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Detection of Toxic Metal Ions in Water Using SiO_2@Ag Core-Shell Nanoparticles

Jyoti Boken[1] **and Dinesh Kumar**[2]

[1]*Department of Physics, Banasthali University-304022, Rajasthan, INDIA*
[2]*Department of Chemistry, Banasthali University-304022, Rajasthan, INDIA*

Abstract

In this paper, we have synthesized silver nanoshell for detection of heavy metal ions in water using chemical reduction method. Silver nanoparticles exhibit strong surface plasmon resonance peak at 433 nm whereas silver nanoshell shows surface plasmon resonance peak at 450 nm. The surface plasmon resonance band of silver nanoshells was found to be sensitive to the presence of toxic ions in the water. One of the most exciting accomplishments is the minimum detection limit for Hg^{2+} which is found to be 0.01 mL in water with good sensitivity. The detection of heavy metal ion such as Hg^{2+} using silver nanoshells of size 202 nm with 28 nm shell thickness was developed. The sizes and shapes of nanoshells were tuned by selecting the reducing and capping agents. The nanoparticles have been characterized by UV-Vis spectroscopy and Transmission electron microscopy.

Keywords: Mercury (II) ions detection; Silver nanoparticles; Silver nanoshells; Surface plasmon resonance.

1. Introduction

In recent years, selective and sensitive chemosensors which are broadly used in heavy metal ions determination have been considerable attention worldwide because these metals play important roles in living systems and have a toxic impact on the environment. Among them, mercury is considered as one of the most dangerous metal ions for environment and has most commonly toxic risks for human contacting areas because it is widely distributed in water, soil and air and it is toxic element that exists in metallic, inorganic and organic forms [1]. According to the Environmental protection agency (EPA) guidelines, tolerance limits for mercury in drinking water are no greater than 0.002 mg/L. Mercuric ion (Hg^{2+}) is the most stable from of inorganic mercury which exists in water surface because of its high water solubility and it cause several health problems that can damage the brain, nervous system, kidneys [2]. Therefore, it is critical to be able to detect and measure the level of Hg^{2+} in both biological and environmental samples under aqueous conditions with high sensitivity and selectivity. Several methods have also been developed for the detection of Hg^{2+} such as electrochemical analysis, atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, inductively coupled plasma mass spectrometry and molecular fluorescence spectroscopy. Most of these methods are expensive, complicated and very difficult for in detection. Therefore, it is important to develop a simple, fast and inexpensive method for detecting metal ions in water samples [3].

Colorimetric sensors provide the immediate optical feedback have been considerable attended due to their simplicity, rapidity, high sensitivity and ease of measurement. Optical sensors which require no longer any special instrumentation are particularly attractive for the visual detection of metal ions. Metal nanoparticles have been extensively studied and used due to of their attractive optical, electronic, biological and catalysis properties [4]. Metal nanoparticles, particularly Silver nanoparticles with well-controlled size have been focus of great attention because the color changes associate with surface plasmon absorption band which depends on a several parameters such as the size and shape of the particles, absorbed species, dielectric properties of the medium and distance between particles. Silver nanoshells show enhanced surface plasmon resonance band than silver nanoparticles therefore detection of metal ions carried out using silver nanoshells will be considerably much more sensitive towards smaller quantity present in drinking water [5]. With this idea, a test for the detection of heavy metal ions such as Hg^{2+} using silver nanoshells was developed.

2. Materials and Methods

2.1 Chemicals

Silver nitrate, trisodium citrate and tetraethylorthosilicate (TEOS) purchased from Sigma Aldrich were used as received without any further purification. Ammonium hydroxide and ethanol and mercuric chloride were purchased from Merck. All the solutions have been freshly prepared for the synthesis of nanoparticles. Distilled water passed through a Millipore system (resistivity=18MΩ.cm) has been used for all the solution preparation and throughout the experiments. All glassware has been first rinsed with aqua regia and then thoroughly with distilled water which was followed by Millipore water.

2.2. Preparation of SiO_2@ Ag core-shell

First silica particles were fabricated according to the protocol of Stöber [6], on these silver particles was coated in the second step. The method exploits the presence of opposite charges on the surface of silica particles and silver ions, Ag nanoparticles can be deposited on the surface of SiO_2 particles by the electrostatic attraction among the particles and the medium. Silver nitrate (0.002 M) was reduced in presence of silica particles (0.03 gm) using trisodium citrate (0.02 M). These particles were centrifuged and washed with water 2-3 times. Yellow colour precipitate was again re-dispersed in water. To enhance the thickness of coating the second step was repeated again till the desired thickness was obtained. Thickness of shell can be tuned by modifying the reaction conditions such as amount of silica particles added in the reaction mixture. SiO_2@Ag core-shell particles were centrifuged at 3000 rpm for 10 min and then washed 3-4 times with water.

3. Results and Discussions

Silver nanoshells were fabricated by reduction method using trisodium citrate. These particles are stabilized by an electric double layer arising from absorbed citrate and corresponding cations. This layer is very sensitive due to its electron transfer interactions as well as well adsorption on the surface of silver nanoshells. This sensitivity has been developed for the detection of toxic ions present in the solution. The changes in the position and shape of plasmon absorption band along with its damping due to chemisorption of these ions onto the surface of silver nanoshells. The assays and changes in the UV-Vis absorption spectra were performed and monitored at room temperature.

The surface plasmon absorption band of SiO_2@ Ag core-shell in aqueous solution is strongly damped when a nucleophilic regent is absorbed on the surface of colloidal nanoshell particles. After the addition of Hg^{2+} ions (10mM) of in the solution, damping of plasmon band was observed at concentrations 0.01ml, 0.1 ml, 0.2 ml as shown in Fig. 1(a). It means, Hg^{2+} ions get adsorbed on the surface of nanoshells which results in the damping of plasmon absorption band. Mie theory predicted that a change in refractive index of the medium would lead solely to the shift in the position of band maximum and would not influence the spectral width. Therefore it is possible that the adsorbed ions from a layer surrounding the silver nanoshells and the optical properties of core-shell themselves by changing their dielectric medium. At the higher concentration (0.3 ml - 0.6 ml) plasmon band has been completely vanished. However change in color of dispersion was also monitored. The effect of addition of cations on the intensity of surface plasmon resonance band is shown in Fig. 1(b). This figure shows reduction in intensity of surface plasmon resonance band with in concentration of added ions for Hg^{2+}. Absorption of cations on the surface of nanoshells is due to gradual reduction in intensity.

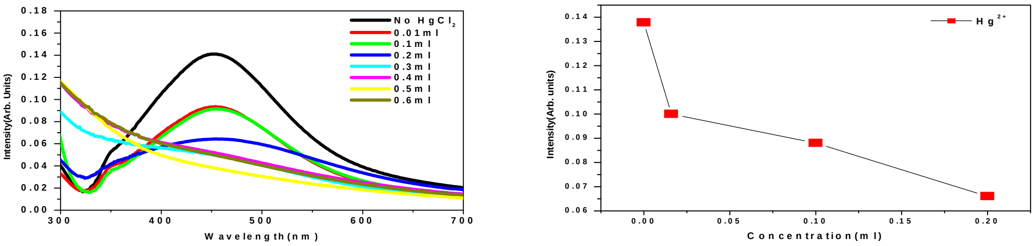

Figure 1: (a) Effect of Hg^{2+} ions on the surface plasmon resonance of SiO_2 @Ag, (b) Intensity of surface plasmon resonance band as a function of added Hg^{2+} ions in solution.

TEM analysis of Silica and $SiO_2@Ag$ core-shell particles were carried out as shown in Fig. 2. Monodispersed silica particles are obtained as shown in Fig. 2(a). Particles completely covered with silver shell can be seen in the Fig 2. (b). It can be concluded that silica particles can be coated with silver nanoparticles without using any primer. Electrostatic attraction between the core and shell can be developed for covering core particle with shell material uniformly. These particles show very intense surface plasmon resonance band originating from the silver nanoparticles present on their surfaces.

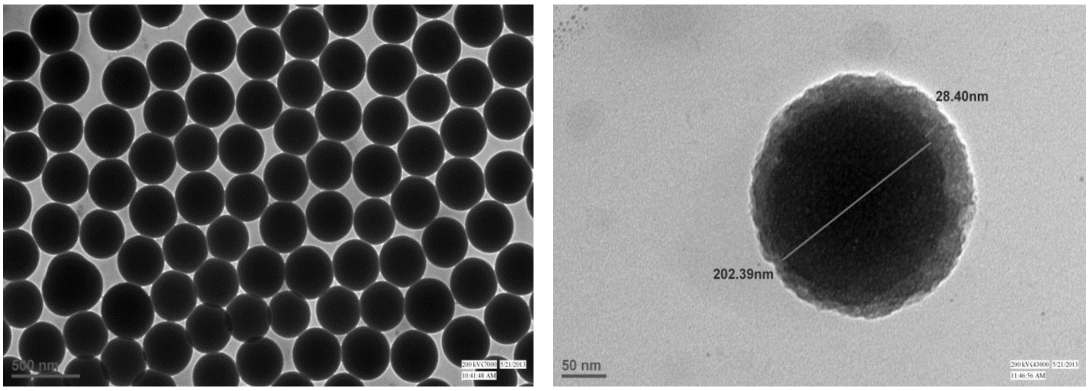

Figure 2: (a) TEM image of silica particles, (b) Core-shell Nanoparticles

4. Conclusions

In summary, a simple, label free, cost effective, portable, selective and sensitive detection method has been developed using $SiO_2@Ag$ core-shell for the detection toxic ions present in drinking water. The presence of Hg^{2+} can be monitored by naked eye and UV-Vis spectrometer. Influence of various metal ions has also been developed using this techniques. The technique utilizes variations associated with the position and intensity of surface plasmon resonance band of $SiO_2@Ag$ core-shell. This colorimetric technique does not need to use any complexation of Hg^{2+} ion to any ligands, DNA, fluorescent compounds or dyes and temperature control unit to probe Hg^{2+} in aqueous solution.

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