Physicochemical Studies on Nano Silver Particles Prepared by Different Techniques

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Abstract: AgNPs were synthesized by liquid – phase reduction method at room temperature and a large enough concentration of Triethanolamine (TEA) had a very small grain size. It was supposed that the surface-capped AgNPs with significantly increased stability and dispersibility. Silver nanoparticles (AgNPs) were prepared in different sizes by reduction of AgNO₃ using citric acid as a reducing agent, (TEA) as the stabilizer agent and different Techniques during preparation as Sonochemical, and Hydrothermal. The morphology and particle sizes were studied by Transmission Electron Microscopy (TEM) and the data revealed that different sizes of AgNPs were formed. The appearance of surface Plasmon band in the ultraviolet-visible spectra (420-445 nm) is due to the formation of AgNPs in different sizes. Also The data was clarified the TEA molecules coordinate to the surface of Nano-Ag particles through their head-groups. XRD also studied. Antibacterial activity of Ag-PVA nanocomposites indicating that Highest antibacterial activity was detected with film A₁.

Key words: Silver nanoparticles, surface Plasmon resonance, optical properties, Antibacterial activity.

INTRODUCTION

Nanocrystallites exhibit novel material properties which largely differ from the bulk materials due to their small sizes, including quantum size effect on photochemistry, nonlinear optical properties of semiconductor or the emergence of metallic properties with the size of the particles. These nanoparticles have a wide range of applications (Cao et al., 2002; Wang et al., 2001 and Sun et al., 2000). Thus, synthesis of nanoparticles is of a great interest field during the past few years. As nanomaterials of noble metals, silver has been widely investigated for its excellent properties like the highest electrical and thermal conductivities among all metals and its applications, such as antibacterial materials (Jiang et al., 2004), antistatic materials, cryogenic superconducting materials (Hirano et al., 2003), biosensor materials (Ren et al., 2002) and so on. Morphologies and structures are found to have great influence on their properties, and great attention has been paid to the synthesis of silver nanorods, nanowires and microwires. Extensive works have been carried out to synthesize silver nanoparticles with controllable shape and size and desired electric and optical properties (Sherry et al., 2005; Wiley et al., 2006; Lu et al., 2006 and Maillard et al., 2003).

Generally, specific control of shape, size and size distribution is often achieved by varying the synthesis methods and reaction conditions such as reducing agents, stabilizers, etc. (Sherry et al., 2005 and Wiley et al., 2006). During the last few years, many methods have been developed to prepare silver nanomaterials e.g., chemical reduction, photochemical method, ultrasonic-assisted reduction, electrochemical method, template, irradiating reduction and biochemical method.

In this work, we presented the synthesis of silver nanoparticles from silver nitrate by different methods (chemical, sonication and hydrothermal techniques) in aqueous solution of Triethanolamine (TEA) surfactant. Citeric acid acts as reducing agent. a reasonable way to prepare silver particles with tunable size is to choose a reductant with suitable reactivity to mediate the nucleation and growth processes of the particles.

MATERIALS AND METHODS

AgNPs were synthesized by liquid – phase reduction method at room temperature (Guo et al., 2010) Silver nitrate, citric acid and triethanolamine were reagent grade. Deionized water was used for all the preparations. silver powder was obtained by reaction of AgNO₃ with citric acid. In a typical preparation of silver powder 0.3 g AgNO₃ was dissolved with 50 deionized water in 250 ml. beaker with sodium hydroxide or nitric acid solution adjusting pH To a certain value, and then the solution was diluted to 100ml. with deionized water. In the same. 0.27 citric acid and a certain dosage of dispersing agent were dissolved with 50 ml. deionized water in 250 ml. beaker with sodium hydroxide or nitric acid solution adjusting pH to a certain value and then the solution was diluted to 100 ml. with deionized water. The reactant solutions were mixed in three – neck flask drop by drop with the aid of a dropping funnel. At the same time, the reaction was kept under agitation at a constant rate and in water bath to maintain a constant temperature of 40°C. It was stirred continuously for 5 min after dripped off.
Then put it aside until most of the silver powders precipitated, and the silver powder was separated from the solution ultrasonically washed three times by deionized water and anhydrous ethanol, respectively. Subsequently, it was dried in a vacuum oven at 60°C for 12h. Finally it was sifted by a 500-mesh sieve. The same experiment was repeated using ultrasonic bath (1), room temperature (2) and Hydrothermal (3) techniques.

Measuring of the antimicrobial activity of nanocomposite films by disk diffusing method (DDM). The Ag-PVA nanocomposite films were prepared by casting. The samples were tested against different strains of bacteria namely: Gram positive bacteria (Staphylococcus aureus, Bacillus cereus and Bacillus subtilis) and Gram negative bacteria (Escherichia coli and Pseudomonas aeruginosa) using DDM. In this method, the pure cultures were used (18-24 h) and the turbidity of the bacterial culture was standardized until the suspension contains approximately $1 \times 10^8 - 2 \times 10^8$ CFU/ml. Then the bacterial suspension was cultured on plates covered with Mueller-Hinton Agar (Bryaskova et al., 2010) (26 ref). The impregnated disks were further placed on the surface of the inoculated agar plates and incubated at 35°C for 24 hours. The inhibition zone was measured. The assay was performed in duplicate.

UV-Vis spectra of colloidal solution were measured with an UV-Vis spectrometer (6100 Jasco, Japan). Images of colloidal particles were measured with a TEM operated at 200 KV. TEM samples were prepared by dropping a small amount of the colloidal solutions onto a copper micro-grid and were dried in a desiccator. X-ray powder diffraction (XRD) measurements were carried out on D8 Advance X-Ray diffractometer; Emyrean Series 2 (P Analytical, Netherlands) operated at (40 kV and 40 mA) with CuKα radiation of wavelength ($\lambda = 1.5406\text{Å}$) at 25°C. Scanning rate was 0.04°/s for 2θ ranging from 20° to 80 and a scanning speed was 1°/min.

RESULTS AND DISCUSSION

Citric acid was chosen as reducing agent in this study due to its middle reduction power. In this process, the following chemical reaction occurred:

$$2\text{AgNO}_3 + \text{C}_6\text{H}_8\text{O}_7 = 2\text{Ag} \downarrow + \text{C}_6\text{H}_6\text{O}_6 + 2\text{HNO}_3$$

According to Eq. (1), it is seen that AgNO3 is two times than citric acid in the molar ratio. In the experiment, we usually added excess citric acid than the theoretical ones to ensure that AgNO3 was completely reduced (Guo et al., 2010).

1. TEM:

The transmission electron microscope (TEM) is currently the imaging technique of choice for the characterization of structure and size distribution of materials. To determine the sizes of the as-prepared silver nanoparticles by different techniques TEM were performed Figure.1 and their sizes were presented in Table 1. Different techniques were used to probe their effect on the size of the resulting nanoparticles. Most of Silver nanoparticles show spherical morphology, and the average size of a spherical particle. Also, from the images it was observed that AgNPs are the best homogeneous and size distributions at Room temperature and the average value of particle sizes are 24, 2.5, and 14 nm respectively. The results indicated that the particle sizes were increased in the following order reduction at room temperature A1 is smaller than hydrothermal A3 and sonochemical A1. If the number nuclei increased faster than that of total ions, smaller particles would be obtained. (2) If the increase of nucleus number was proportional to that of total ion number, the particle size might remain unchanged. (3) When the number of nuclei remained constant or increased slower than that of total ions, the particle size would become larger with the increase of ion concentration. Based on the above observation, our case appears to belong to the three situation. According to this correlation, silver nanoparticle can be efficiently prepared with controlled size.

2. X-Ray Diffraction:

The XRD patterns of the as-received samples are shown in Fig. 2. For materials A1 observes distinct diffraction lines corresponding to crystalline phases. For samples A2 and A3 see only a wide ‘halo’ typical for amorphous materials. As-received materials show that for A2 they are fully amorphous and for A3 they contain crystalline grains embedded in amorphous matrix.

3. UV-VIS Spectroscopy:

Figure (3) shows the UV-Vis absorption spectra of AgNPs. The absorption band appeared at 420 nm for the sample (A1) which prepared using ultrasonic techniques, The as-prepared samples were synthesized using different techniques. AgNPs (A2) exhibit absorption band with a maximum at 390 nm. (A3) sample prepared using hydrothermal techniques exhibit absorption band with a maximum at 380 nm. It is cleared in table (1) the relation between particle size and band gap.
It is well known that triethanolamine is a strong base due to the lone pair of electrons on the nitrogen atom and Ag⁺ has sp hybrid orbital, which can accept lone pairs of N and O atoms of TEA to form coordination bonds. The absorption band appeared was assigned to the surface Plasmon band of TEA capped AgNPs (De et al., 2000; He et al., 2002 and Michaels et al., 1999). The shift of the Plasmon band is due to different size and the capping material. Also, it can be ascribed to the bond formation of the N and O with lone pairs of electrons and the Ag atoms of the nanoparticles and provides clear evidence for the adsorption of the TEA on the surface of silver particles and as shown in the structure (1) (Kerker 1985).

It can be observed a long tail in the spectrum due to the presence of some rodlike particles with the spherical AgNPs (Bohren et al., 1983; Jin et al., 2001; Klasu et al., 1999 and Brown et al., 2000). The intensity, wavelength position and half-width of the well-known surface Plasmon absorption band in the case of metallic silver particles are very sensitive towards chemical modifications of the surface. The changes in the intensity and shape of the Plasmon absorption band can be explained quantitatively by the change in the density of the electron in the metal particles that donated or removed by free radical attack. With increasing Ag particle size the Plasmon band was shifted to higher wavelength. It can be suggesting that the AgNPs became uniform with nearly narrow size distribution and the particle size was increase with decreasing of the time of preparation. The absorption spectrum is then composed of the sum of absorption and scattering modes, each of which has a contribution that depends on the particle size. Higher-order modes become more dominant with increasing particle size causing the Plasmon absorption band to red shift while the bandwidth increases. Physically, this can be explained by the fact that for larger particles the light cannot polarize the nanoparticles homogeneously and retardation effects lead to the excitation of higher-order modes (Kreibig and Vallmer 1995). As the optical absorption spectra depend directly on the size of the nanoparticles, this is regarded as an extrinsic size effect (Link and El-Sayed 2003).

Formation of a great number of nuclei and raising the Ag⁺ concentration above the nucleation threshold, without formation of additional nuclei. The formed nuclei aggregated rapidly together to form small nanoparticles, and then the formed small nanoparticles soon aggregated to become large nanoparticles because of high density of small nanoparticles. In the process of the aggregation, there is less capping agent adsorbed on the particles. This is an nonequilibrium process. The formed large particles are not stable. The large particles will be broken into small parts because of the fact that TEA prevalingly links the surface of Ag nanoparticles, which can make the small nanoparticles separate from the large nanoparticles. This reaction goes on, and more silver ions are reduced to silver atoms. Finally, the particle size stops decreasing and starts to increase at a certain

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**Fig. 1:** TEM images of AgNPs prepared at different techniques.

**Table 1:** Relation between particle size and the band gap for prepared Ag NPs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wavelength (nm)</th>
<th>Band gap (eV)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>420</td>
<td>2.95</td>
<td>24 nm</td>
</tr>
<tr>
<td>A₂</td>
<td>390</td>
<td>3.18</td>
<td>2.5 nm</td>
</tr>
<tr>
<td>A₃</td>
<td>380</td>
<td>3.26</td>
<td>14 nm</td>
</tr>
</tbody>
</table>

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reaction moment. The whole process is a dynamic one; that is, during the increase of the particle size there are some larger particles to decompose into smaller nanoparticles. This is also true for the reverse process (He et al., 2001 and Oliveira et al., 2005). With the presence of less, the process of separating small nanoparticles from the large nanoparticles will be less efficient and the formed AgNPs will be polydisperse.

Fig. 2: X-ray diffraction patterns for as-received samples of AgNPs prepared at different techniques (A₁) Ultrasonic (A₂) room temp and (A₃) Hydrothermal techniques.

The band gap for A₁ is found to be 2.95 eV. Figure 3 shows absorption spectrum of Ag NPs 1 showed an absorption edge at about 420 nm and the band gap (E₉) calculated was 2.95 eV and, an absorption edge for A₂ at about 390 nm and the band gap (E₉) calculated was 3.18 eV. For Ag3 an absorption edge at about 380 nm and the band gap (E₉) calculated was 3.26 eV. Since the absorption edge was an index of particle size, smaller particles have larger band gaps and absorb at shorter wavelengths (Brus 1983).

4. Antibacterial activity of Ag-nanocomposites:

The antibacterial activity of the films was tested by using Disk Diffusion Method (DDM) in which the inhibition zone was monitored. It was found that all films exhibit bactericidal activity by appearance of inhibition zone except films A₂ and A₃ which indicating no activity against Bacillus cereus and Bacillus subtilis (Table 2). Highest antibacterial activity was detected with film A₁. The higher antibacterial activity against
Gram-positive bacteria is probably driven by the differences in the structure of cell walls between Gram-negative and Gram-positive bacteria. The cell wall of Gram-negative bacteria consists of lipids, proteins and lipopolysaccharides (LPS) that ensure more effective defense against biocides in comparison to Gram-positive bacteria where the cell wall does not contain outer membrane of LPS (Lei et al., 2008), thus leading to higher antimicrobial activity.

![Graph](image)

**Fig. 3:** Ultraviolet-visible spectra of AgNPs prepared at different techniques (A1) Ultrasonic (A2) room temp and (A3) Hydrothermal techniques.

**Structure (I)**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Staphylococcus aures</th>
<th>Bacillus cereus</th>
<th>Bacillus subtilis</th>
<th>Escherichia coli</th>
<th>Pseudomonas aeruginosa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>13</td>
<td>13</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>12</td>
<td>-</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>-</td>
<td>11</td>
<td>11</td>
<td>12</td>
</tr>
</tbody>
</table>

The bactericidal activity is presumably due to certain changes in the membrane structure of bacteria cell wall as a result of the interaction with the embedded silver nanoparticles which leads to the increased membrane permeability of the bacteria and consequently, leading to their death (Gong et al., 2007).

**4. Conclusion:**

Ultrafine Silver nanoparticles (AgNPs) were prepared by reduction of AgNO₃ using citric acid as a reducing agent, Triethanolamine (TEA) as the stabilizer agent. TEM showed different particle sizes of TEA capped silver nanoparticles synthesized by different techniques. UV-Vis results suggest that the silver nanoparticles are capped by TEA and different band gaps. Both reducing agents Citric acid, stabilizing agent, Hydrothermal and sonochemical techniques play important roles for controlling the particle sizes and shapes. Antibacterial activity of Ag-nanocomposites indcating that the highest antibacterial activity was detected with nanocomposite film of PVA - A1.

**REFERENCES**