

Proceedings

Interaction of Colloidal Silver Nanoparticles with Ni²⁺: Sensing Application †

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Abstract: We report on synthesis of silver nanoparticles (AgNPs) capped with specific thiol suitable to detect heavy metal ions in water. The sensing mechanism is based on a change of an optical properties of the silver colloids, namely the surface plasmon resonance (SPR) when small amounts of contaminants are present in solution. We detected a specific sensitivity to nickel ions and we investigated the interaction of the AgNPs with Ni²⁺ in the concentration range of 0.5–2.0 ppm.

Keywords: silver nanoparticles; surface plasmon resonance; heavy metal ions; optical sensors; optical absorption

1. Introduction

Metal nanoparticles are widely used in several different fields, from biotechnology and biomedicine, to optics and optoelectronics, and recently also as nanosensors for air and water pollution [1–11]. These innovative materials have peculiar physical (mechanical, magnetic, optical, etc.) and chemical (reactivity, catalytic, etc.) properties that make them extremely amazing [12,13]. Among others silver nanoparticles (AgNPs) are extensively studied because of their particular properties. In fact, AgNPs have good conductivity, chemical stability, catalytic and antibacterial activity, and they are often used for surface enhanced spectroscopy (SERS), since it partly requires an electrically conducting surface [14–16]. Another peculiar property of colloidal silver nanoparticles is the optical absorption which shows an intense surface plasmon resonance (SPR). The SPR occurs upon irradiating silver nanoparticles with visible light, which causes the oscillation of free electrons in the conduction band of nanoparticles, and the position of SPR peak depends mainly on the particle size and shape. The high surface to volume ratio typical of the nanoparticles and the surface chemistry make the AgNPs extremely reactive with the external environment. All these properties allow silver nanoparticles to be used in sensing applications [17–20]. In particular, recently AgNPs were widely applied for the control of environmental pollution and, in particular, for the detection of heavy metals in water. This is becoming a topic of primary importance both for the heightened public sensitivity to the problem and for an actual worsening of this issue.

In this work, AgNPs capped with 3-mercapto-1propanesulfonic acid sodium salt (3-MPS) were synthesized by well established methods with the aim to optimize the surface functionalization in view of sensing application. In particular, AgNPs with diameter of about 6nm were used as sensing interactive materials for Ni²⁺ ion in water. The interaction was studied evaluating the influence of the Ni²⁺ concentration (0.5, 1, 2 ppm) on the SPR. The AgNPs @Ni²⁺ systems were investigated by means of Uv-vis and FTIR spectroscopies and DLS technique to verify the composition, size and dispersity.

2. Materials and Methods

3-mercapto-1propanesulfonic acid sodium salt (C₃H₇S₂O₃Na, 3MPS, SigmaAldrich, 98%), silver nitrate (AgNO₃, Sigma-Aldrich, 99.5%) and sodium borohydride (NaBH₄, Sigma-Aldrich, 98%) were used as received. Deionized water (electrical conductivity less than 1 μΩ/cm at room temperature) was obtained from a Millipore Milli-Q water purification system. AgNPs were prepared following a procedure reported elsewhere [21].

Morphological characterization has been accomplished with a Transmission Electron Microscope (TEM), model Tecnai 12 G2 Twin, FEI Company. UV-vis spectra of water suspensions were collected using a Perkin-Elmer Lambda 19 spectrophotometer. A Malvern Zetasizer Nanoseries instrument (Malvern, UK) was used to obtain the DLS measurements on the AgNPs colloidal suspensions (0.2 mg/mL) at T = 25.0 ± 0.2 °C. The average hydrodynamic radius of the diffusing objects was calculated, as reported in previous studies [22]. The ζ-potential was calculated from the measured electrophoretic mobility by means of the Smolukovsky equation [23]. Reflection Absorption Infrared Spectroscopy (RAIRS) analysis was performed by means of a VECTOR 22 (Bruker) FTIR interferometer equipped with a DTGS detector and operating in the wavenumber range 400–4000 cm⁻¹. Measurements were carried out by means of a Specac Monolayer/grazing angle accessory GS19650 operating at 70° incidence. Samples were prepared as thin films by solvent evaporation on Ti substrates from the mother solution; a clean Ti surface was used for recording the background.

AgNPs contained in a fixed volume of water was added to a fixed volume of water solution containing the Ni²⁺ ions, at specific concentration. After five minutes of interaction (ions/AgNPs), in order to allow a complete interaction, the absorption spectra were collected.

3. Results

The interaction of the Ni²⁺ ions with AgNP-3MPS, causes the modification of the shape and wavelength peak of the SPR. Figure 1a shows the normalized optical absorption spectra of the reference solution of AgNPs and AgNPs @Ni²⁺. We measured a redshift of the peak wavelength with the increasing ion concentration from 405 nm (reference) up to 433 nm for 2 ppm concentration. The data of the SPR peak wavelength as a function of concentration of the nickel are reported in Figure 1b. We measured also a broadening of the absorption band as reported in Figure 1c. The Full Width at Half Maximum (FWHM) goes from 114 nm for the reference to 160 nm for 2 ppm concentration. By measuring the FWHM of the normalized spectra, it is possible to have a qualitative idea of the broadening of the nanoparticles dimension distribution.

Ni²⁺ adsorption does not produce significant modification in the FTIR spectra (data not shown); the position of the peaks related to 3MPS is not affected. DLS measurements were carried out showing an increase of the <R_H> of the AgNPs after interaction with Ni²⁺. Figure 2 shows the dimension growth with the Ni²⁺ concentration: from 9 ± 1 nm for reference, i.e., AgNPs alone, to 10 ± 1 nm for 0.5 ppm, to 40 ± 4 nm for 1 ppm, to 1020 ± 80 nm for 2 ppm of Ni²⁺ concentration. Moreover, the ζ potential changes in presence of Ni²⁺: AgNPs showed ζ potential of -44 mV, while in presence of 2 ppm of Ni²⁺ the ζ potential becomes +4 mV, indicating an effective interaction of positive ions with NPs.

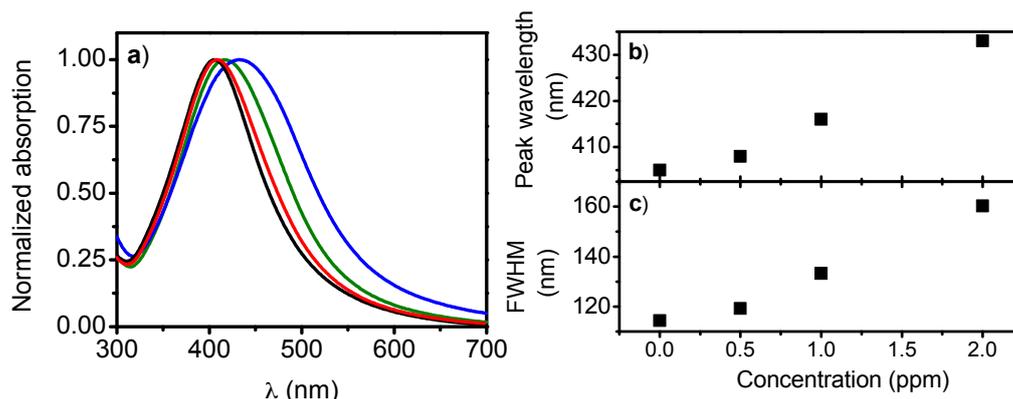


Figure 1. (a) normalized absorption spectrum of the AgNP-3MPS with tree different Ni²⁺ concentration: 2 ppm (blue), 1 pp (green), 0.5 ppm (red). The black curve is the reference. (b) trend of the maximum of the absorption peak and (c) of the FWHM booth as a function of Ni²⁺ concentration.

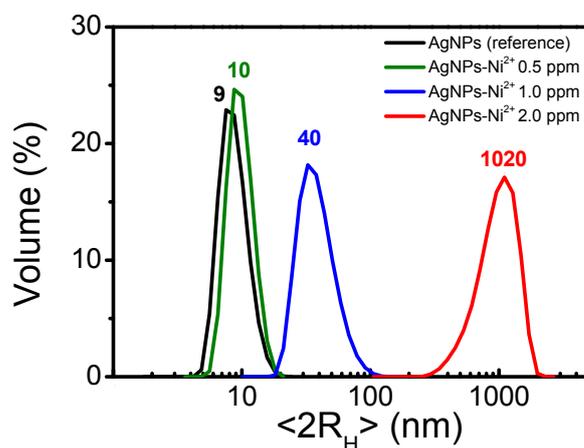


Figure 2. DLS measurements of AgNPs before and after interaction with Ni²⁺ at different concentration.

4. Discussion

The FTIR spectra remain similar before and after AgNPs interaction with Ni²⁺: the main peaks at high wavenumber are attributed to O-H (3300 cm⁻¹) and C-H (2800–2900 cm⁻¹) stretching, the latter due to the aliphatic chain of 3MPS; a peak at 750 cm⁻¹ is also related to rocking vibration of the methylene groups of 3MPS. The peak at 1350 cm⁻¹ could be attributed to S=O stretching of the sulphonate groups of 3MPS. The UV-vis and DLS measurements confirmed the hypothesis of aggregation of AgNPs in presence of Ni²⁺: showing the increment of hydrodynamic radius from 9 nm for AgNPs alone, up to 1020 nm for 2 ppm of Ni²⁺.

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Conflicts of Interest: The authors declare no conflict of interest.

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