

Systematic circular dichroism study of systems containing cysteine and silver nanoparticles

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Abstract

Mixtures containing silver nanoparticles (~45 nm) prepared by citrate reduction of AgNO₃ and cysteine were prepared. Influences of cysteine concentration, mixture pH, and time on the circular dichroism spectra were studied. The mixtures were also analyzed by absorption spectroscopy in UV–Vis range and by surface-enhanced Raman scattering. The results showed interesting behavior of circular dichroism spectra and surface-enhanced Raman scattering spectra.

Introduction

The behavior of nanoparticles in the presence of chiral compounds is in the field of interest of several scientists due to possible application in heterogeneous catalysis [1], material science [2], development of chemical sensors [3], and nanocatalysis [4]. The first such chiral system was described by Shaaf et al. in 1998 for glutathione modified gold nanoparticles [5]. Several years later Choi et al. described electronic circular dichroism (ECD) of silver nanoparticles (AgNPs) 6.4 nm in diameter in the presence of L-cysteine and D-cysteine [6].

Here we report a systematic circular dichroism study of systems containing cysteine and silver nanoparticles. This work is a detailed study of our previous preliminary results [7].

Results and discussion

Characterization of prepared AgNPs showed that nanoparticles have different shape and size (Fig. 1A) with average size of 45 nm. The wavelength of surface plasmon absorbance (415 nm, Fig. 1B) corresponds to the average diameter estimated by TEM [8].

The immobilization of cysteine on the AgNPs was proved by surface-enhanced Raman scattering (SERS) spectra of systems containing AgNPs and cysteine. Bands in Raman spectrum of pure cysteine (Fig. 2A) corresponds to SERS spectrum of AgNPs in the presence of cysteine (Fig. 2B). Control experiment with only AgNPs (Fig. 2C) showed different bands in SERS spectrum.

Moreover, we were able to detect the presence of cysteine even in a concentration of $5 \cdot 10^{-9}$ mol L⁻¹ (Fig. 2D), although in this spectrum are also bands corresponding to citrate that stabilize surface of AgNPs.

For a concentration study AgNPs were diluted eight times in order to obtain values of absorbance at the wavelength of surface plasmon absorbance (415 nm) where Lambert-Beer law still holds true, i.e. values around 1 (for 1-cm cuvette).

To the diluted AgNPs solutions concentrated aqueous solutions of L- and D-cysteine were added resulting in mixtures with different concentrations of L- and D-cysteine (10^{-6} , $5 \cdot 10^{-5}$, 10^{-5} , $5 \cdot 10^{-5}$, 10^{-4} , $5 \cdot 10^{-4}$, 10^{-3} , $5 \cdot 10^{-3}$, and 10^{-2} mol L⁻¹). After incubation overnight UV-Vis and ECD (Fig. 3 and 4) spectra were measured.

With increasing concentration of cysteine in the solution the absorbances of surface plasmon band slightly decrease and aggregation occurred in the presence of high concentrations of cysteine, as can be seen from the presence of a new band at 700 nm. This observation is similar to the results published before for gold nanoparticles [9].

In the case of ECD spectra the situation is more complicated due to several contributions that form the resulting spectrum. The spectral region below 250 nm corresponds to dissolved cysteine only (i.e. not bonded to AgNPs surface) [10] and the signal in this region increases with increasing cysteine concentration (Fig. 3 and 4). In the region above 250 nm the signal comes from chemisorption of cysteine on AgNPs [10] and this signal has a maximum for 10^{-4} mol L⁻¹ cysteine concentration for both enantiomers (Fig. 3 and 4).

Acknowledgment

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References

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Figures

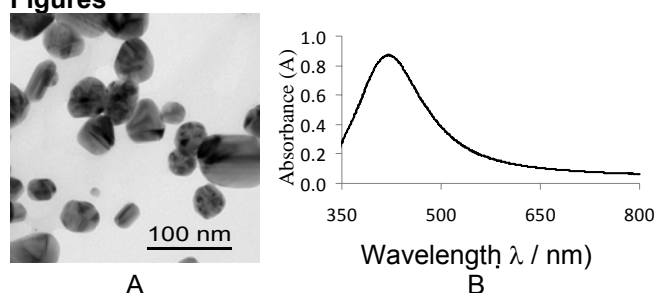


Fig. 1 TEM image (A) and UV-Vis spectrum (B) of AgNPs.

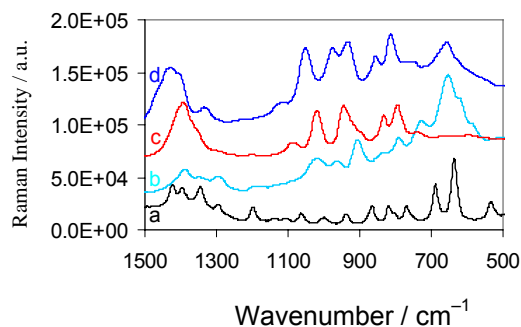


Fig. 2 Raman spectrum of L-cysteine (a), SERS spectrum of silver nanoparticles in the presence of L-cysteine ($c = 1.10 \cdot 10^{-4} \text{ mol L}^{-1}$) (b), SERS spectrum of silver nanoparticles (c), SERS spectrum of silver nanoparticles in the presence of L-cysteine ($c = 5.10 \cdot 10^{-9} \text{ mol L}^{-1}$) (d).

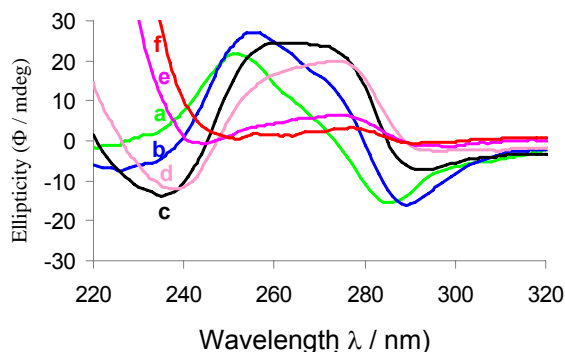


Fig. 3 ECD spectra of AgNPs with various concentrations (mol L^{-1} ; a: $5.10 \cdot 10^{-5}$; b: 10^{-4} ; c: $5.10 \cdot 10^{-4}$; d: 10^{-3} ; e: $5.10 \cdot 10^{-3}$; f: 10^{-2}) of L-cysteine.

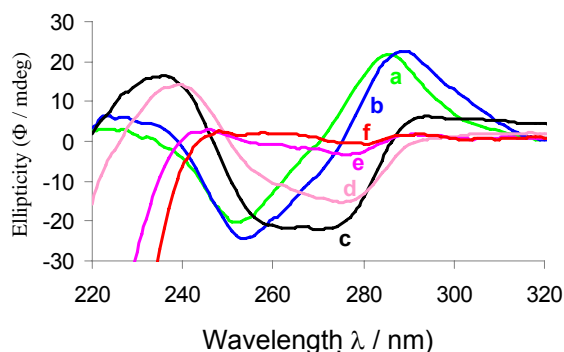


Fig. 4 ECD spectra of AgNPs with various concentrations (mol L^{-1} ; a: $5.10 \cdot 10^{-5}$; b: 10^{-4} ; c: $5.10 \cdot 10^{-4}$; d: 10^{-3} ; e: $5.10 \cdot 10^{-3}$; f: 10^{-2}) of D-cysteine.