Adsorption of sulfur onto a surface of silver nanoparticles stabilized with sago starch biopolymer

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Abstract
Adsorption of sulfide ions onto a surface of starch capped silver nanoparticles upon addition of thiourea was investigated. UV–vis absorption spectroscopy revealed that the adsorption of the sulfide ion on the surface of the silver nanoparticles induced damping as well as blue shift of the silver surface plasmon resonance band. Further increase in thiourea concentration led to shift of the resonance band toward higher wavelengths indicating the formation of the continuous Ag2S layer on the silver surface. Thus fabricated nanoparticles were investigated using electron microscopy techniques (TEM, HRTEM, and HAADF-STEM) and X-ray photoelectron spectroscopy (XPS), which confirmed their core–shell structure.

1. Introduction

In the last decades, there has been considerable interest in the fabrication of nanocomposite structures that comprise metal or semiconductor nanoparticles and polymers. This has become an important area of the composite research, not only because of the fundamental properties of the nanocomposites but also because of the wide range of their possible applications [1–3]. It is well known that inorganic nanoparticles often show characteristic electronic, optical and other properties, different from those of the bulk phase. These properties can be successfully utilized by incorporation of the nanoparticles (either in situ or ex situ methods) into polymer matrices, since a polymer can be easily designed into almost any shape required by a particular application. Moreover, in an in situ preparation method, a polymer matrix can also act as the controlled environment for the growth of the nanoparticles.

Recently, biopolymers, such as chitosan [4–7], alginate [8–11] and starch [12–24] have been introduced as capping agents and/or matrices for semiconductor, metal and semiconductor–semiconductor core–shell nanoparticles. Because macromolecular chains of these biopolymers possess a large number of hydroxyl groups, they can complex well with metal ions, which further enables a good control of size, shape and dispersion of the nanoparticles formed. In a preceding study, Ag and Ag2S nanoparticles were synthesized in the presence of a sago starch biopolymer [16]. Sago starch proved to be a good choice as a host material, since it could be used as a capping agent for the nanoparticles in solution and as a matrix for the solid nanocomposite. It was also shown that the obtained silver-starch nanocomposite can be potentially used as a material with antimicrobial activity. On the other hand, the application of silver as an antimicrobial material is governed by its strong affinity towards sulfur, i.e. by its interaction with sulfur containing functional groups from membrane-bound enzymes [25]. For this reason, in the present paper we decided to combine previously introduced methods for preparation of Ag and Ag2S nanoparticles in the starch matrix in order to study the adsorption of sulfide ion onto a surface of silver nanoparticles. We believe that this approach can mimic to a certain extent the processes that could take place when the biopolymer capped silver nanoparticles are in the presence of the sulfur rich medium (such as a living cell).

The adsorption of the sulfide ion was monitored by UV–vis spectroscopy. The adsorption finally results in formation of a continuous Ag2S layer and detailed microscopic investigations were performed on Ag–Ag2S core–shell nanoparticles obtained in this...
way. Also, oxidation of silver (i.e., formation of Ag⁺ ion) by the interaction with sulfur can induce the shift in the binding energies and this effect was studied by using X-ray photoelectron spectroscopy (XPS). XPS is a perfect tool for investigation of these processes and it can provide additional information about the sulfur adsorption. The other aspect of the particles properties that will be also studied is the dependence of the position of the silver surface plasmon band on the thickness of the Ag₂S absorbing shell layer.

2. Materials and methods

2.1. Materials

A commercial sample of sago starch was used in this study. It has an average particle size of 32 μm, amylose content of 27% and natural moisture content of 12.5%. Silver nitrate, thioacetamide and sodium borohydride were supplied by Sigma–Aldrich and used as received.

2.2. Adsorption of sulfide ions on the surface of the sago starch capped silver nanoparticles

Silver capped sago starch nanoparticles were prepared using the reported procedure [16]. Silver nitrate (0.195 mmol) was added to a hot aqueous solution of sago starch (0.25 g of sago in 25 ml of water). After stirring for 5 min, 0.195 mmol of sodium borohydride was added and boiled for another 5 min. For the investigation of the adsorption of sulfide ions on the surface of the Ag nanoparticles, thioacetamide was used as an ion source. The procedure was carried out in such way that the reduction of silver salt to the metallic state using sodium borohydride was immediately followed by interaction of the obtained nanoparticles with sulfur. Throughout the procedure, the concentration of the AgNO₃ was kept constant (0.195 mmol) while the concentration of thioacetamide was varied. The formation of the adsorbed layer was followed via UV–vis spectroscopy. Table 1 outlines the denotation of the samples and the preparation conditions. For the structural and morphological analysis the S-CS5 sample was used. A nanocomposite film of this sample, dark red in color, was obtained after evaporation of the solvent.

2.3. Characterisation

UV–vis absorption spectra of the composite samples dissolved in water were obtained by using a Perkin Elmer Lambda 5 UV–vis spectrophotometer.

Transmission electron microscopy (TEM) analysis was performed on a Philips CM20 microscope, operating at 200 kV. High resolution transmission electron microscopy (HRTEM) observations were made on a JEOL 4000EX microscope. Scanning transmission electron microscopy (STEM) experiments were performed on a JEOL 3000F microscope collecting the high angle annular dark field (HAADF) signal. For TEM experiments, the samples were prepared by grinding small pieces of polymer nanocomposite with a small quantity of ethanol. For HRTEM and STEM specimens were prepared using a different procedure—the polymer matrix was dissolved in hot water, mixed with ethanol, and a few drops of the solution were deposited on to a TEM grid.

X-ray diffraction (XRD) measurements were performed on a Philips PW1050 X-ray diffractometer (Cu Kα₁ radiation, λ = 0.154 nm).

X-ray photoelectron spectroscopy (XPS) experiments were performed on a Physical Electronics Quantum 2000 instrument using Al Kα radiation (1486.6 eV). Prior to the analysis, the S-CS5 sample was sputtered using a 2 keV argon ion beam. The C 1s, O 1s, Ag 3d, S 2p, core levels were recorded at 29.35 eV pass energy and at 55° take-off angle. The peak shift due to charge accumulation was corrected using the C 1s level at 284.4 eV as an internal standard [26]. The XPS peaks are assumed to be linear combinations of Lorentzian and Gaussian line shapes and were resolved into individual components after proper subtraction of the baseline using the Shirley background subtraction method.

3. Results and discussion

3.1. Optical properties

Fig. 1a shows the change in the UV–vis spectra with adsorption of sulfur ions onto silver nanoparticles in the presence of the sago starch. Initially, the surface plasmon resonance (SPR) band of starch capped silver nanoparticles in water is located at 398 nm [16]. The introduction of thiourea into the solution induces a strong damping and broadening of the plasmon band which eventually, after formation of the pure Ag₂S nanoparticles, disappears. At low concentrations of thiourea, the band slightly blue shifts, which is the result of an increase in the electron density of the silver due to chemisorption of sulfur [27]. With a further increase in thiourea concentration (starting from the S-CS4 sample), a shift of the SPR band towards higher wavelengths takes place (Fig. 1a). The observed red shift is a result of the formation of the continuous Ag₂S layer on the nanoparticle surface [28]. For this reason, we have chosen sample S-CS5 for our structural investigation. Concerning the observed damping of the SPR bands, it is mainly a consequence of the charge transfer between the adsorbed sulfur ions and silver surface [29] as well as of the overall reduction of the nanoparticles surface area. The more pronounced damping noticed at higher thiourea concentration can be related to the presence of the absorbing silver sulfide shell [30].

In order to illustrate this, we have calculated a series of extinction cross-section curves presented in Fig. 1b. In this figure, curve 1 represents an extinction cross-section of the silver nanoparticles in water capped with the starch layer of volume fraction g = 0.68 calculated previously in Ref. [16]. The influence of adsorbed sulfur on the SPR bands of silver nanoparticles was introduced in the calculations (curves 2–4) both via the increase in relative electron density of silver δn and the phenomenological parameter A that describes size and interface effects in the light scattering process [29]. The corresponding silver bands were calculated by Mie theory extinction cross-section [30]:

\[ C_{ext}(\omega) = \frac{12\pi^3\varepsilon_m^{3/2}}{c} \frac{\omega}{(\Re \varepsilon(\omega) + 2\varepsilon_m)^2 + (\Im \varepsilon(\omega))^2} \times (1 + \delta n), \]  \hspace{1cm} (1)

using modified, Drude-like, dielectric function of silver,

\[ \varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_P^2}{\omega^2 + i\omega\Gamma}, \]  \hspace{1cm} (2)

In the preceding relations, \( \omega \) and \( c \) are the frequency and the velocity of the incident light, \( \varepsilon_m \) is the dielectric constant of the medium, \( \Gamma \) is the size dependent damping frequency and \( \omega_p \) is

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starch (g)</th>
<th>AgNO₃ (mmol)</th>
<th>Thioacetamide (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-Ag</td>
<td>0.25</td>
<td>0.195</td>
<td>0</td>
</tr>
<tr>
<td>S-CS1</td>
<td>0.25</td>
<td>0.195</td>
<td>0.003</td>
</tr>
<tr>
<td>S-CS2</td>
<td>0.25</td>
<td>0.195</td>
<td>0.0055</td>
</tr>
<tr>
<td>S-CS3</td>
<td>0.25</td>
<td>0.195</td>
<td>0.008</td>
</tr>
<tr>
<td>S-CS4</td>
<td>0.25</td>
<td>0.195</td>
<td>0.0105</td>
</tr>
<tr>
<td>S-CS5</td>
<td>0.25</td>
<td>0.195</td>
<td>0.016</td>
</tr>
<tr>
<td>S-CS6</td>
<td>0.25</td>
<td>0.195</td>
<td>0.0215</td>
</tr>
<tr>
<td>S-Ag₂S</td>
<td>0.25</td>
<td>0.195</td>
<td>0.195</td>
</tr>
</tbody>
</table>
the bulk plasmon frequency of silver. The size dependent damping frequency was estimated from the relation,

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

where \( r \) is the radius of the nanoparticle, \( \Gamma_0 \) is the bulk damping frequency, \( v_f \) is the Fermi velocity and \( A \) is the constant that includes details of the scattering process typically of the order of 1. An additional factor \((1 + \bar{n})\) in Eq. (2) was introduced assuming that the chemisorption of sulfur leads to an increase in electron density \( \bar{n} \) and, thus, to an increase in a bulk plasmon frequency of silver \( \omega_p \) or, accordingly,

\[ \omega_p = \sqrt{\frac{\varepsilon_0 \varepsilon_r}{m_e}} \sqrt{(N + \Delta N)} \frac{e^2}{m_e} = \omega_p \sqrt{1 + \frac{\Delta N}{N}} \]

where \( m \) is the electron mass, \( \varepsilon_0 \) is the dielectric constant of silver for \( \omega \to 0 \), and \( \Delta N \) is the change in the number of electrons. In the calculations of the extinction cross-section the following parameters were used [31]: the silver bulk plasmon frequency \( \omega_p = 9.5 \text{eV} \), the damping frequency \( \Gamma_0 = 0.0987 \text{eV} \), the Fermi velocity \( v_f = 1.4 \times 10^6 \text{ms}^{-1} \) and the contribution of the vacuum and interband electronic transitions \( \varepsilon_\infty = 5 \). For these parameter values, the best agreement between the Drude dielectric function and corresponding experimental values [32] of bulk silver was found. Finally, the dielectric constant of the medium was estimated from the relation \( \varepsilon_m \approx \varepsilon + \frac{g(\varepsilon - \kappa)}{3} \) [16], where \( \varepsilon = 1.78 \) and \( \varepsilon_s = 2.34 \) are dielectric constants of water and starch, respectively. According to the performed calculations, we estimated that the adsorption of sulfur onto a silver surface results in an increase in electron density, \( \bar{n} \), of approximately 1.5%.

Curves 5–7 were calculated using extinction cross-sections for coated spheres [30]:

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

where \( k = 2\pi /\lambda \) is the wave vector of the incident light and the Mie scattering coefficients \( a_n \) and \( b_n \) are complex expressions of Riccati–Bessel functions (see Appendix A for details). Since \( \text{Ag}_2\text{S} \) absorbs light in the investigated wavelength range (Fig. 1a), in this procedure the values of complex dielectric function of silver sulfide at particular wavelengths were obtained from the experimental values of the optical constants of a 38.3 nm thick \( \text{Ag}_2\text{S} \) film [33]. The thickness of the \( \text{Ag}_2\text{S} \) shell, \( r_s \), was introduced in the calculations through the ratio of the radii of the core \( (r_1) \) and core–shell \( (r_2 = r_1 + r_s) \) nanoparticle, \( \rho = r_1/r_2 \). With increasing thioacetamide concentrations the silver plasmon band red shifts indicating an increase in thickness of the \( \text{Ag}_2\text{S} \) layer. In the case of S-CS5 sample, which was further investigated by electron microscopy techniques, the peak position at 410 nm corresponds to \( \rho = 0.9 \).

Fig. 1. (a) UV–vis absorbance spectra of the aqueous solution of starch capped Ag (dotted line), Ag–Ag–S nanoparticles (solid line): (1) S-Ag; (2) S-CS1; (3) S-CS2; (4) S-CS3; (5) S-CS4; (6) S-CS5; (7) S-CS6; (8) S-Ag–S. (b) Extinction spectra (1) of starch capped silver nanoparticles in water [16], (2–4) of silver nanoparticles with adsorbed sulfur calculated by using Eq. (1), and (5–7) of core–shell Ag–Ag–S nanoparticles calculated by using Eq. (5).

Fig. 2. XRD spectra of S-Ag, S-CS3, S-CS5, and S-Ag–S nanocomposite films.
3.2. Structural and morphological analysis

XRD spectra of S-Ag, S-CS3, S-CS5 and S-Ag$_2$S samples are shown in Fig. 2. Samples S-Ag and S-Ag$_2$S show typical XRD spectra of cubic Fm$ar{3}$m silver [34] and monoclinic $P2_1/c$ Ag$_2$S [35], respectively. Also, the spectrum of the S-CS3 sample is similar to that of a pure Ag-starch nanocomposite. On the other hand, the S-CS5 sample obviously shows a mixture of both crystal phases where the intensity of the monoclinic Ag$_2$S peaks increases with an increasing the amount of added thioacetamide. The broad peak observed at low angles in the spectra of all four materials is attributed to the sago starch.

A TEM micrograph of the S-CS5 sample is shown in Fig. 3. The Ag–Ag$_2$S nanoparticles are relatively well dispersed in the starch matrix with an average diameter of about 30 nm. The images of a few selected particles were enlarged and shown as insets in Fig. 3. An HRTEM image of a single core–shell nanoparticle is presented in Fig. 4. The surface of the nanoparticle shows crystal
in the interior of the specimen. Since the probability of elastic scattering is proportional to Z^n (where Z is the atomic number and 1 < n < 2), the heavier atoms will scatter more electrons than the lighter atoms and the fractional scattering outside a given angle will increase with Z. The large Z-difference between core and shell is clearly visible in the HAADF images. In Fig. 5 the bright contrast in the interior of the nanoparticles indicates the presence of silver, whereas the lower contrast of the outer shells suggests the presence of the lighter elements such as sulfur.

X-ray photoelectron spectroscopy, which is highly sensitive to the chemical composition and the environments of the elements in the material, was additionally used to study the core–shell nanoparticles in the starch matrix. XPS proved to be a suitable technique for the investigation of the surface composition of the core–shell nanoparticles [36], polymer capped metal nanoparticles [37] and semiconductor nanoparticles in polymer matrices [38]. The initially performed XPS survey scan of the S-CS5 sample revealed the presence of C 1s, O 1s, S 2p, and Ag 3d core levels. The Ag 3d and S 2p spectral regions are shown in Fig. 6. The Ag 3d region of the bulk silver is characterized by two lines, which are the consequence of spin orbital splitting and correspond to Ag 3d_{3/2} and Ag 3d_{5/2} core levels [37]. The same two lines are observed in the Ag 3d region of the S-CS5 sample (Fig. 6a) but each of them can be resolved into another two lines. For the Ag 3d_{3/2} core level, the first line, located at 368.3 eV, corresponds to Ag 3d_{3/2} binding energy of metallic silver [26], while the second line is shifted towards lower energies (367.8 eV) and indicates the presence of Ag⁺ [36,38]. Concerning the S 2p core levels (Fig. 6b), it can be noticed that the majority of the sulfur is in the Ag₂S state at 162 eV. A spectral line that originates from oxidized sulfur (probably SO₄²⁻) is also present at higher energies (~168 eV). The obtained results for the S-CS5 sample imply the presence of both, metallic silver and oxidized silver in the form of Ag₂S.

In Fig. 7, Ag 3d and S 2p spectral regions of the nanocomposite with pure Ag₂S nanoparticles (S-Ag₂S sample) are shown. As can be seen (Fig. 7a), the Ag 3d_{3/2} level is represented as a single peak at 367.8 eV which means that all of the silver is in the Ag⁺ state. We tried to resolve this line into two peaks, as in the case of the Ag 3d_{3/2} line of the S-CS5 sample, but a significantly poorer fit was obtained and, which is even more illustrative, both lines were shifted towards lower energies with respect to the Ag 3d_{3/2} binding energy of Ag₀ silver (368.3 eV). This also suggests that the line resolved at 368.3 eV in Fig. 6a can be related to the silver core. The S 2p spectrum in Fig. 7b of the S-Ag₂S sample is similar to the spectrum of the S-CS5 sample (Fig. 6b). These results are in agreement with the S 2p core level spectra of PbS-polymer nanocomposites reported recently by Asunskis and Hanley [38].

4. Conclusions

The adsorption of sulfur onto a surface of the Ag nanoparticles was followed via UV–vis spectroscopy. The introduction of thioacetamide in the synthesis procedure induced a strong damping and the blue shift of the plasmon band as an indication of the sulfur absorption on a surface of silver nanoparticles. At higher thioacetamide concentrations additional red shift was observed due to formation of a continuous Ag₂S shell layer. The influence of the thickness of the Ag₂S absorbing shell layer on the silver surface plasmon band is discussed in terms of the Mie theory. The silver nanoparticles with a shell layer were investigated by TEM, HRTEM, and HAADF-STEM techniques. XPS measurements prove that the obtained nanoparticles have a hybrid structure, since the Ag 3d_{3/2} level could be resolved into two lines from which the first corresponds to metallic silver (Ag₀) and the second to Ag⁺. The XPS spectrum of the S 2p level, on the other hand, shows that the majority of the sulfur is in the S²⁻ state, confirming that the shell layer is indeed Ag₂S.

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Appendix A

The extinction cross-section, $C_{ext}$, of a single spherical core–shell particle of radius $r_2$ with core radius $r_1 = r_2 (\rho < 1)$ is given by Eq. (5). Mie scattering coefficients $a_n$ and $b_n$ used in calculation of $C_{ext}$ have the following form:

$$a_n = \frac{\varphi_n(m_2 y) - A_n \psi_n(m_2 y)}{\varphi_n(m_2 y) - A_n \psi_n(m_2 y)} - \frac{B_n \varphi_n(m_2 y)}{\varphi_n(m_2 y) - A_n \psi_n(m_2 y)}$$  \hfill (A1 a)

$$b_n = \frac{m_2 \varphi_n(m_2 y) - B_n \psi_n(m_2 y)}{\varphi_n(m_2 y) - A_n \psi_n(m_2 y)} - \frac{m_2 \psi_n(m_2 y) - B_n \psi_n(m_2 y)}{\varphi_n(m_2 y) - A_n \psi_n(m_2 y)}$$  \hfill (A1 b)

where

$$A_n = \frac{m_2 \varphi_n(m_2 y) \psi_n(m_1 y) - m_1 \psi_n(m_2 y) \psi_n(m_1 y)}{m_2 \varphi_n(m_2 y) \psi_n(m_1 y) - m_1 \psi_n(m_2 y) \psi_n(m_1 y)}$$ \hfill (A2 a)

$$B_n = \frac{m_2 \psi_n(m_2 y) \psi_n(m_1 y) - m_1 \psi_n(m_2 y) \psi_n(m_1 y)}{m_2 \psi_n(m_2 y) \psi_n(m_1 y) - m_1 \psi_n(m_2 y) \psi_n(m_1 y)}$$  \hfill (A2 b)

Riccati–Bessel functions $\psi_n$ and $\chi_n$ are by definition $\psi_n(z) = \frac{\varphi_n(z)}{\epsilon_n}$ and $\chi_n(z) = -2y_n(z)$, where $J_n$ and $Y_n$ are spherical Bessel functions of first and second kind [39], respectively and $\epsilon_n = \sqrt{\epsilon_1 \epsilon_2}$. The argument variables $m_1$, $m_2$, $x$, and $y$ in the preceding relations are

$$m_1 = \sqrt{\epsilon_1 / \epsilon_m}, m_2 = \sqrt{\epsilon_2 / \epsilon_m}, x = \sqrt{\epsilon_1} k r_1, \quad \text{and} \quad y = \sqrt{\epsilon_2} k r_2,$$

where $\epsilon_1(x)$ and $\epsilon_2(x)$ are complex dielectric functions of the core and the shell.

References


V. Djoković et al. / Colloids and Surfaces B: Biointerfaces 73 (2009) 30–35