

Microwave-assisted synthesis of silver nanoparticles using benzo-18-crown-6 as reducing and stabilizing agent

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Abstract Benzo-18-crown-6 is employed to work as both reducing and stabilizing reagent in the reaction for synthesis of silver nanoparticles. Silver nanoparticles are analyzed using transmission electron microscope and UV–visible spectroscopic technique. The silver nanoparticles prepared in this way are uniform and stable, which can be stored at refrigerator for 5 months. Appearance of surface plasmon band at 420 nm indicated the formation of silver nanoparticles. Highly monodispersed stable silver nanoparticles were obtained within 3 min of microwave irradiation. Through transmission electron microscopy, silver nanoparticles were observed to be spherical.

Keywords Silver nanoparticles · Benzo-18-crown-6 · Microwave

Introduction

In the last few years, there have been considerable efforts dedicated to the preparation, characterization and applications of metal nanoparticles (NPs) (Pal and Deb 2012a, b, c, d, e; Pal et al. 2012, 2013; Pal et al. 2009; Shah et al. 2010; Bahgat et al. 2012; Kannan et al. 2012; Karuppuchamy et al. 2012; Nafees et al. 2012). Metal NPs are usually prepared by reduction of metal ions in solution. Meanwhile, because of the trouble-some aggregation of NPs induced by their high surface energy, surface passivating reagent and

capping reagent are usually involved in the reaction system (Manna et al. 2001; He et al. 2001). The choice of the capping agent is very critical because it determines the stability, solubility, reactivity and even the size and shape of the NPs during the synthesis. Crown ether is a macrocyclic polyether whose structure contains hydrogen, carbon and oxygen atoms. Each oxygen atoms are confined between two carbon atoms and exhibits a conformation with a hole. The common names of crown ethers have a prefix to designate the total number of atoms in the cycle and a suffix to designate the number of oxygen atoms in the cycle. Compared with general heating treatment, microwave synthesis is in favour of homogeneous heating and easy nucleation of noble metal NPs (Thiebaut et al. 1993; Correa et al. 1998; Patel et al. 2005). So, here microwave is employed to synthesize silver nanoparticles (AgNPs). Noble metal nanomaterials have attracted attention because of their potential applications in catalysis, energy, electronics and biotechnology (Xu et al. 2004; Jiangmei et al. 2009).

In our experiment, we find that benzo-18-crown-6 can work as both reducing and stabilizing reagent in the synthesis of AgNPs. Further, no other reagent is needed in the reaction except AgNO₃. The particles were characterized by transmission electron microscopic (TEM) and UV–visible spectroscopy studies.

Experimental section

Materials

AgNO₃ (Merck) and benzo-18-crown-6 (Fluka) employed were of analytical grade. They were used without further purification. All the aqueous solutions were prepared using triple distilled water.

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Apparatus

Glasswares were cleaned with ultrasonic cleaning bath, Spectra Lab India, model UCB-40 using mild detergent and after proper washing rinsed with ultrapure water. Cleaning normally lasts between 3 and 6 min. Ultrasonic cleaning uses cavitation bubbles induced by high frequency pressure (sound) waves (usually from 20 to 400 kHz) to agitate a liquid. The agitation produces high forces on contaminants adhering to substrates like metals, plastics, glass, rubber and ceramics. This action also penetrates blind holes, cracks and recesses. A Samsung CE2877 domestic microwave oven (850 W), Samsung India Electronics Ltd. New Delhi, India was employed for irradiating solutions. Absorption spectra were recorded in a Varian Carry 50 UV–visible spectrophotometer equipped with a peltier temperature controller unit. The particle size and morphology of the NPs were characterized by Morgagni 268D TEM operating at 80 KB (Mega view III Camera CCD) at the All India Institute of Medical Sciences (AIIMS), New Delhi.

Preparation of AgNPs

In a typical procedure, 1 ml of 0.2 M benzo-18-crown-6 and 10 ml of 0.0001 M AgNO_3 were taken in a 50-ml conical flask and placed in a microwave oven that was operated at the 300 W for 3 min. The colourless solution instantaneously turned into the characteristic pale yellow colour, indicating the formation of AgNPs.

Results and discussion

Formation of AgNPs

The advantage of microwave-mediated synthesis over the conventional heating is the improved kinetics of the reaction generally by one or two orders of magnitude, due to rapid initial heating and the generation of localized high-temperature zones at reaction sites (Liu et al. 2005). The TEM image of the AgNPs is shown in Fig. 1. The AgNPs, which were obtained in benzo-18-crown-6 under microwave irradiation after 3 min are nearly uniform and spherical in shape and well dispersed. It is interesting to find that AgNPs can be synthesized with benzo-18-crown-6 and AgNO_3 promoted by microwave. Figure 2 shows the corresponding particle size distribution histogram of the AgNPs. The size distribution histogram reveals that such AgNPs range from 6 to 11 nm in size. About 25 % of these NPs consist of particles with 6 nm diameter, 15 % particles were of 7 nm size, 25 % particles were of 8 nm size and size of the remaining particles was in the range of



Fig. 1 TEM image of AgNPs

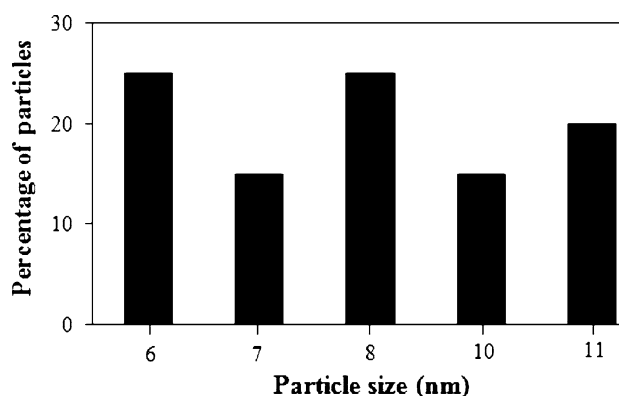


Fig. 2 Size distribution of the AgNPs synthesized under optimum experimental conditions

10–11 nm diameter. Figure 3 shows the typical UV–visible spectra of the silver colloidal solution. It can be observed that stronger absorbance peak appears at about 420 nm. The peak is symmetrical and there is no obvious absorption range of 450–700 nm, which indicates that negligible aggregation occurs in this reactive system and the NPs are well dispersed.

Effect of microwave irradiation time and power

The position and shape of plasmon absorption of noble metal nanoclusters are strongly dependent on particle size, dielectric medium and surface-adsorbed species (Kamat et al. 1998; Heilmann et al. 1999). The formation process and the optical properties of the AgNPs can also be identified from both the colour change and UV–visible spectra of the solutions. The UV–visible absorption spectra of the aqueous solutions containing prepared AgNPs are shown in Figs. 4 and 5. The changes of shape of the absorption spectra were obvious during the whole reaction process. As shown, the heating time ranges taken were 3, 6, 9, 12 min. (Table 1) and the power ranges taken were 180, 300,

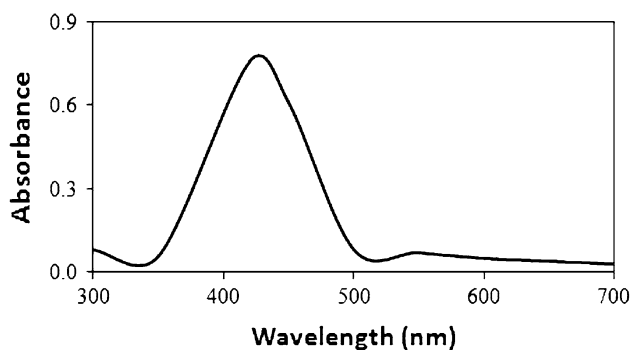


Fig. 3 UV-visible spectra of AgNPs

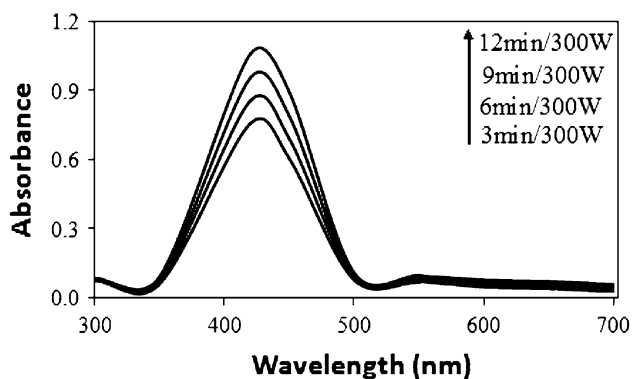


Fig. 4 UV-visible spectra of AgNPs at different heating time under microwave irradiation

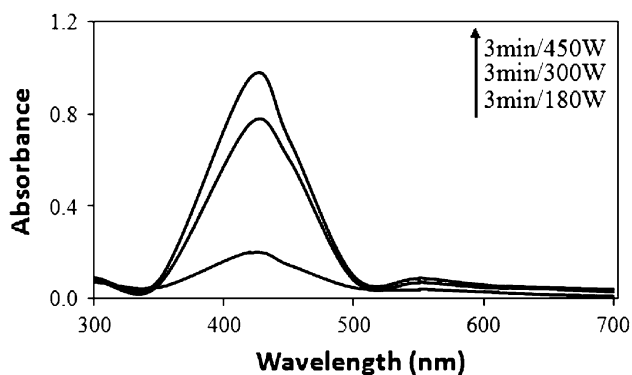


Fig. 5 UV-visible spectra of AgNPs at different heating power under microwave irradiation

450 W (Table 2). The solution was observed to change from colourless to transparent yellow to dark yellow indicating the formation of larger number of NPs with increased heating time. There is only one symmetric absorption peak at 420 nm which is the characteristic surface plasmon resonance of spherical AgNPs (He et al. 2001). According to Mie's theory, small spherical nanocrystals should exhibit a single surface plasmon band, whereas anisotropic particles should exhibit two or three

bands, depending on their shape. Similarly, the gradual increase in heating power also produces the same effect due to the reasons mentioned as above.

Stabilization of AgNPs

As shown in Fig. 6, the absorbance spectra of silver colloidal solution have been only slightly changed in position and absorbance intensity, but exhibit invariability in shape and symmetry, after the solution has been stored for 5 months at refrigerator ($-4\text{ }^{\circ}\text{C}$) and the solution is still clear yellow with no obvious change of colour. The result

Table 1 Effect of microwave irradiation time at constant power on the formation of AgNPs

S. No.	Solution composition	Irradiation time/W	Optical property of resulting solutions
1	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	3 min/300 W	Pale yellow
2	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	6 min/300 W	Comparatively dark yellow
3	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	9 min/300 W	Comparatively dark yellow
4	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	12 min/300 W	Comparatively dark yellow

Table 2 Effect of microwave irradiation power at constant time on the formation of AgNPs

S. No.	Solution composition	Irradiation time/W	Optical property of resulting solutions
1	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	3 min/180 W	Very light yellow
2	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	3 min/300 W	Pale yellow
3	0.0001 M AgNO_3 + 0.2 M benzo-18-crown-6	3 min/450 W	Comparatively dark yellow

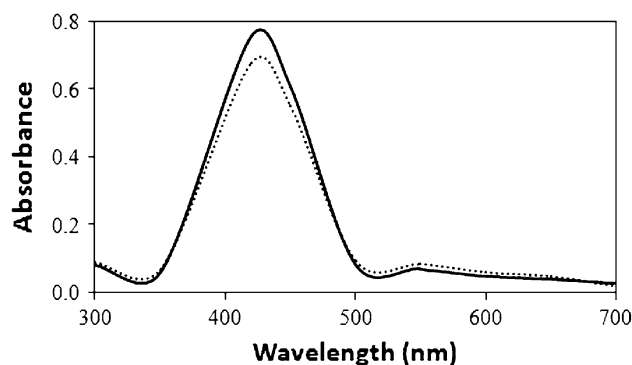


Fig. 6 UV-visible spectra of AgNPs after it is stored for 5 months at refrigerator

implies that the AgNPs prepared by this method are very stable with negligible aggregation.

Conclusions

AgNPs were synthesized under microwave irradiation using benzo-18-crown-6 as both reducing and stabilizing reagent. 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 AgNPs in the current study. Silver colloidal solution was characterized by UV–visible spectroscopy. The UV–visible spectra showed that these synthesised samples have absorbance peak at 420 nm. The AgNPs prepared in this way are uniform and stable, and can be stored at refrigerator for 5 months without any visible change.

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