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ORIGINAL ARTICLE

Extracellular bio-synthesis of silver nanoparticles



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Abstract The effect of cetyltrimethylammonium bromide, CTAB has been studied on the optical properties and morphology of advanced Ag-nanoparticles (AgNPs) using *Oriental plane* leaves extract as a reducing-, stabilizing- and capping-agent for the first time. The formation of Ag-nanodisks was monitored by measuring the UV–vis spectra at different time intervals (5, 10, 20 and 30 min) after adding the leaves extract (from 1 to 5 cm³) to the different AgNO₃ solutions ([Ag⁺] = 4.0, 8.0, 12.0, 16.0 × 10⁻⁴ mol dm⁻³). The sigmoidal nature of the reaction-time plots suggests the involvements of an autocatalytic reaction path. In the presence of CTAB, the peak at 450 nm is shifted to shorter wavelength, i.e., 425 nm and sharpness of the surface resonance plasmon (SRP) band also decreases. The results confirm a significant change in the morphology and/or agglomeration tendency with CTAB. Transmission electron microscopy (TEM) results show the formation of stable AgNPs at different concentration of AgNO₃ gives mostly spherical particles with diameter ranging from 10 to 30 nm.

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1. Introduction

Cetyltrimethylammonium bromide exhibits a number of roles in the synthesis of spherical, nonspherical (wires/rods, disks, sheets/plates, cubes, prisms, hollow structures, multi-branched and/or multi-pods metallic gold and silver nanoparticles) (Chen et al., 2003; Sau and Murphy, 2004; Kuo and Huang, 2005; Bakshi, 2009). It has been established that surfactant aggregates, especially micelles, reverse micelles and macro-

emulsions, will get an edge over other stabilizers (Pileni, 1993). Syntheses of branched metal nanostructures need a surfactant, especially CTAB, as a shape-directing agent (Lou et al., 2006; Bakr et al., 2006). Surfactant chains tend to self-associate, resulting in the formation of various aggregates (micelles, microemulsions, vesicles, etc.) (Fendler, 1982; Tascioglu, 1996; Tondre and Hebrant, 1997; Bunton, 2006). Reduction ability of natural plants extract came directly from the various constituents containing –NH₂, –COOH, –OH, –SH, etc., groups. The role and use of shape-directing cetyltrimethylammonium bromide in the similar investigations involving greener reducing agents has been neglected (Khan et al., 2012a, 2012b; Zaheer and Rafiuddin, 2013). Gardea-Torresdey et al. (2002) and Gardea-Torresdey et al. (2003) prepared the gold and silver nanoparticles by using living plants for the first time. Very recently, the literature is replete with the investigations to the use of natural products (azadirachta

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indica leaf broth (Shiv Shankar et al., 2004), aloe vera plant extract (Chandran et al., 2006), camellia sinensis (Vilchis-Nestor et al., 2008), lemongrass leaves extract (Shankar et al., 2005), natural rubber (Abu Bakar et al., 2007), starch (Vigneshwaran et al., 2006), sesbania drummondii (Sharma et al., 2007), seed extract of jatropha curcas (Bar et al., 2009), nyctanthes arbortristis flower extract (Das et al., 2011) as an alternate source of the toxic reductants for the synthesis of advanced nanosilver particles).

In this article, we describe a one-pot chemical reduction method to the formation of AgNPs using aqueous leaves extract of *Oriental plane*, is large, deciduous tree of the Platanaceae family. Large number of molecules such as platanin, tannin, allantoin (diureide of glyoxylic acid), phlobaphene (insoluble phenolic substances), mannitol (sugar alcohol; osmotic diuretic agent and a weak renal vasodilator), platanolic acid (hydroxy-carboxylic acid), and platanol are the bioactive constituent of chinnar leaves. Keeping in view the role of citric acid, ascorbic acid, sugars and amino compounds (Al-Thabaiti et al., 2008; Khan and Talib, 2010; Khan and Al-Nowaiser, 2011; Rafey et al., 2011; Hussain et al., 2011; Khan et al., 2012, 2013) for the synthesis of advanced AgNPs we are interested in developing a 'green' route to synthesize AgNPs using *Oriental plane* leaves extract as reducing as well as capping agent. Therefore, this study aimed at exploring the possibility of synthesizing AgNPs using a bio-chemical reduction method and CTAB (a shape-directing stabilizer) under normal atmospheric conditions. To the best of our knowledge, this is the first ever report on *Oriental plane*-assisted green synthesis of AgNPs. In the present study, we show that an extract of *Oriental plane* leaves placed in an aqueous solution of AgNO_3 , resulted in the reduction of the Ag^+ ions and formation of stable AgNPs. The method is simple, clean and the required only reactants (extract and AgNO_3) and water, and this method has an advantage in higher scale production of AgNPs over the chemical and physical methods.

2. Materials and methods

2.1. Synthesis of silver nanoparticles

To the preparation of aqueous solution of chinnar leaves extract, 10 g fresh leaves collected from the Srinagar, Jammu and Kashmir, India, 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 Whatman filter paper No. 40. The perfect transparent clear filtrate contains only soluble organic moieties of the chinnar leaves and the solid residue is discarded. This resulting aqueous solution used for the reduction of Ag^+ ions to the metallic Ag. A fresh stock solution of AgNO_3 (molecular weight: 169.87 g/mol, assay: 99%; Merck, India) was prepared by dissolving requisite solid AgNO_3 in double-distilled water. Exactly 5.0 cm^3 of the extract was added to 50 cm^3 reaction mixture (0.01 mol dm^{-3} ; 8.0 cm^3 AgNO_3 + 37 cm^3 water) in a 250 ml Borosil flask and kept it at room temperature for the reduction process. As the reaction time increases, appearance of pale-yellow observed which indicates the formation of AgNPs (Al-Thabaiti et al., 2008; Khan and Talib, 2010;

Khan and Al-Nowaiser, 2011; Rafey et al., 2011; Hussain et al., 2011; Khan et al., 2012, 2013).

2.2. Characterization of silver nanoparticles

The appearance of silver sol (reduction of Ag^+ ions by leaves extract) was monitored by UV-vis spectroscopy (Shimadzu UV-vis spectrophotometer; model UV-1800, Japan) as a function of time by using a quartz cuvette with water as reference. The morphology of AgNPs was determined by using transmission electron microscope (Hitachi 7600 with an accelerating voltage of 120 kV). The selected area electron diffraction (SADE) data were also recorded. Sample for TEM analysis was prepared by coating of aqueous AgNPs drops on carbon-coated copper grids, and kept for 5 min; the extra solution was removed using blotting paper at room temperature.

3. Results and discussions

3.1. Visual observations and UV-vis spectra

A preliminary visual observation shows that the initial color of the reaction mixture after the addition of leaves extract to the aqueous AgNO_3 solution was nearly colorless. Interestingly, the color of the reaction mixture changed from pale-yellow, pink-yellow, light brown, wine-red to dark brown exponentially with reaction-time as aggregation proceeds. Colourlessness of reaction mixture at the initial stage and the final deep reddish-brown color after the completion of the reaction are shown in (Fig. 1), which indicates the AgNPs shape, size and the size distribution altering with the reaction time at different stages (Khan et al., 2012). The color change might be due to the excitation of SPR in the production of AgNPs (Mulvaney, 1996). The spectra of the biosynthesis production of AgNPs are noted at different time intervals and are shown in Fig. 2 for the 5.0 cm^3 of leaves extract. The SRP peak observed at 450 nm confirms the influence of aqueous chinnar leaf extract in reducing Ag^+ ions to AgNPs from aqueous AgNO_3 solution. Absorbance intensity of broad SRP band increases steadily as a function of reaction time. A weak absorbance peak was observed at 450 nm with 1.0 cm^3 of extract after 5 min. Interestingly, the position of the maximum absorption was shifted to a shorter wavelength (from 450 to 425 nm; blue shift). Sharpness of the peak increases with time indicating that much smaller AgNPs were generated with time (Fig. 3). In addition to a sharp peak at 425 nm, a weak shoulder also developed at 475 which might be due to the anisotropic growth of AgNPs. The broadness of the peak indicates the wide size distribution of the nanoparticles in the biomolecules constituents of leaves extract (Song and Kim, 2009).

3.2. Kinetics and mechanism

The reaction-time curves show that the Ag^+ ions reduction into Ag^0 occurs very rapidly and more than 90% of the reduction of Ag^+ ions will be completed in 10 min. From 10 to 30 min, the reaction stops as the intensity of the reaction shows almost a parallel line with x -axis with respect to time (Fig. 4). No appreciable change in absorbance was noticed after 10 min

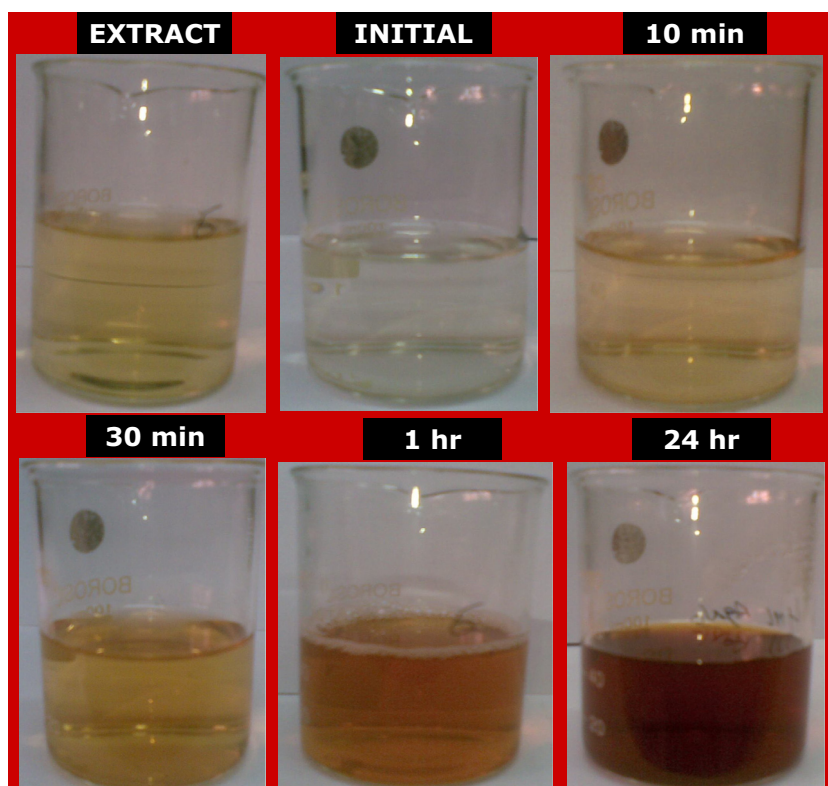


Figure 1 Optical images of chinnar leaves extract and its reaction product with AgNO_3 at different time intervals. *Reaction conditions:* $[\text{Ag}^+] = 16.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{extract}] = 5.0 \text{ cm}^3$, temperature = 30°C .

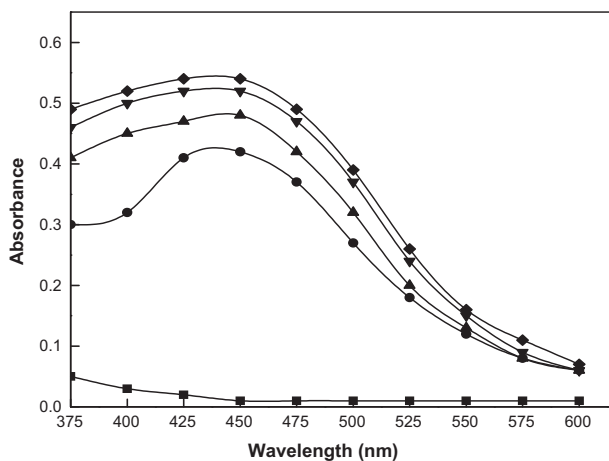


Figure 2 UV-vis bioreduction kinetics of the reaction of *Oriental plane* leaves extract with aqueous AgNO_3 with different time intervals. *Reaction conditions:* $[\text{Ag}^+] = 16.0 \times 10^{-4}$, $[\text{extract}] = 5.0 \text{ cm}^3$; (■; only leaves extract), time = 5 (●), 10 (▲), 20 (▼) and 30 min (◆).

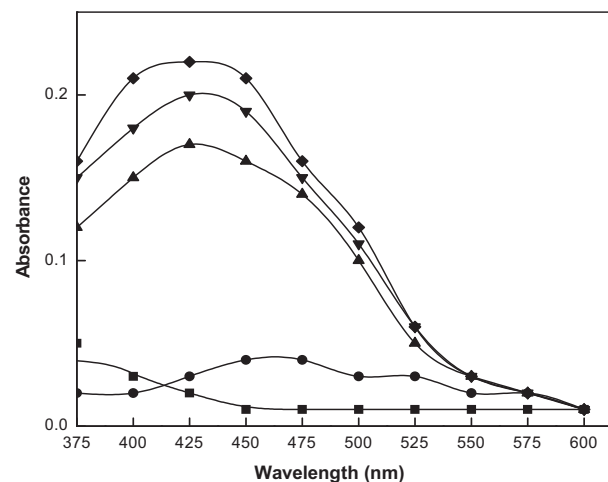


Figure 3 UV-vis bioreduction kinetics of the reaction of *Oriental plane* leaves extract with aqueous AgNO_3 with different time intervals. *Reaction conditions:* $[\text{Ag}^+] = 16.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{extract}] = 1.0 \text{ cm}^3$; (■; only leaves extract), time = 5 (●), 10 (▲), 20 (▼) and 30 min (◆).

for all the $[\text{Ag}^+]$ used in the entire study, confirming the complete reduction of Ag^+ ions to AgNPs. The sigmoidal shape of the reaction-time curves clearly suggests that autocatalysis was involved in the path of AgNPs formation (Huang et al., 1993; Mehta et al., 2010). Surprisingly, formation of transparent pale yellow color silver sol was not observed at lower $[\text{Ag}^+]$ ($\leq 2.0 \times 10^{-4} \text{ mol dm}^{-3}$) whereas, yellowish-white

precipitate was also formed at higher $[\text{Ag}^+]$. Therefore, it can now be stated confidently that formation of AgNPs is not directly proportional to the $[\text{Ag}^+]$; small $[\text{Ag}^+]$ being enough to initiate the formation of metal nucleation center which acts as a catalyst for the reduction of other Ag^+ present in the reaction mixture.

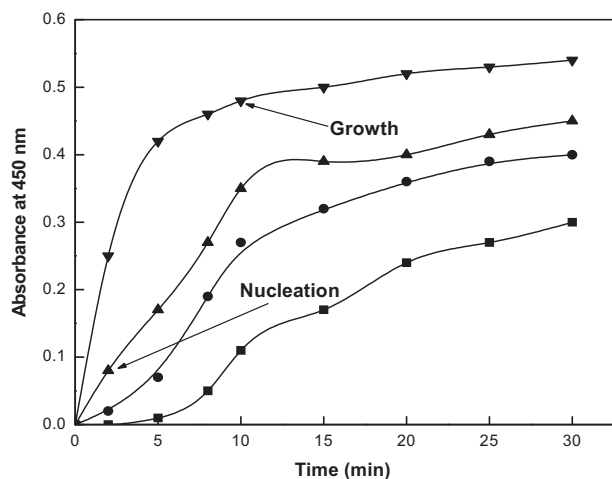
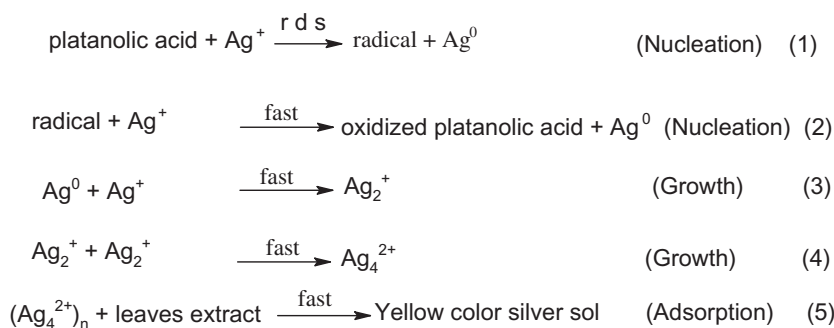


Figure 4 Reaction-time curves showing the effect of $[Ag^+]$ on the nucleation and growth of Ag-nanoparticles at room temperature. Reaction conditions: [extract] = 5.0 cm^3 , $[Ag^+] = 4.0$ (■), 8.0 (●), 12.0 (▲) and $16.0 \times 10^{-4} \text{ mol dm}^{-3}$ (▼).

Before attempting to propose a mechanism for the Ag-nanoparticles (reduction of Ag^+ ions into Ag^0 ; nucleation), it is necessary to discuss the species of silver metal particles existing in aqueous solution. Various species of colloidal silver such as Ag_2^+ , Ag_3^+ , Ag_4^+ , Ag_8Ag^+ or Ag_9^+ and Ag_6^{4+} exist in aqueous solution and in zeolites, as suggested by various investigators (Khan et al., 2012b; Mulvaney, 1996; Huang et al., 1993; Henglein, 1993). Out of these species, only Ag_4^{2+} can be stabilized for a long time in the presence of a polyanion even under air and growth stops at the stage of this species. On the basis of above results and discussion, Scheme 1 mechanism to the reduction of Ag^+ ions by constituents of chinnar leaves extract is proposed.

Hydroxy groups of reducing sugars and/or platanolic acid reduce Ag^+ into Ag^0 (Eq. (1); rate-determining step (RDS)). The neutral atom Ag^0 reacts with Ag^+ to form the relatively stabilized Ag_2^+ clusters as shown in Eq. (3). Ag_2^+ clusters dimerize to yield Ag_4^{2+} (yellow-color silver sol; stable species) (Eq. (4)) (Henglein, 1993). The intervention of free radical was detected by adding acrylonitrile as a scavenger, and the formation of white precipitate (Signorella et al., 1996) appeared slowly as the reaction proceeded indicating in situ generation of free radicals. Control experiments with Ag^+ ions and leaves extract did not show formation of a precipitate.



Scheme 1 Mechanism to the formation of AgNPs.

3.3. Shape-directing effect of CTAB

Surfactants are the amphiphilic molecules, which create highly anisotropic interfacial regions lining the boundary formed by the highly polar aqueous and nonpolar hydrocarbon regions. Micelles, dynamic aggregates can alter morphology and other surface optical properties to different extent depending upon their nature of head group, type of counter-ions and length of hydrophobic tail (Yu and Yam, 2004; Pal et al., 1997). Bakshi (2010) and Bakshi (2009) used different surfactants, anionic, cationic and Gemini to the synthesis of multibranch advanced Ag and Au NPs and reported these stabilizers acted as shape-directing agents. In order to see insight into the sub- and post-micellar role of shape-directing CTAB, a series of experiments were performed at two different [CTAB] i.e., 4.0×10^{-4} and $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ at fixed concentrations of other reagents. The observed results are summarized in Fig. 5 as absorbance–wavelength profiles. The intensity of the SRP band was increased rapidly with time. However, the position of the maximum absorption was shifted to a shorter wavelength with the variation of reaction-time, indicating that much smaller AgNPs were generated in the presence of CTAB. The peak at short wavelength may be attributed to the out-of-plane quadrupole (Jin et al., 2001; Kelly et al., 2003). In the present study, we did not observe any significant effect of sub- and post-micellar [CTAB].

3.4. TEM images and SADE patterns

Fig. 6 shows typical TEM images and SADE ring patterns of AgNPs prepared in the absence and presence of CTAB using chinnar leaves extract. These results suggest that the obtained AgNPs were mostly irregular and agglomerated in an unsymmetric manner on to the surface of Ag^0 , reduction species of Ag^+ , with a larger size of 30 nm (Fig. 6A). The reason for the aggregation is due to the presence of excess amounts of reducing moieties. The TEM analyses corroborate well with the results drawn from the corresponding reaction-time curves (Fig. 3). In the presence of CTAB, the interactions and solubilization of reducing molecules occur with the positive head group of CTAB. The AgNPs are also adsorbed and/or bound with the CTAB, which in turn, altered the morphology drastically and the number of spherical shaped AgNPs was also increased (Fig. 6C). TEM micrographs clearly indicate the presence of coatings surrounding the AgNPs which might be due to the terpenoids and/or reducing sugars present in the

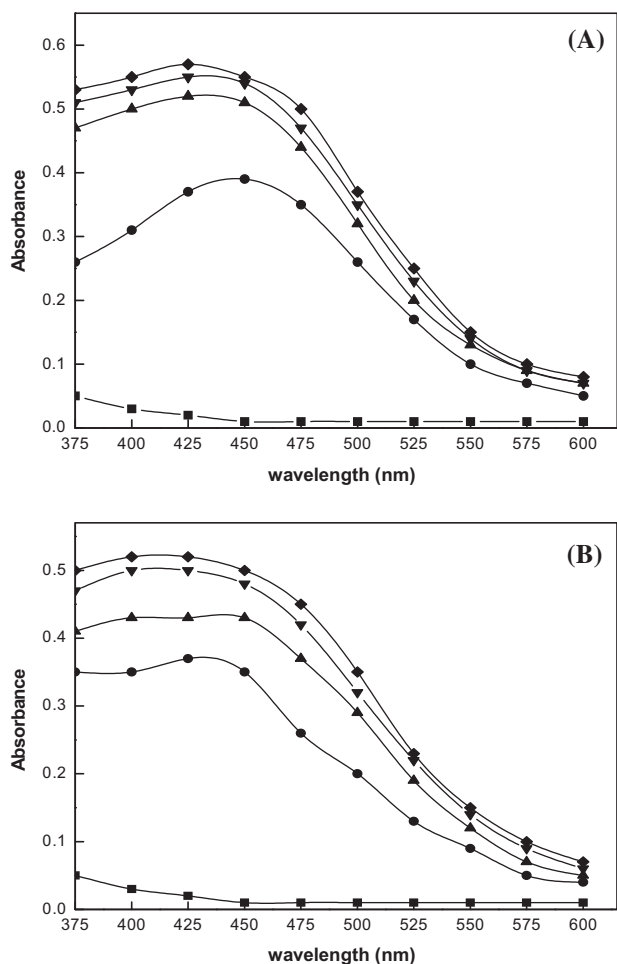


Figure 5 Absorption spectra of extract (■) and its reaction product with $[Ag^+]$ ($=16.0 \times 10^{-4} \text{ mol dm}^{-3}$) at different time intervals. *Reaction conditions:* $[CTAB] = 4.0$ (A) and $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ (B); $[extract] = 5.0 \text{ cm}^3$, time = 5 (●), 10 (▲), 20 (▼) and 30 min (◆).

leaves extract acted as reducing- and capping-agents (Shankar et al., 2004; Rai et al., 2006). Fig 6B indicates that the AgNPs aggregated and/or deposited in a symmetric manner, resulted in the formation of beautiful silver (tiles-like structures with dimensions between 8 and 40 nm). The typical selected-area diffraction pattern is shown in Fig. 6C. The ring patterns are consistent with the plane families $\{110\}$, $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$, $\{331\}$ and $\{422\}$, of pure face-centered cubic silver structure (Huang and Yang, 2008; Guzman et al., 2008; Serra et al., 2009).

4. Conclusions

We have used *Oriental plane* leaves extract for the biogenic reduction of Ag^+ ions for the first time. The morphology (particle size and shape), shape of the spectra (intensity of peak and position of SRP band) and the stability of the resulting AgNPs are highly dependent on the concentration of $AgNO_3$, leaves extract, CTAB, and pH. Platanolic acid (hydroxy carboxylic acid, triterpene) of chinarr leaves extract was mostly responsible for the reduction of silver ions to nanosized silver particles.

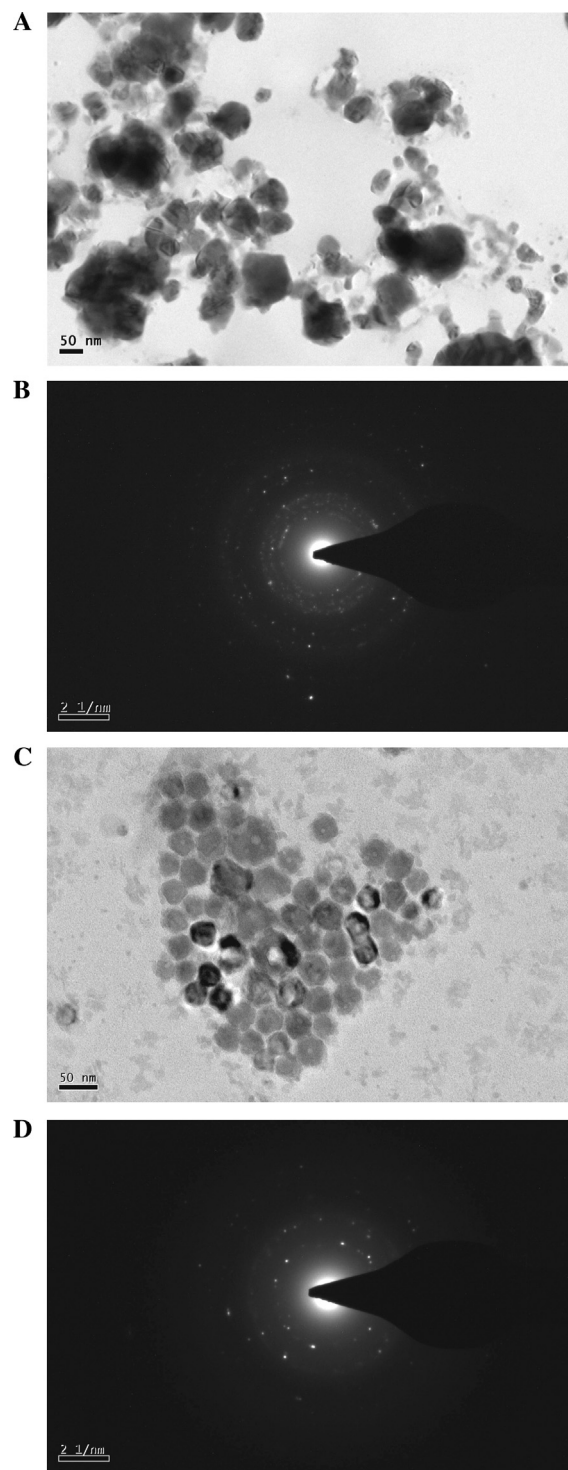


Figure 6 TEM images and SAED patterns of AgNPs synthesized using chinarr leaves extract (5.0 cm^3) in the absence (A and B) and presence of CTAB (C and D). *Reaction conditions:* $[Ag^+] = 16.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[CTAB] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[extract] = 5.0 \text{ cm}^3$.

TEM images show the ring of bilayer on the surface of the AgNPs. UV-vis spectroscopic data exhibit blue-shift of the SPR band with reaction time. AgNPs remain stable in the presence of high concentrations of leaves extract. The present

method may be helpful in the development of similar stable systems with other metal nanoparticles.

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