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Impact of Ph on the Properties of Spherical Silver Nanoparticles Capped by PVA

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ABSTRACT

Spherical shaped silver nanoparticles have been synthesized through chemical reduction method using tri sodium citrate as reductant and PVA as surfactant. We have studied the pH influence on the properties of synthesized silver nanoparticles. Broadened XRD peaks confirmed the formation of small nano-sized silver particles with face centered cubic (FCC) structure. The average particle size of the silver nanoparticles decreased from 32 nm to 20 nm when the pH is increased from 6 to 10. The particle size decreased with increasing pH value was confirmed by both XRD and FESEM studies. FTIR measurements concluded that intact of PVA with silver nanoparticles

Introduction

Nanotechnology is rapidly growing technology and one of the most promising areas of research in modern material science. A combination of nanotechnology and biology can address several biomedical problems, and can modernize the field of health and medicine because the majority of the natural processes also take place in the nanometer scale regime [1]. Advances in nanotechnology largely depend on the ability to synthesize nanoparticles of various materials, sizes, shapes, and assembling them into complex architectures.

In recent years, metallic nanoparticles have attracted strong research focus because of their unique functional properties which lead to diverse applications in the areas of plasmonics [2], surface enhanced Raman scattering [3], catalysis, medicine and biological sensing [4, 5]. It is well known that the synthesis of well-controlled shapes and the size of particles could be critical on which catalytic reactivity depends for extensive applications [3] in different fields.

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Silver nanoparticles have been intensively investigated due to their excellent unique properties associated to novel metals such as conductivity, chemical stability, catalytic activity, optical behavior, and antimicrobial activity. Silver nanoparticles can be synthesized by various methods such as chemical reduction [6], microwave-assisted synthesis [7], metal evaporation [8], electrochemical [9], γ-radiation [10], photochemical [11], laser ablation [12] etc. The most extensively used one is chemical reduction method, which is simple, but the great care must be exercised to make stable and reproducible nanoparticles.

One of the problems of chemical synthesis is that the lifetime of the atoms in the dispersion is short and nanoparticles tend to come close together and resulting in agglomeration. This problem is often overcome by the use of capping agents, which coat the particles in order to reduce high surface energies [13]. In the present work, we used poly vinyl alcohol (PVA) as surfactant. A strong adsorption of polymer stabilizer would occupy the growth sites and thus reduce the growth rate of nanoparticles. By changing the reaction parameters such as molar ratio of the reductant/silver precursor, pH, and temperature of the reaction, the particle size can be tuned. In the present work, we have studied the influence of pH on the properties of prepared silver nanoparticles.

Experimental Section:

All the chemicals were of analytical reagent grade and used without any further purification.In a typical synthesis process, 0.01 M of silver nitrate ($AgNO_3$) solution is prepared with ethanol. Then 0.1 M of tri sodium citrate (reducing agent) and 2 ml PVA (1%) which acts as surfactant are added drop by drop to the above solution under continuous stirring. Then after, NaOH is added drop wise in order to attain pH of the reaction system to 6 and the above solution was kept sealed under continuous stirring for 4 hrs maintaining at a temperature of 75^oC. PVA isadsorbed on the surface of the silver nanoparticles with the alkyl chains on the outside resulting in the hydrophobic nature preventing the agglomeration of formed silver nanoparticles. By simply varying pH of the reaction system, we can tune the size of the nanoparticles. When, the reaction is completed products were collected and thoroughly washed for several times with ethanol, and finally subjected to vacuum dried at 80^0C for 3 hrs. to obtain silver nanoparticles. The above procedure is reiterated by varying the pH 8 and pH10.

The as-synthesized silver nanoparticles were subjected to various characterization studies. The X-ray diffraction patterns of the samples were collected on a Mac Science M18XHF-SRA X-ray diffractometer. Elemental compositions for the prepared samples were analyzed through EDAX using Oxford Inca Penta FeTX3 EDS instrument attached to Carl Zeiss EVO MA 15 Scanning Electron Microscope. The FESEM measurements were obtained using a ZEISS, SUPRA55. FTIR spectra of the freeze-dried samples were recorded with ATR-FTIR using Bruker Vertex-80 spectrometer.

Results and discussions:

Structural analysis:

The X-ray diffraction patterns for the prepared silver nanoparticles are shown in Figure 1.

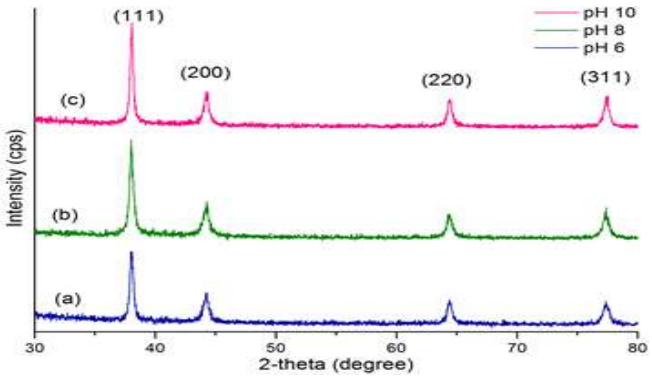

Figure1. Representative XRD patterns of silver nanoparticles (a) pH 6 (b) pH 8 (c) pH 10

From the figure it is obvious that distinct peaks at 2θ values of about 38^o, 44.5^o, 64.5^o and 77.5^o representing (111), (200), (220) and (311) Braggs reflections of fcc structure of silver, confirms the formation of silver nanoparticles which are in consistent with the JCPDS (No.04-0783) data. The broadening of Bragg's peaks indicates the formation of small silver nanoparticles. The average particle size of silver nanoparticles was calculated using Debye-Scherrer's equation [14]

$$D = K\lambda / \beta \cos\theta \quad \ldots\ldots [1].$$

The average sizes of the particles at different pH values 6, 8, 10 are of 32, 26, and 20 nm, respectively. From the particle size determination it is observed that with increasing pH the particle size is decreased.

Compositional analysis:

The EDAX spectra of as prepared silver nanoparticles at pH 6 and pH 10 values are shown in Figure. 2(a) and 2(b). From the EDAX profiles it is observed that the presence of elemental composition of silver.

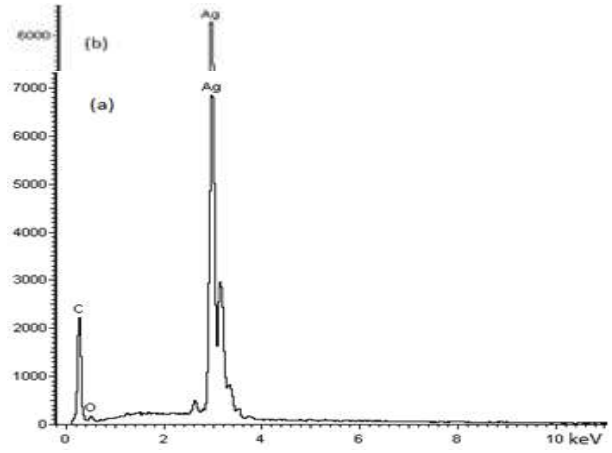

Figure 2. EDAX spectra of silver nanoparticles prepared at (a) pH 6 (b) pH 10.

Identification lines for silver in the range 2.5 - 4 keV [15] are observed due to Surface Plasmon Resonance and these correspond with peaks in the spectrum, thus giving evidence that silver has been correctly identified. Besides, elemental silver there exist weak signal of elemental carbon likely to be due to adhesion of carbon tape on to the stud. Hence, from the EDAX spectra it is confirmed that the reduction of silver ions to elemental silver and formation of pure silver nanoparticles.

Morphological analysis:

The size and morphology of the synthesized silver nanoparticles prepared at different pH values have observed by FESEM measurements. The FESEM images of silver nanoparticles with pH values 8 and 10 have shown in Figure. 3(a) and 3(b).

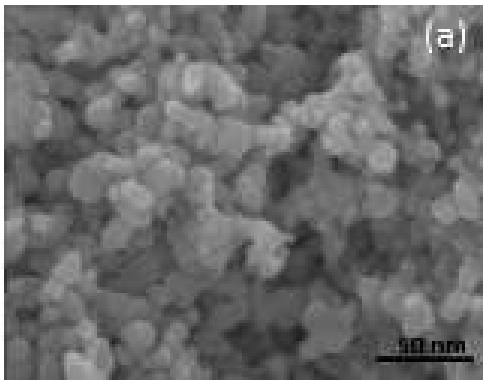

Figure 3.FESEM images of silver nanoparticles at a) pH 8 (b) pH 10

The prepared silver nanoparticles are mostly spherical in shape and had found to be homogeneous with no substantial aggregation. The average particle sizes prepared at pH values of 8.0 and 10.0 are of 25 nm and 19 nm respectively. The average particle size decreased with increase in pH, which is also consistent with previous XRD results.

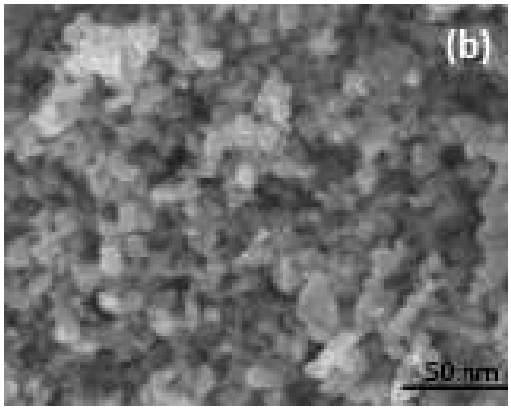

Figure 3.FESEM images of silver nanoparticles at a) pH 8 (b) pH 10

FTIR analysis:

Spectra of pure PVA and PVA capped silver nanoparticles (pH 10). The pure PVA sample shows strong absorption peaks at 3450 cm^{-1} (typical hydroxyl bands for free alcohol), 3240.41 cm^{-1} (attributed to hydrogen bonded band), 1639 cm^{-1} (the symmetric stretching of carboxylate anion (-COO-)), 1404 cm^{-1} (due to O-H and C-H bending), 1082 cm^{-1} (related to C-O stretching) [16]. In addition bands corresponding to the (-CH2-) asymmetric and the symmetric stretching are at 2926 cm^{-1} and 2854 cm^{-1} respectively for pure PVA.The spectrum of PVA capped silver nanoparticles showed major peaks at 3446, 3269.34, 2964.59, 2924.9, 1589, 1394, 1078 cm^{-1}. From this, we can observe shifting in the bands due to the interaction of O-H bonds of PVA with the surface of silver nanoparticles by chemical adsorption. Hence, we can suggest that prepared silver nanoparticles are encapsulated by PVA.

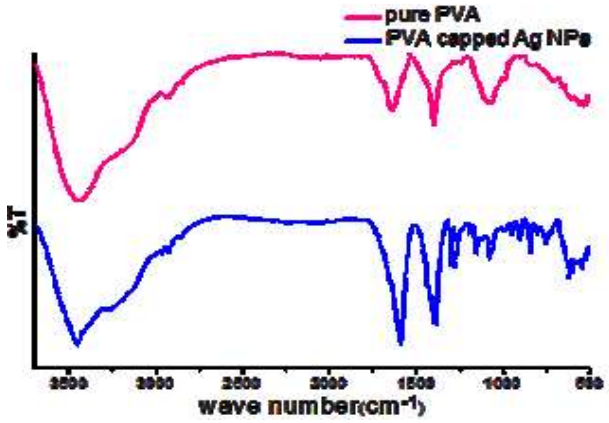

Figure 4.FTIR spectrum of pure PVA and PVA capped silver nanoparticles

Conclusion:

Figure 4.FTIR spectrum of pure PVA and PVA capped silver nanoparticles uniform sized spherical PVA capped silver nanoparticles have been successfully synthesized by chemical reduction method in the presence of trisodium citrate as reduction agent and PVA as surfactant. The influence of pH on the properties of silver nanoparticles wasstudied. The particle size of the silver nanoparticles was tunable by simply changing the pH of the reaction. The formation of silver nanoparticles was monitored via XRD, FESEM and FTIR measurements. The EDAX analysis showed the formation of elemental silver. With increasing in pH the particle size is decreased as confirmed by both XRD and FESEM results. From the FTIR it is observed that the prepared silver nanoparticles were capped by PVA. The obtained silver nanoparticles were bio and eco compatible.

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