



Chiral supramolecular nanoparticles: The study of chiral surface modification of silver nanoparticles by cysteine and its derivatives



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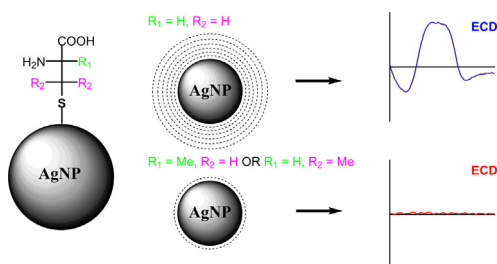
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HIGHLIGHTS

- Cysteine, penicillamine, α -methylcystein immobilization on nanoparticles was proved.
- Different nanoparticles have similar optical activity in the presence of cysteine.
- Chiral ECD bands are provided only in the presence of cysteine.
- Adsorbed cysteine derivatives molecules are lesser than cysteine molecules.
- 3D supramolecular structure of adsorbed molecules is needed to origin of ECD signal.

GRAPHICAL ABSTRACT



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ABSTRACT

Many studies dealing with modified nanoparticles are based on the assumption that organic molecules form single-layer structure on their surface. In this work, we suggest a novel approach to study the important phenomenon of supramolecular chirality at metal nanoparticle surfaces. Self-assembly layers of several ligands, namely L-cysteine, L-penicillamine and α -methyl-L-cysteine, on different silver nanoparticles were studied by means of absorption and electronic circular dichroism spectroscopy in UV–vis range and surface enhanced Raman scattering spectroscopy. The amount of ligands bonded to the surface of nanoparticles was quantified by absorption spectroscopy. Quantification was performed indirectly by measuring concentration of free ligands in solution after incubation with absorption labels 4-toluenesulfonyl chloride or 1-fluoro-2,4-dinitrobenzene. Data were obtained for ligands at concentration levels from 10^{-6} to 10^{-3} mol L⁻¹. The results showed the significantly lower adsorbed molecules of methyl derivatives of cysteine than for cysteine themselves. This fact could explain the unexpected behavior of silver nanoparticles that provide ECD bands in the presence of cysteine and not in the presence of its derivatives.

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1. Introduction

Nanoparticles (NP) are nowadays frequently discussed topic in many scientific disciplines. A considerable attention has been devoted to the optical activity or chirality of nanoparticles [1–3],

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noble metals nanoparticles particularly [4,5]. This property is usually measured on rather complicated systems of metal nanoparticles and organic ligands adsorbed on the surface and few mechanism of optical activity origin were proposed [6,7]. In general, optical activity of nanoparticles may arise from the cluster itself (inherent chirality) or ligands adsorbed on the surface of the particles (chirality of adsorbates or supramolecular chiral pattern of adsorbed molecules) [8–11]. Both of these major mechanisms were described in literature before and it is also possible to find out more detailed insight into origin of nanoparticles optical activity – for example dipole interactions between molecules and nanoparticles [12]. A crystal structure of an inherent chiral gold cluster was published recently [13,14]. Chirality resulting from ligands shell can be obtained in systems either of well-defined composition with diameter close to or below 2 nm [15,16] or with larger nanoparticles diameter and broader size distribution of nanoparticles [17,18]. Optical activity of such systems is mostly demonstrated on gold or silver NP modified by thiol ligands [19,20]. Supramolecular optically active assemblies of nanoparticles on suitable carriers have been also discussed in the literature [21–25].

Circular dichroism (CD) spectroscopy is commonly used to study conformation states of peptides or proteins such as α -helix, β -sheet, etc. Changes in conformation itself or representation of conformation states are easily detectable. It is also possible to measure other assemblies of optical active molecules and this makes CD spectroscopy powerful technique for detecting optical activity of nanoparticles. The difference between molecular and surface plasmon resonance optical activity can also be distinguished based on the energy of circular dichroism [26].

Measurements of nanoparticles chirality could provide important information about molecular orientation [27] and interface effects. This is interesting especially due to practical applications for example in heterogeneous enantioselective catalysis [28].

In the past, it has been shown that modification of silver NP by cysteine provides strong CD signals. This effect is commonly explained by supramolecular pattern of molecules due to mutual H-bond network on the surface [29]. In typical studies, authors presume that molecules form single layer on the surface [30]. In this work, we suggest a novel approach to study this phenomenon of supramolecular chirality and extend the previously published thesis, which discussed circular dichroism of large (45 nm) silver NP modified by chiral ligands [18,31]. To our best knowledge, there are not reports so far focused on the influence of the amount of molecules bonded on the nanoparticles on circular dichroism spectra.

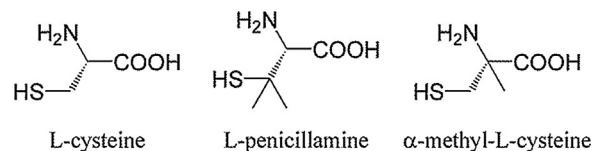


Fig. 1. Structures of the investigated compounds.

2. Experimental

2.1. Chemicals and materials

Sodium carbonate monohydrate, L-cysteine (Fig. 1), silver nitrate, 1-fluoro-2,4-dinitrobenzene, 4-toluensulfonyl chloride, sodium borohydride, trisodium citrate, and L-penicillamine (Fig. 1) (all Sigma–Aldrich, St. Louis, MO, USA), and ultrapure water (Milli-Q grade, Merck Millipore, Billerica, MA, USA). α -Methyl-L-cysteine (Fig. 1) was prepared according previously published procedure [32].

2.2. Equipment

Transmission electron microscopy (TEM, JEOL JEM-3010 microscope, Japan), UV–vis absorption spectroscopy (Varian Cary 400 SCAN UV-Vis spectrophotometer, Varian, USA), Raman spectroscopy (Raman NIR Advantage spectrometer DeltaNu with laser excitation line 785 nm, power 100 mW in the range of 100–2000 cm^{-1} with mean spectral resolution ca. 4 cm^{-1} ; integration time was 15 s and results spectra are average of five repetitive measurements), and electronic circular dichroism spectroscopy (ECD, J-850, Jasco, Japan) were used.

2.3. Synthesis of silver nanoparticles

Two types of silver nanoparticles were prepared. They differed in diameter, size distribution and optical parameters. First type of nanoparticles was prepared by citrate reduction of silver nitrate and it is indicated below as AgNPC. Second type was prepared by borohydride reduction and it is indicated below as AgNPB. The synthesis of AgNPC was described previously [31]. Shortly, to 100 mL of boiling water (under reflux) 1 mL of aqueous solution of silver nitrate (9.3 mg, 54.7 μmol) and 1 mL of 1% aqueous solution of the trisodium citrate dihydrate (10 mg, 34.0 μmol) were added. Heating was continued for 20 min during which time the solution had changed color from colorless to brown-yellow. After that the reaction vessel was allowed to cool down to the room temperature.

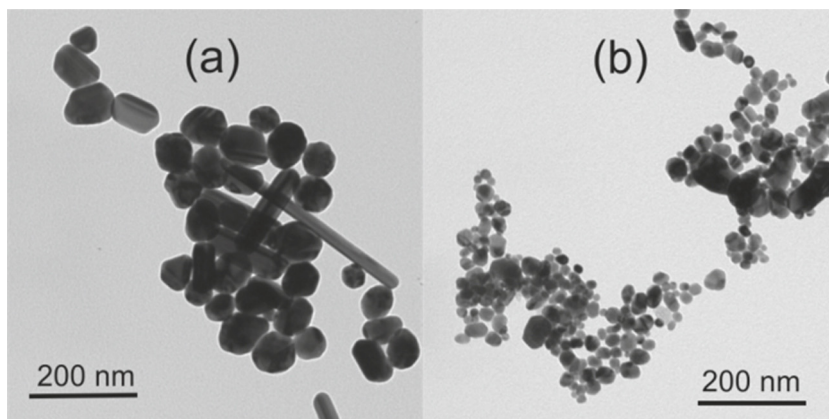


Fig. 2. TEM images of (a) AgNPC and (b) AgNPB.

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