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ORIGINAL ARTICLE

Shape-directing role of cetyltrimethylammonium bromide on the morphology of extracellular synthesis of silver nanoparticles

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Abstract *Oriental plane* leaf extracts were used as a reducing-, stabilizing- and capping-agent for the preparation of silver nanoparticles (AgNPs) for the first time. The size, shape, size distribution and optical properties strongly depend on the experimental conditions, absence, and presence of shape-directing cetyltrimethylammonium bromide (CTAB). UV–vis spectroscopy, transmission electron microscopy and selected electron diffraction ring patterns were used to determine the morphology of resulting AgNPs at different time intervals. The spectra showed a surface Plasmon resonance (SPR) peak at 450 nm which is the characteristic of spherical AgNPs (diameter ranging from 10 to 30 nm). The peak shifted to shorter wavelength (blue shift) from 450 to 425 nm and sharpness of the peak also decreases in the presence of CTAB which might be due to the capping action of CTAB. A layer of ca. 3 nm around a group of the AgNPs in which the inner layer is bound to the AgNPs surface via the active groups of the extract has been observed.

1. Introduction

The use of different surfactants (normal and Gemini) as stabilizers and/or capping agents has been the subject of various researchers for two decades (Mulvaney, 1996; Chen et al., 2003). Morphology of gold and silver AgNPs (cubes, hollow structures, disks, prisms, sheets/plates, wires/rods, multi-branched and/or multi-pods) strongly depends on the nature and presence of stabilizer (Bakshi, 2009). Bakshi et al. (2008) used the seed-mediated approach to synthesize gold nanoparticles by using twin tail alkylammonium cationic Gemini surfactant such as hexamethylene-1,6-bis(dodecyldimethylammonium bromide) (12-6-12) and didodecyldimethylammonium bromide (12-0-12) as capping agents in aqueous phase. Spherical and nanorods were obtained in the presence of 12-6-12 while no anisotropic growth was observed with 12-0-12 as a

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capping agent. Salavati-Niasari and his co-workers synthesized copper indium sulfide nanocrystals, CdSe/CdS core/shell nanoparticles by using the micro wave, ultrasonic, and precipitation methods (Sabet et al., 2013; Amiri et al., 2013, 2014a). They also investigated the photo catalyst activity of CdSe/CdS core/shell nanoparticles (Amiri et al., 2014a) and application of copper indium sulfide nanoparticles for solar cell (Amiri et al., 2014b). Mono-dispersed lanthanum hydroxide nanoparticles and nanorods, and bismuth sulfide nanorods were reported by Salavati-Niasari et al. (2012, 2013). The literature is replete with the investigations of the use of different stabilizers during the synthesis and characterization of advanced nanomaterials of various metals. But the use of shape-directing cetyltrimethylammonium bromide in the similar investigations involving plants leaves and seeds as reducing agents has been neglected (Pileni, 1993; Khan et al., 2012a,b). Various natural reducing agents such as medicinal plants, leaves, flowers, seeds and their bark are used as an alternate source of the toxic reductants (Shiv Shankar et al., 2004; Sharma et al., 2007; Al-Thabaiti et al., 2008). Reduction ability of natural reducing agents strongly depends on the reduction potentials of reducing agents.

The leaves of *Oriental plane* are used for the treatment of astringent, dysentery, heal wounds, chilblains and ophthalmia. A large number of molecules such as platanin, tannin, allantoin, glyoxylic acid, phlobaphene, mannitol, platanolic acid and platanol are the bioactive constituents of chinar leaves. Recently, we have reported the use of various reducing agents (citric acid, ascorbic acid, sugars and amino acids) in the synthesis of advanced AgNPs in the presence of shape-directing CTAB (Al-Thabaiti et al., 2008; Khan et al., 2012; Hussain and Khan, 2014). In this paper, we describe a one-pot chemical reduction method for the synthesis of AgNPs using aqueous leaf extracts of *Oriental plane* (deciduous tree of the Platanaceae family). To the best of our knowledge, this is the first ever report on *Oriental plane*-assisted extracellular green synthesis of advanced AgNPs in the absence and presence of shape-directing CTAB cationic surfactant. The method is simple, clean and requires only the extract and $AgNO_3$. In addition, this method has an advantage in higher scale production of AgNPs over the various methods reported in the literature.

2. Experimental

2.1. Chemicals

Deionized double distilled (first time from alkaline $KMnO_4$), CO_2 and O_2 free water was used as the solvent. All glassware was washed with aqua regia (3:1 HCl and HNO_3), rinsed with water, and dried prior to use. Silver nitrate ($AgNO_3$, oxidant, Merck India, 99.99%), and CTAB (99%, stabilizer, Fluka) were used without further purification. Fresh chinnar leaves collected from the Srinagar, Jammu and Kashmir, India, were perfectly washed, chopped into small pieces and added to a Borosil conical flask containing 250 ml double distilled deionized water. The reaction mixture was kept on a boiling water bath for 30 min, cooled and filtered through What-man filter paper no. 40. The perfect transparent clear filtrate contains only soluble organic moieties of the chinnar leaves stored in an amber glass bottle. This resulting aqueous solution is used for the reduction of Ag^+ ions to the Ag^0.

2.2. Preparation and characterization of AgNPs

In a typical experiment, fresh solution of $AgNO_3$ was added to the reaction mixture containing required amounts of leaf extracts and kept at room temperature for the reduction process. As the reaction time increases, appearance of pale-yellow is observed indicating the formation of AgNPs (Hussain and Khan, 2014; Zhang et al., 2004). Shimadzu UV–vis spectrophotometer; model UV-1800, Japan and transmission electron microscope (Hitachi 7600 with an accelerating voltage of 120 kV) were used to record the spectra and determine the morphology (size, shape and the size distribution) of resulting AgNPs, respectively. Selected area electron diffraction (SADE) data were also recorded. XRD patterns of the samples were recorded using Ni-filtered Cu Kα radiation (λ = 1.54056 Å) of a Rigaku X-ray diffractometer operating at 40 kV and 150 mA at a scanning rate of 0.02^0 per step in the 2θ range of $10^0 \leqslant 20^0\ \theta \leqslant 80^0$.

3. Results and discussion

3.1. Visual observations and UV–vis spectra

It has been established that metallic silver in nano and/or colloidal state gives different colors in aqueous solutions due to the excitation of electron from the valence bond to conduction bond (Mulvaney, 1996). In the first set of experiments, observation shows that the required amounts of leaf extracts and aqueous $AgNO_3$ solution were colorless. As the reaction time increases, the color of the reaction mixture changed from pale-yellow, pink-yellow, light brown, and wine-red to dark brown. Optical images of leaf extracts, $AgNO_3$ and different colors formed after the reduction of Ag^+ ions with extracts are given in Fig. 1. Appearance of different colors at different time intervals (from initial to final stage) indicates that the morphology of AgNPs (shape, size and the size distribution) alters with the reaction time. The appearance and/or change of color strongly depend on the reaction conditions and [extract] and/or [Ag^+] which is due to regular aggregation. The position and shape of the SRP absorption depend on the particle size, shape, and dielectric constant of the surrounding medium and surface-adsorbed species. The broadening of the absorption band with [Ag^+] indicates that initially reduced AgNP grows to form larger particles, and finally, Ag^+ acts as a shape-directing agent. The shift of the plasmon peak to higher wavelengths may happen due to various reasons (Zhang et al., 2004). The spectra of the synthesized AgNPs are also recorded at different time intervals for the variation of leaf extracts (Fig. 2). The surface Plasmon resonance (SPR) peak observed at 450 nm confirms the influence of aqueous chinnar leaf extracts in reducing Ag^+ ions to Ag^0 (formation of AgNPs from aqueous $AgNO_3$ solution). Absorbance intensity of broad SPR band increases steadily as a function of reaction time suggesting the anisotropic growth of AgNPs. A weak absorbance peak was observed at 450 nm with 1.0 cm^3 of extracts after 5 min. Interestingly, the position of the maximum absorption was shifted to a shorter wavelength (from 450 to 425 nm; blue shift). The red- and/or blue-shifting of the absorption band with [extract] indicate that initially small AgNPs grow to form larger particles and finally extracts act as shape-directing agents (Linnert et al., 1990). The blue-shifting is probably due to the interparticle interaction in the