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Synthesis of silver nanoparticles using N^1,N^2-diphenylbenzamidine by microwave irradiation method

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Silver nanoparticles have been prepared under microwave irradiation from a solution of silver nitrate in the presence of N^1,N^2-diphenylbenzamidine (DPBA) or simply amidine without any stabilizing agent. Different morphologies of silver colloids with charming colors could be obtained using N^1,N^2-diphenylbenzamidine (DPBA). The structures of silver colloids were determined by TEM. UV-Vis spectroscopy was used to follow the reaction process and to characterize the optical properties of the resultant silver colloids. The influence of unconventional reducing agent on the morphology of silver was investigated.

Keywords: Silver nanoparticles; Microwave; Optical properties

1. Introduction

In the last few years the preparation and characterization of nanostructured materials have become a topic of extreme interest because of their distinctive properties and potential uses in technological applications. It is found that the optic, electronic, magnetic, and catalytic properties of these particles depend on their size and shape. So, one of the challenges in nanoparticle synthesis is to control not only the particle size but the particle shape and morphology as well [1–4]. Their uniqueness arises from their high ratio of surface area to volume (aspect ratio) as these materials typically have a diameter of 100 nm or less [5, 6]. Novel metal nanocrystallites such as silver and gold provide a more interesting research field due to their close-lying conduction and valence bands in which electrons move freely. The free electrons give rise to a surface plasmon absorption band, which depends on both the particle size and chemical surroundings [7]. Thus, the color of the colloids varies depending on the method of preparation and the state of aggregation [8]. Silver nanoparticles create physical phenomena in their electronic, optical, and magnetic properties because of their small size. Several different

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methods can be used to make silver nanoparticles and keep them from oxidizing and agglomerating. Same size and shape nanoparticles can be tightly packed to create a high density. In general, metal nanoparticles can be prepared and stabilized by various methods such as photochemical reduction [9, 10], electrochemical techniques [11, 12] and chemical reduction [13, 14]. In general terms, to obtain small particle sizes with narrow size distributions and good stability is the goal. However, along with the development of nanotechnology, multi-dimensional novel metal colloids with interesting optical properties may have wider applications. As a quick, simple and energy efficient method, microwave synthesis has been developed and is widely used for the synthesis of solid materials [15]. Compared to conventional heating, microwave dielectric heating results from dipolar polarization as a consequence of dipole–dipole interactions between polar molecules and the electromagnetic field, and has become a very popular and useful technology as a non-conventional energy source in materials science [16].

In this study, a non-conventional reducing agent such as N^1,N^2-diphenylbenzamidine (DPBA) was used to synthesize silver nanoparticles using the microwave irradiation method. Silver colloids were successfully prepared by chemical reduction under microwave irradiation. Different sized silver nanoparticles of interesting colors were synthesized. The influences of the reducing agent on the optical properties and the morphologies of the silver particles have been investigated. The advantage of using non-conventional agent in preparation of silver nanoparticles has also been discussed.

2. Materials and method

All chemicals and reagents used were of analytical grade (BDH/Merck). All aqueous solutions were prepared in triple distilled water. 1.0×10^{-4} mol l^{-1} silver nitrate ($AgNO_3$), 0.001 mol l^{-1} N^1,N^2-diphenylbenzamidine (DPBA) was used.

The apparatus used for the preparation was a Samsung CE2877L domestic microwave oven (850 W) Samsung India Electronics Ltd., New Delhi, India.

2.1. *Formation of silver nanoparticles in DPBA*

Silver nanoparticles were synthesized through the preparation of different amidine solutions containing silver nitrate. The solutions were then put into the microwave oven where $AgNO_3$ was reduced to silver nanoparticle. In a typical procedure, the reaction solutions were prepared by dissolving 0.001 mol l^{-1} N^1,N^2-diphenylbenzamidine (DPBA) in ethanol and 1.0×10^{-4} mol l^{-1} $AgNO_3$ (20 ml) in a 50 ml Pyrex flask to obtain a homogeneous reaction mixture. It is important to mention that this synthesis was done in the absence of any stabilizer. Thereafter the vial was topped with a screw cap to prevent the evaporation of toxic and corrosive solvent. Then the vial was placed on the turntable of the microwave oven. The mixture was irradiated at a power of 300 watt for the duration of the reaction discontinuously to prevent an increase of pressure. After irradiation, the dilute colloidal solutions with striking colors were cooled to room temperature for characterization.

2.2. *Experimental techniques*

The ultraviolet-visible (UV-Vis) spectra were used to follow the reaction process and to characterize the optical properties, and were measured in quartz cuvette with Perkin-Elmer Lambda 20 UV-Vis spectrophotometer. Distilled water was used as a reference. Transmission electron microscopic (TEM) analyses were performed with Morgagni 268D Transmission electron microscope operating at 80kB (Mega view III Camera CCD), All India Institute of Medical Sciences (AIIMS), New Delhi. Samples were prepared by drying a drop of the colloid on a TEM grid with the sample allowed to dry completely at room temperature. Approximately 100 nanoparticles from each sample were measured manually for size distribution. Triple distilled water was used for solution preparation.

3. Results and discussion

3.1. *TEM analysis*

The TEM images of the as-prepared silver nanoparticles in DPBA are shown in figure 1. It is apparent that silver nanoparticles formed in different timings have different sizes. As shown in figure 1(a), the silver colloids, obtained in

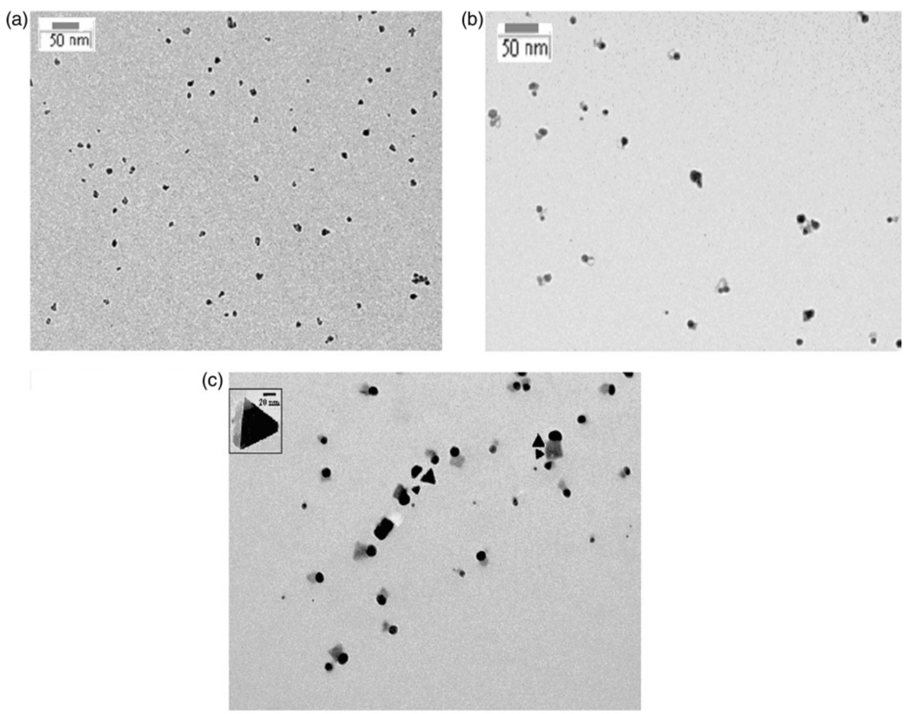

Figure 1. TEM images of silver nanoparticle sample prepared in DPBA (microwave conditions: 300 W, irradiated for (a) 3 minutes, (b) 8 minutes, (c) 12 minutes, inset shows a single silver nanoprism.

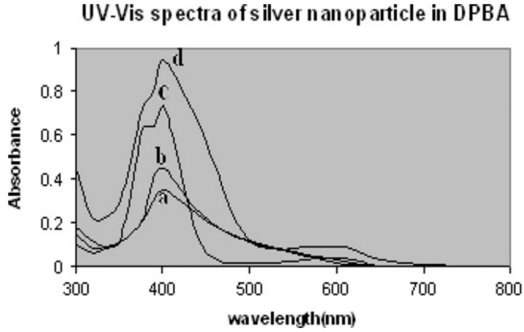

Figure 2. UV-Vis spectra of silver nanoparticles prepared in DPBA, at different time under microwave irradiation. Microwave conditions (300 W): (a) 3 minutes, (b) 8 minutes, (c) 12 minutes, (d) 16 minutes.

N^1,N^2-diphenylbenzamidine (DPBA) under microwave condition after 3 minutes, are nearly uniform spherical in shape and well-dispersed. The average diameter of particles is below 12 nm with a narrow size distribution, which may be due to the coordinating ability of the N-atom in N^1,N^2-diphenylbenzamidine (DPBA). It is interesting to note that silver nanoparticles obtained in DPBA after 8 minutes irradiation have regular geometrical shape. Most of them are triangular (edge length ~50–100 nm) or truncated triangular nanoprisms (figure 1(c), which will be discussed further in the optical properties section (figure 2). The range selected for microwave radiation power was between 300–650 W, but 300 W was found appropriate for the required solution.

3.2. *Optical properties*

The position and shape of plasmon absorption of noble metal nanoclusters are strongly dependent on particle size, dielectric medium, and surface-adsorbed species [17, 18]. The formation process and the optical properties of the silver nanoparticles can also be identified from both the color change and UV-Vis spectra of the solutions. The UV-Vis absorption spectra of the aqueous solutions containing as-prepared silver nanoparticles are shown in figure 2. The change of peak position and the shape of the absorption spectra were obvious during the whole reaction process. The heating time ranges taken were 3, 8, 12, 16 minutes. Using DPBA as reducing agent, as the reaction progressed, the solution was observed to change from colorless to transparent yellow to light brown, and then to mauve with some opalescence. The yellow to yellowish brown colors observed in different solutions are symptomatic of the presence of silver nanoparticles in the solution. As shown in figure 2, when the sample was irradiated for 3 minutes, an intense absorption peak at 403 was observed attributed to the characteristic surface plasma excitation of silver nanoparticles (figure 2) [19]. After irradiation for 8 minutes, a shoulder at 376 nm was observed altogether with a peak at 403 nm. As the reaction time was further increased the same shoulder was observed at 376 nm. The color change and the presence of shoulder indicate the existence of silver particles of various sizes and shapes at various irradiation times, and that the final product has an anisotropic morphology. It is well known that the shape and size of inorganic nanocrystals control their widely varying electrical, optical and catalytic properties. All of these silver colloidal aggregates were stable for several months.

4. Conclusions

Silver nanoparticles obtained by chemical irradiation and chemical reduction of silver ions in DPBA have been studied. It can be concluded that microwave radiation significantly promoted the nucleation of the nanoparticles without interfering considerably with the particle growth process. Not only the heating is faster through microwave radiation, but also the temperature distribution of the solution is more uniform. As such, this has led to the fast reaction rate and narrow size distribution of the Ag nanoparticles in the current study. Each solution was characterized by UV-Vis spectroscopy. The UV-Vis absorption spectrums of such particles are noticeably different from those obtained with pure metals. The average particle size of different preparations is found to be between 10 nm to 35 nm. It is important to mention here that the particles prepared in amidine or DPBA without stabilizer shows stability towards coagulation/aggregation as compared to that prepared in stabilizer. The shoulders obtained in the UV-Vis spectra of DPBA altogether with a peak at 403 nm may be possibly due to the anisotropic behavior of silver nanoparticles, as given by Mie's theory [20]. Metal nanoparticles with controlled shape are of great interest because of their morphology dependent properties [21] and potential applications in a lot of fields. El-Sayed *et al.* [22] have synthesized the controlled shape of the nanoparticles, which can be utilized for catalytic reactions as they depend not only on the size but also on the shape of the particles.

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