<td>384</td>
<td>40</td>
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<tr>
<td></td>
<td>II</td>
<td>415</td>
<td>50</td>
</tr>
<tr>
<td>(c_3)</td>
<td>I</td>
<td>398</td>
<td>52</td>
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<tr>
<td>(c_4)</td>
<td>I</td>
<td>398</td>
<td>47</td>
</tr>
</tbody>
</table>
Theory of the optical behaviour of small metallic particles in a dielectric medium

**Mie theory**

\[
C_{\text{ext}}(\omega) = \frac{12\pi r^3 \varepsilon_m^{3/2} \omega}{c} \frac{\text{Im} \varepsilon(\omega)}{(\text{Re} \varepsilon(\omega) + 2\varepsilon_m)^2 + \text{Im} \varepsilon(\omega)}
\]

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \times (1 + \delta n)
\]

\[
\omega_c = \frac{\omega_p}{\sqrt{\varepsilon_\infty + 2\varepsilon_m}}
\]

\[
\Gamma = \Gamma_0 + A \frac{v_f}{r}
\]

\[
\omega_p = \sqrt{\frac{N e^2}{m\varepsilon_0}} \rightarrow \sqrt{(N + \Delta N)e^2} = \omega_p \sqrt{1 + \frac{\Delta N}{N}} = \omega_p \sqrt{1 + \delta n}
\]

**Mie theory for capped and core-shell metal particles**

\[
C_{\text{ext}} = \frac{2\pi}{\varepsilon_m k^2} \sum_{n=1}^{\infty} (2n+1)\text{Re}(a_n + b_n)
\]

\[
\rho = \frac{r}{r + d}
\]

\[
a_n = \frac{\psi_n'(y) [\psi_n'(m_2 y) - A_n \chi_n'(m_2 y)] - m_2 \psi_n'(y) [\psi_n(m_2 y) - A_n \chi_n(m_2 y)]}{\xi_n'(y) [\psi_n'(m_2 y) - A_n \chi_n'(m_2 y)] - m_2 \xi_n'(y) [\psi_n(m_2 y) - A_n \chi_n(m_2 y)]}
\]

\[
b_n = \frac{m_2 \psi_n(y) [\psi_n'(m_2 y) - B_n \chi_n'(m_2 y)] - \psi_n'(y) [\psi_n(m_2 y) - B_n \chi_n(m_2 y)]}{m_2 \xi_n(y) [\psi_n'(m_2 y) - B_n \chi_n'(m_2 y)] - \xi_n'(y) [\psi_n(m_2 y) - B_n \chi_n(m_2 y)]}
\]
Maxwell-Garnett (M-G) effective medium theory

\[
\varepsilon_{av}(\omega) = \varepsilon_m \left( \frac{(1 + 2f)\varepsilon(\omega) + (1 - f)2\varepsilon_m}{(1 - f)\varepsilon(\omega) + (2 + f)\varepsilon_m} \right)
\]

\[
f = F \frac{r^3}{(r + s)^3}
\]

\[
\alpha_{av} = \frac{\omega \text{ Im}(\varepsilon_{av}(\omega))}{c n_{av}}
\]

\[
\omega_c = \frac{\omega_p}{\sqrt{\varepsilon_{\infty} + \frac{2 + f}{1 - f}\varepsilon_m}}
\]
Adsorption of sulfur on the surface of starch capped silver nanoparticles

\[
\delta n \approx 1.5\% \\
\rho \approx 0.9
\]

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*Coll Surf B: Biointerf* in press
TEM and HRTEM analysis of Ag@Ag$_2$S core-shell nanoparticles in sago starch
HAADF-STEM analysis
XPS analysis
• The recent results on the other nanocomposite structures that comprise biopolymers and inorganic nanoparticles.
Sago starch-CdS nanocomposite

The Brus equation:

\[
\Delta E = \frac{\hbar^2}{8R^2} \left( \frac{1}{m^*_e} + \frac{1}{m^*_h} \right) + \frac{e^2}{4\pi\varepsilon_0\varepsilon_r R}
\]

\[
d = 2R = 4.1 \text{ nm}
\]

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Sago starch-CdSe nanocomposite
Sago starch-PbS nanocomposite

- Particle diameter $D$ (nm):
  - $D_c = 9.2$ (3) nm
  - $\sigma_c = 3$ nm
  - $D_{\text{LN}} = 8.2$ nm
  - $\sigma_{\text{LN}} = 0.26$
  - $N = 100$

- Absorbance (a.u.):
  - Wavelength $\lambda$ (nm)
  - Absorbance $\alpha$ (a.u.)

- X-ray diffraction peaks:
  - (111)
  - (200)
  - (220)
  - (311)
  - (222)
Colaborators

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- T. Radhakrishnan, M.K. Georges, University of Toronto at Mississauga
- D. Božanić, R. Krsmanović, N. Bibić, “Vinča” Institute
Thank you for your attention!