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Enantioselective silver nanoclusters: Preparation, characterization and photoluminescence spectroscopy

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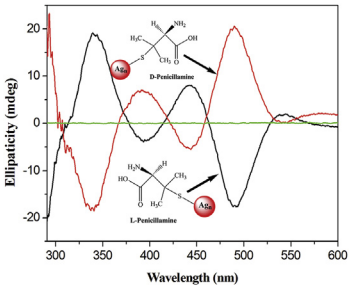
HIGHLIGHTS

- New wet chemistry method to prepare mirror image small silver clusters protected by penicillamine.
- Preparation enantioselective catalysts by easy wet chemistry method.
- The synthesized silver clusters have photoluminescence properties.
- The synthesized silver clusters show high Anisotropy factors up to 3×10^{-4}.
- The adsorption isotherms of all synthesized clusters are mainly of type II of Brunaue's classification.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report a new wet-synthesis method to separate some water-soluble chiral silver nanoclusters with high yield. The cluster material was obtained by the reduction of silver nitrate with $NaBH_4$ in the presence of three ligands L-penicillamine (L-pen), D-penicillamine (D-pen) and racemic mixture of penicillamine (rac-pen), functioning as capping ligand. For characterizing all silver cluster samples, the particle size was assessed by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) and their average chemical formula was determined from thermogravimetric analysis (TGA) and elemental analysis (EA). The particles sizes of all three clusters are 2.1 ± 0.2 nm. The optical properties of the samples were studied by four different methods: UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), photoluminescence spectroscopy (PL) and circular dichroism (CD) spectroscopy. The spectra are dominated by the typical and intense plasmon peak at 486 nm accompanied by a small shoulder at 540 nm. Infrared spectroscopy was measured for the free ligand and protected silver nanoclusters, where the disappearance of the S-H vibrational band (2535 $-2570\ cm^{-1}$) in the silver nanoclusters confirmed anchoring of ligand to the cluster surface through the sulfur atom. PL studies yielded the fluorescent properties of the samples. The main focus of this work, however, lies in the chirality of the particles. For all silver clusters CD spectra were recorded. While for clusters capped with one of the two enantiomers (D- or L-form) typical CD spectra were observed, no significant signals were detected for a racemic ligand mixture. Furthermore, silver clusters show quite large asymmetry factors (up to 3×10^{-4}) in comparison to most other ligand protected clusters. These large factors and bands in the visible range of the spectrum suggest a strong chiral induction from the ligand to the metal core. Textural features of the prepared silver nanoclusters were investigated using nitrogen adsorption-desorption at $-196\ ^{\circ}C$. Specific surface area S_{BET}, pore volume and average pore diameter were calculated.

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1. Introduction

Monolayer-protected nanoclusters (MPNCs) of noble metals (Au and Ag) have gained much attention in the last decade due to their physicochemical properties [1–7] and possible applicability in enantioselective catalysis [1], enantioseparation [2], material science, energy technology, biology, and medicine [3–5], as well as materials for liquid crystal displays [6], and optoelectronics [7].

Chiroptical properties in thiolate-protected metal clusters were first observed by Whetten and co-workers in 1998 by studying gold nanoclusters protected by L-glutathione (L-GSH) [8]. After purification of the clusters, CD spectra were recorded and Cotton effects were observed for transitions at higher wavelengths than that of the free glutathione ligand. The circular dichroism (CD) spectroscopy measures the difference between the absorbance for left- and right-handed light and a non-zero CD signal is detected if the sample contains achiral species. In the case of clusters, chiral structures exist and therefore CD signals are observed, as well [9,10]. Circular dichroism requires not only rotation of linearly polarized light but also the presence of a discrete electronic transition in the metal core and/or of the ligand molecule of monolayer protected metal clusters. The magnitude of the CD effect for an electronic transition is directly related to the product of the electric dipole and magnetic dipole transition moments and thus is also proportional to the optical absorption. In our previous work, small silver clusters protected by glutathione as ligand show strong chiroptical activity in the electronic transitions which are metal-based across the near-infrared, visible, and near-ultraviolet regions [11], however, large silver clusters just give very weak or not even any optical activity in this region [12].

Many researchers in the last decades tried to explore the origin of chiroptical effects of clusters and several models have been discussed in the literature. It was proposed that the clusters either have intrinsically chiral cores [13,14], or that the electrons feel a dissymmetric field that is created by chiral adsorbates, without a change in the geometric lattice of clusters [15]. While the latter is predicted by theory using a particle-in-a-box model, it is believed that intrinsically chiral structures of the core result from the interaction of the chiral ligand energetically favoring one specific chiral structure of the cluster.

The optical absorption spectra of small silver Ag_n ($n = 10, 20, 35, 56, 84, 120$) clusters was calculated by time-dependent density functional theory. It was found that Ag_n cluster spectra evolve from molecular-like to plasmon-like transitions with increasing (n). Furthermore, the plasmon width increases with decreasing cluster size for typical cluster shape distributions as predicted by Mie theory [16]. A similar size-dependent behaviour was also found experimentally: Larger silver nanoclusters in the 2 nm regime generally exhibit a broad plasmon resonance peak at around 450 nm in the visible region [11,12,17]. In contrast to clusters, such nanoparticles do not exhibit molecule-like properties and develop an optical absorption band originating from surface plasmon resonances. Smaller silver clusters with only several tens of atoms (up to about 1 nm), on the other hand, exhibit molecule-like optical transitions [11]. In this case more than one absorption maximum is visible in their spectra and a strong dependence of the spectral behaviour on the number of atoms in the cluster is observed [11,12,17].

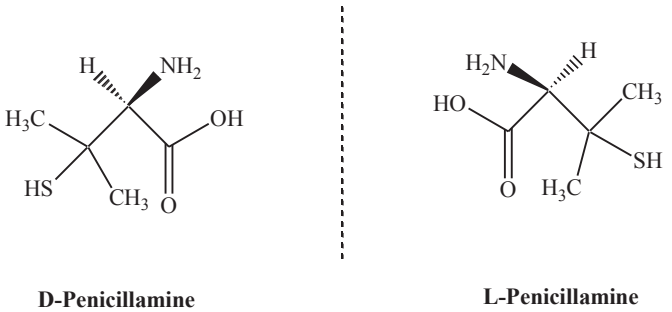
Several quantum clusters (QCs) of silver with known chemical composition have been identified by mass spectrometry such as water soluble Ag_7 [18], $Ag_{7,8}$ [19] and Ag_9 [20] as well as organic soluble Ag_{44} [21], ~Ag_{140} [22] and Ag_{152} [23]. These thiols protected silver clusters possess molecule-like behaviour in their optical properties but systematic changes in these properties were not seen due to size and structural differences in cores (such as Ag_6^{4+}, Ag_8^{6+} and Ag_{22}^{12+}) [24]. For example, while Ag_{14} is yellow emissive, Ag_{16} and Ag_{32} exhibit blue emission [24]. A toluene solution from $Ag_{152}(SCH_2CH_2Ph)_{60}$ silver clusters showed an absorption maximum at 460 nm [23]. These silver clusters exhibited photoluminescence at near-infrared (NIR) region with an emission wavelength of 800 nm, upon excitation at 375 nm. This NIR emission is attributed to the silver core [23].

The photoluminescence of metal (silver and gold) nanoparticles/clusters has become a heavily investigated research field in chemistry due to the potential applicability of metal nanoparticles/clusters as sensors [25], in biolabelling for drug delivery or for efficient energy transfer [25]. However, the origin of fluorescence is still discussed. For example, recently Wu and Jin [26] studied the fluorescence properties of Au_{25} clusters protected by several different, mostly hydrophobic, molecules to elucidate the role of the cluster's charge state and of the ligand on the photoluminescence. From this study they suggested two possible mechanisms. According to their interpretation the fluorescence either may arise from the metal core or from the interaction of the metal core and the surface ligands. In the latter case, either charge transfer through the metal-sulphur bonds, or direct donation of delocalized electrons from electron-rich groups in the ligand molecules may be responsible for the interaction of the ligands with the cluster [26].

In this study, we report on a new method for the synthesis of silver clusters protected by chiral L- and D-penicillamine (Scheme 1), as well as their racemic mixture (rac-pen). This method is purely based on wet chemistry and has an advantage of producing a high yield of the cluster material. Silver clusters are directly produced with a very narrow size distribution (2.1 ± 0.2 nm) from the synthesis method without using any purification techniques like gel electrophoresis [27]. The optical properties of enantioselective silver clusters were studied by UV-vis, circular dichroism (CD) and photoluminescence spectroscopy (PL). The size and chemical composition of synthesized monolayer protected silver clusters were assessed by transmission electron microscopy (TEM), powder X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA) and elemental analysis. The complete isotherm of the synthesized clusters were measured using nitrogen adsorption-desorption at −196 °C, specific surface area S_{BET}, pore volume and average pore diameter were calculated.

2. Experimental

In this work several cluster samples were isolated and studied. Three different types of silver clusters (**1**–**3**) were prepared by the same method, but with different enantiomeric forms of the ligand.



D-Penicillamine **L-Penicillamine**

Scheme 1. L- and D-penicillamine (L- and D-pen) used as ligands for protecting the clusters.