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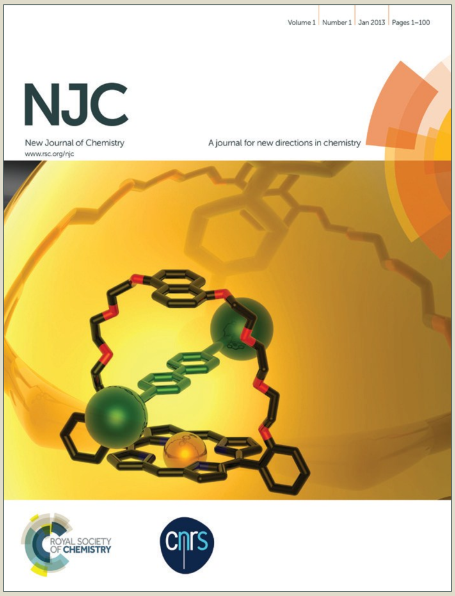

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Cyclodextrin encapsulated monometallic and inverted core-shell bimetallic nanoparticles as efficient free radical scavengers

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ABSTRACT

An effective method for the synthesis of monometallic and inverted core-shell bimetallic nanoparticles of silver and gold using four different cyclodextrins (α-CD, β-CD, γ-CD or HP β-CD) in aqueous alkaline medium at room temperature, stable for several months and having radical scavenging activity is reported. UV-visible absorbance spectra showed surface plasmon absorption maxima at 407 and 528 nm, for silver and gold respectively. The inverted core-shell bimetallic nanoparticles showed absorption maxima between the peaks corresponding to pure silver and pure gold nanoparticles & changed linearly with increasing concentration of shell metal precursor in the bimetallic nanoparticles. TEM showed the presence of uniform spherical particles in the range of 12-14 nm size and incase of bimetallic nanoparticles shows the inverted core-shell nanostructures in the range of 15-17 nm. All the encapsulated nanoparticles showed radical scavenging behavior as observed from the rapid quenching of the DPPH light absorption.

KEY WORDS: Cyclodextrin, silver-gold, monometallic and bimetallic inverted core-shell nanoparticles, free radical scavenger

INTRODUCTION

Metallic nanoparticles have been extensively investigated because of their unique electronic and optical properties that are substantially different from bulk materials.[1] A lot of effort has been devoted to the synthesis and characterization of stable dispersions of nanoparticles made of silver, gold, and other noble metals.[2] Part of the reason lies in the fact that these colloidal particles are useful in a broad range of areas, such as photography,[3] catalysis,[4] biological imaging,[5] photonics,[6] optoelectronics,[7] and surface-enhanced Raman scattering (SERS) detection.[8] A number of methods have been demonstrated in the past decades for preparing these nanoparticles; notable examples include condensation in the vapor phase,[9] chemical reduction in the solution phase,[10] photon or ultrasound-induced reduction in solutions or reverse micelles,[11] chemical vapor deposition (CVD) or electrostatic spraying on solid substrates,[12] and thermal decomposition of precursors in solvents, sol-gel matrixes, and polymer films.[13] The dispersions of these nanoparticles usually display a very intense color due to plasmon resonance absorption, which can be attributed to the collective oscillation of conduction electrons that is induced by an electromagnetic field.[14] It has been shown that the size, morphology, stability, and properties (chemical or physical) of these nanoparticles have a strong dependence on the specificity of the preparation method and the experimental conditions.[15] In recent research, several methods have been developed and described for the preparation of metal nanoparticles by using a reducing agent such as $NaBH_4$, citrate, hydrazine and ascorbate. The use of these strong reducing agents, produces small particles, but controlling the generation of the larger particles become difficult.[16] Moreover, such reducing agents are associated with environmental toxicity or biological hazards and also for the stabilization of metallic nanoparticles, wide range of polymers and reagents are used, which disturbs the composition and properties of metallic nanoparticles. In addition, in most of the cases, hazardous solvent has been used, the use of environmentally benign water would be beneficial as choice of reaction medium. It is essential that the production of nanoparticles be achieved by using minimum amount of material, which can function both as the reducing agent and the protecting agent, exclusive of external energy sources in an aqueous medium including the avoidance of impurities in the final products and as well as the reduced production cost. In order to overcome these difficulties for the synthesis and stabilization of metal nanoparticles, we have adopted "green chemistry approach" by using water-soluble supramolecular molecules "cyclodextrins" as a reducing agent and stabilizing agent in aqueous medium. Cyclodextrins (CDs) are nontoxic water-soluble cyclic oligosaccharides of D-glucopyranose units connected by 1,4-α-glycosidic linkages. The most common CDs are α, β and γ-CD, composed of six, seven and eight D-glucopyranose units, respectively.[17] CDs have a hydrophobic inner non-polar cavity and a hydrophilic polar exterior. The supramolecular chemistry of CDs in aqueous solution is a topic of commercial interest with a variety of applications.[18] These naturally and commercially available CDs have unique ability to form an inclusion complex with a wide variety of hydrophobic guest molecules in both solid and liquid state, polar and non-polar media and widely used in pharmaceutical industries.[19,20] It was shown previously that [60]fullerene does form an inclusion complex with β-cyclodextrin and the complex could behave as an efficient radical scavenger.[21] In this article, we describe a simple, effective and green approach for the synthesis of Ag, Au monometallic and Ag-Au, Au-Ag inverted core-shell bimetallic nanoparticles in aqueous mildly alkaline medium by using different CDs and show their efficient radical scavenging property. Here the CDs act as reducing agent as well as stabilizing agent and give stability to the nanoparticles for several months without agglomeration and the complex solution is an efficient free radical scavenger.

MATERIALS AND METHODS

β-cyclodextrin was obtained from Signet Chemical Corporation, Mumbai as a gift sample. α-cyclodextrin, HP β-cyclodextrin, γ-cyclodextrin, silver nitrate ($AgNO_3$), tetrachloroauric (III) acid (AuCl4), 2,2'-diphenyl-1-picrylhydrazyl (DPPH) (stored in dry ice) and iodine crystals were purchased from Sigma-Aldrich. All cyclodextrins were dried overnight under vacuum at 60^oC, and used without further purification. For the synthesis of metallic nanoparticles, 10 mM metals ($AgNO_3$ and $AuCl_4$) solutions as a metal salt precursor and 7 mM cyclodextrin solutions as a reducing as well as stabilizing agent were prepared in double distilled water. Double distilled deionised water was used throughout the work. Optical properties of the nanoparticles were determined using Shimadzu-2450 UV-visible spectrophotometer. Size and shape of the nanoparticles were measured on an energy-filtering transmission electron microscope [EF-TEM, EM 912 OMEGA (ZEISS, S-4700), 120 kV]. Samples were prepared for TEM analysis by placing a drop of the solution on a polymer coated copper grid and then dried under electric bulb for 30 min. The particle size distribution was measured using Static light scattering (SLS) by MiniDawn Tri-Star, Wyatt technology. FT-IR spectra were recorded on a Shimadzu-8400S infrared spectrophotometer at 30 scans using a KBr pellet method.

RESULTS & DISCUSSION

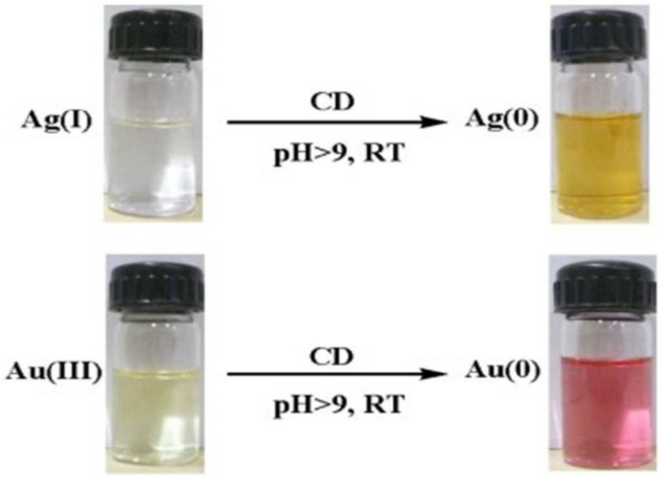
Synthesis of monometallic nanoparticles using cyclodextrins

Synthesis of Ag and Au monometallic nanoparticles were carried out as follows. To the 10 mL (7 mM) γ-CD solution, 0.05 mL (10 mM) metal solution and after two minutes 0.05 mL 0.1N NaOH were added so that the pH of the solution became 10-12 and reaction was carried at room temperature (in case of α-CD and β-CD gentle warm condition) for 20 min without extra reducing agent and stabilizing agent. The transparent colorless solution was converted to the characteristic pale yellow color in case of Ag nanoparticles and yellow color solution converted to the pink-violet color in case of Au particles, indicating the formation of silver and gold monometallic nanoparticles. The stability of these solutions was observed to be more than six months without changing its physicochemical properties at room temperature.

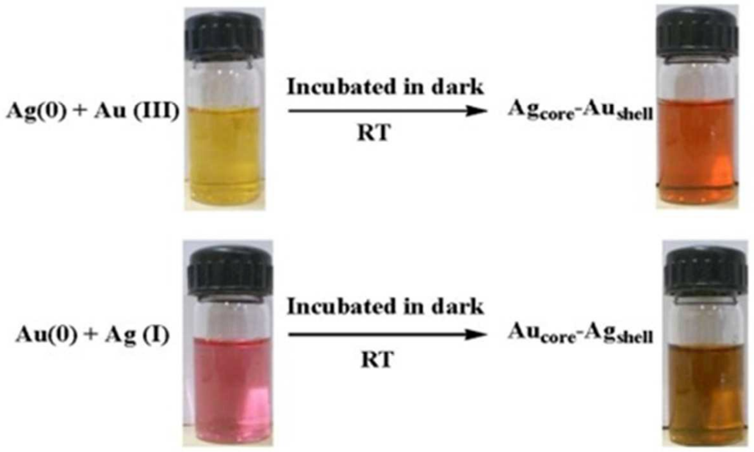
Synthesis of inverted core-shell bimetallic nanoparticles using cyclodextrins

Synthesis of Au_{core}-Ag_{shell} bimetallic nanoparticles were carried out as follows: An aliquot of 0.05 mL of $AgNO_3$ (10 mM) was added drop wise to 10 mL of the preformed gold colloidal solution. The solution was allowed to incubate for 20 min. After about 20 min, the pink color of the solution turned to reddish yellow, indicating the formation of a silver shell on the gold particles, i.e., the formation of Au_{core}-Ag_{shell} bimetallic nanoparticles. No extra CD or NaOH solution was added to induce the chemical reduction of silver ions and their deposition on the gold seed particles. The alkalinity of the gold colloidal solution helps to induce the chemical reduction of Ag (I) ions and their deposition on the gold particles. Similarly Ag_{core}-Au_{shell} bimetallic nanoparticles were prepared by adding 0.05 mL 10 mM $AuCl_4$ solution to preformed silver colloidal solution. In case of Ag_{core}-Au_{shell} nanoparticles, the initial yellow color of the solution gradually deceased, and a reddish wine color developed. Here, also, no extra CD or NaOH solution was added to induce the formation of core-shell particles.

In present study, an efficient strategy and green method to produced spherical silver, gold monometallic (Scheme 1) and silver-gold, gold-silver inverted core-shell bimetallic (Scheme 2) nanoparticles is developed by reducing metal compounds using supramolecular cyclic oligosaccharides cyclodextrins as reducing agent as well as stabilizing agent. “Cyclodextrins” have primary as well as secondary hydroxyl groups. These functional groups take part in the reduction of metal ions. The primary side (primary hydroxyl group) of cyclodextrins protect the monometallic nanoparticles for the formation of bimetallic inverted core-shell nanoparticles.



Scheme 1. Synthesis of monometallic Ag and Au nanoparticles



Scheme 2. Synthesis of inverted core-shell bimetallic Ag_{core}-Au_{shell} and Au_{core}-Ag_{shell} nanoparticles.

General reduction reaction conditions and schematic representation for the formation of nanoparticles is shown in Figure 1. Usually, apart from the formation of metallic nanoparticles in aqueous medium, the toxicity of reactants and stability of metallic nanoparticles in aqueous solution are equally important issues. Therefore, the use of cyclodextrins in the synthesis is showing promise not only

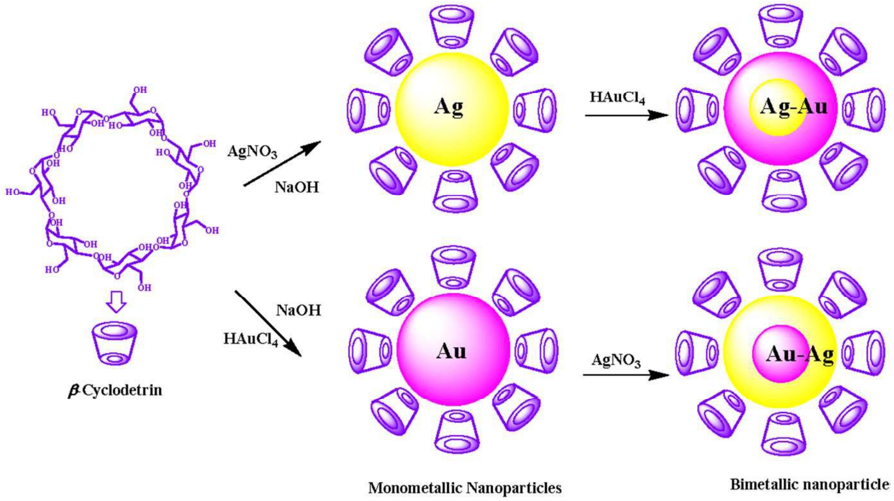


Figure 1. Schematic representation for formation of monometallic and bimetallic nanoparticles.

of the ‘green’ route but it also shows both reducing and stabilizing behavior at a same time to produce monodisperse nanoparticles without any addition of toxic reagents. The reaction rate is strongly influenced by concentration of metal precursor, cyclodextrin concentration, temperature and pH. In case of α-CD and β-CD the solution required gentle warm condition and stirring whereas in the case of γ-CD and HP β-CD solution they do not require temperature or stirring. We observed that the reaction starts immediately after mixing the metal solution with alkaline cyclodextrins solution and within twenty minutes the colorless solution of the silver converts into yellow color and yellow colored solution of gold converts into violet pink color, which are the characteristic surface plasmon absorption of the silver and gold nanoparticles respectively. Similarly for the inverted core-shell bimetallic nanoparticle we can observe the changes in surface plasmon resonance. The γ-CD and HP β-CD show good reducing ability due to their higher solubility compared to α-CD and β-CD.

Characterization

The nanoparticles formed by α-CD, β-CD, γ-CD or HP β-CD were fully characterized. The preliminary visible evidence for the formation of nanoparticles is the characteristic changes in surface plasmon (the coherent oscillation of the free electron is on the surface of metallic and the absorbance of an external electron field occurs due to the resonance) of nanoparticles by UV-visible absorbance spectroscopy. The UV-visible absorbance spectra of silver, gold monometallic and silver-gold, and gold-silver bimetallic inverted core-shell nanoparticles synthesized using γ-cyclodextrin as a reducing agent are given in Figure 2.

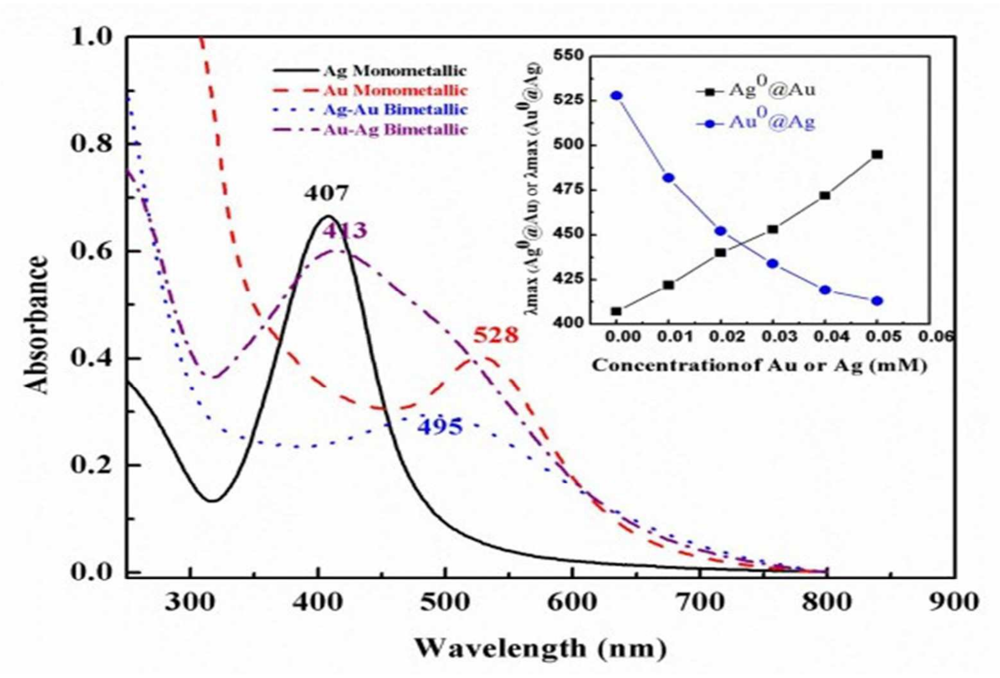


Figure 2. UV-visible absorbance spectra of monometallic and bimetallic nanoparticles, Inset: Surface plasmon bands (λ_{max}) of inverted core-shell bimetallic nanoparticles as a function of Au or Ag concentration from 0.01 mM to 0.05 mM at a constant concentration 0.05 mM of Ag or Au monometallic nanoparticles.

The UV-visible absorbance spectra reveal the formation of silver and gold nanoparticles by showing characteristic surface plasmon absorption maxima at 407 nm and 528 nm for monometallic silver and gold nanoparticles. Similarly for Au-Ag and Ag-Au core-shell bimetallic nanoparticles the surface plasmon absorbance shows at 413 nm and 495 nm, respectively. Thus, the change in surface plasmon of monometallic nanoparticles after addition of metal precursor confirmed the formation of bimetallic inverted core-shell nanoparticles. Further clarifications for the formation of the inverted core-shell architectures, i.e., Au_{core}-Ag_{shell} and Ag_{core}-Au_{shell} structures, typical complexation reactions with iodine were carried out under ambient conditions.[22,23] The successive changes of the surface plasmon absorption of the bimetallic colloids upon dissolution with iodine clearly support the formation of core-shell structures. An aliquot of iodine (10 mM) was added to 5 mL of bimetallic colloids separately, and the changes in absorbance values were measured spectrophotometrically. In the case of Au_{core}-Ag_{shell} particles, it was found that the shell first dissolves slowly and the peak due to the Au_{core}-Ag_{shell} nanoparticles gradually red shifts. On continuous shaking in the presence of oxygen, the yellow-colored solution (Au_{core}-Ag_{shell} nanoparticles) turned pink because of the stepwise removal of silver layers. Finally, bare gold nanoparticles, i.e., seeds, reappeared with the plasmon peak for gold nanoparticles at 528 nm via a double-hump curve. Addition of excess iodine then dissolved the gold nanoparticles, and finally, the solution became colorless. This study confirms that the gold layer was completely covered by silver nanoparticles, i.e., Au_{core}-Ag_{shell} bimetallic nanoparticles formed in solution. In the case of Ag_{core}-Au_{shell} nanoparticles, the Au shell first dissolved, and the color changed from pink to yellow. Because of the dissolution of the Au shell, the peak was blue-shifted to 407 nm for silver, and finally, the yellow color vanished because of the dissolution of the Ag core. The kinetics of the dissolution reaction has been described elsewhere[24] hence, the stepwise vanishing of the surface plasmon oscillation demonstrates that the core-shell structures are dissolved in the presence of iodine under ambient conditions. The surface plasmon maxima changes linearly with increasing concentration of shell metal precursor in the bimetallic nanoparticles as shown in Figure 2 (shown in the inset). TEM images of silver, gold monometallic and silver, gold inverted core-shell nanopartilces are shown in Figure 3.

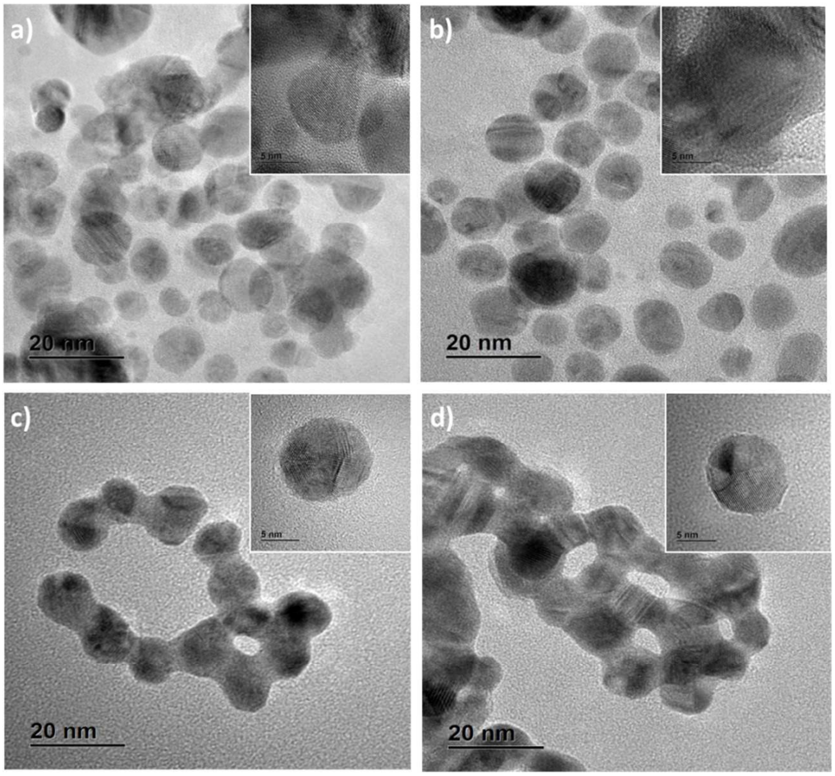


Figure 3. TEM images of (a) Ag, (b) Au, (c) Ag-Au, and (d) Au-Ag nanoparticles. The inset shows the HRTEM images of corresponding metal nanoparticles.

As can been seen, the Ag and Au nanoparticles show crystal lattice structure (shown in inset of Figure 3a and Figure 3b) whereas in the core-shell structures (inset Figure 3c and Figure 3d) we can see the two different lattices corresponding to Ag and Au. In this present method of synthesis of the Ag NPs, the Ag ions are reduced by the cyclodextrin molecules and then stabilized by them. Each β-cyclodextrin molecule has seven primary hydroxyl groups and 14 secondary hydroxyl groups. Here, the reduction of the Ag(I) ions is due to the primary hydroxyl group of the cyclodextrin and not by any additional reductant. Therefore addition of Au(III) leads to its reduction by the cyclodextrin molecules. If any galvanic reaction is happening, each gold atom reduction requires three Ag atoms oxidation. If that were happening in our method of synthesis, then the core would have been very much smaller than what is observed and very importantly, separate Ag NPs would have been observed. Even if there is formation of Ag ions due to the galvanic reaction, they would be reduced by the cyclodextrins and covered with Au. This is supported from the atomic percentage of the core-shell NPs in the EDX. In general, the atomic percent of Ag is less than Au in Ag_{core}-Au_{shell} NPs and atomic percent of Au is more that Ag in Au_{core}-Ag_{shell} NPs. TEM micrographs demonstrate the symmetric spherical shape and very narrow size distribution of all the samples and particles size was 12±2 for monometallic silver and gold nanoparticles and particle size was 15±2 for bimetallic nanoparticles. Generally, the sizes of the observed particles in TEM are in good agreement with the values obtained by SLS as shown in Table 1 for different cyclodextrins. TEM micrographs of bimetallic nanoparticles showed inverted core-shell particles. The EDX spectra for bimetallic nanoparticles confirm the presence of Ag and Au along with cyclodextrin (C and O), (not shown here).

Table 1. Particle size of nanoparticles with different cyclodextrin measured by SLS.

Cyclodextrins (CDs)	Ag Monometallic (nm)	Au Monometallic (nm)	Ag-Au Core-Shell Bimetallic	Au-Ag Core-Shell Bimetallic
α-CD	13±1	12±2	14±3	15±1
β-CD	12±0.5	11±2	15±2	16±2
γ-CD	10±1	11±1	14±1	16±2
HP β-CD	9±1	10±2	14±2	15±1

In order to investigate the binding sites of CDs on the surfaces of nanoparticles, the FT-IR spectra of pristine γ-CD and nanoparticles prepared by γ-CD were recorded and compared. The non-covalent interaction between metal ions and hydroxyl groups of γ-CD was confirmed by FT-IR spectroscopy, shown in Figure 4. The FT-IR spectra of the metallic nanoparticles and parent γ-CD was found to be nearly similar, except that the relative intensity of the transmittance band at 1156 cm^{-1}, 1030 cm^{-1}, 946 cm^{-1}, 756 cm^{-1} and 578 cm^{-1} of typical of the free γ-CD significantly decreased in the blank sample, which is because of the hydroxyl groups interaction with metal ions. Moreover, a shift in the stretching frequency of hydroxyl groups was observed from 3373 cm^{-1} to 3309 cm^{-1} and it was also observed that the broad peak of hydroxyl group after formation of nanoparticles become narrow.

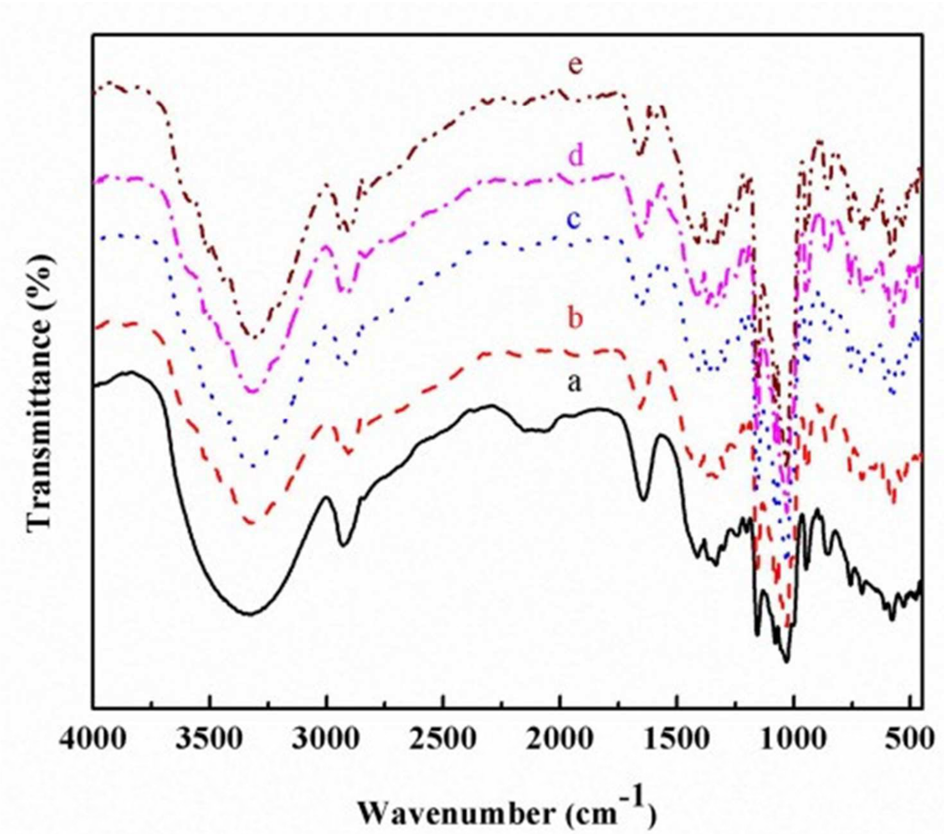


Figure 4. FT-IR spectra of (a) γ-CD (b) Ag-γ-CD, (c) Au-γ-CD (d) Ag-Au-γ-CD and (e) Au-Ag-γ-CD nanoparticles.

Radical Scavenging

In order to demonstrate the antioxidant properties of nanoparticles we have carried out the radical scavenging reaction of the stable free radical DPPH with all the nanoparticles and the progress of the radical scavenging reaction of DPPH with AgNPs visually as well as by UV-VIS absorbance at definite intervals of time is shown in Figure 5. It can be seen that the absorbance at 527 nm maximum decreased steadily with time and it was also visually observed that the deep violet color of the radical (DPPH) being bleached gradually.

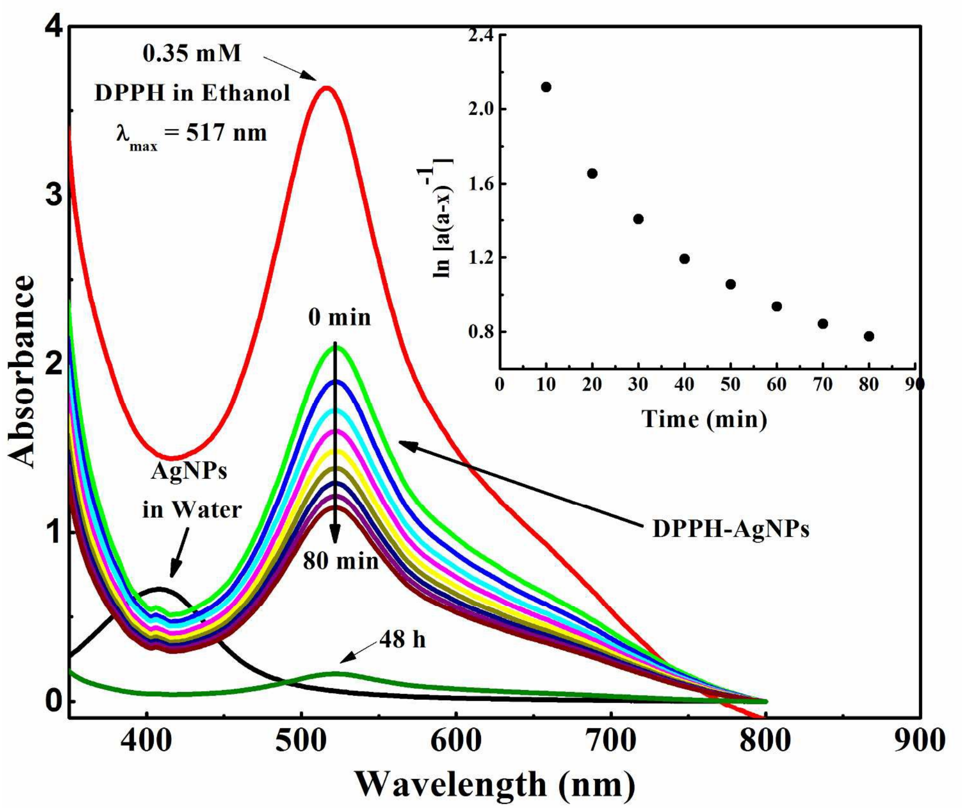
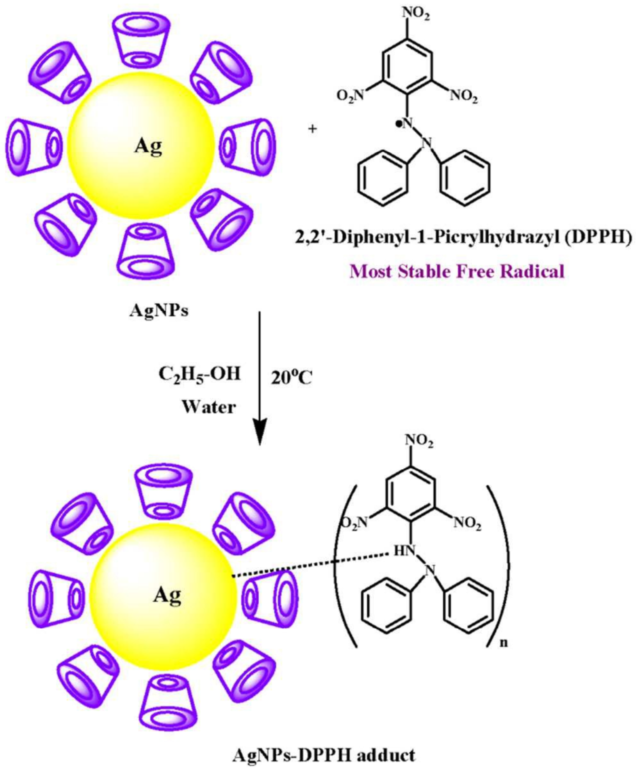


Figure 5. UV-Vis spectra of scavenging of DPPH free radical by AgNPs, Inset: pseudo-first order rate correlations for DPPH reaction with AgNPs.

It shows that the typical absorbance band of DPPH in ethanol undergoes a bathochromic shift from 517 to 527 nm as shown in Scheme 3. The decrease in absorbance is detectable within minutes of the reactions. In order to observe the effect of solvent and pristine cyclodextrin on DPPH scavenging, blank experiment was conducted without AgNPs by mixing DPPH solution and water. However, no considerable change in absorbance at the characteristic peak maximum was observed even after several hours of contact. AgNPs have a large number of reaction sites; each nanoparticle is capable of reacting with a number of DPPH radicals. Hence, in terms of molar equivalents, the concentration of AgNPs in effect is very high as compared to that of DPPH during the initial stages of the reaction, while the concentration of DPPH would decrease steadily with time, the concentration of AgNPs would practically remain constant.



Scheme 3. Reaction scheme for radical scavenging of stable free radical DDPH

A similar behavior was observed for AuNPs and also the bimetallic Ag_{core}-Au_{shell} NPs and Au_{core}-Ag_{shell} NPs. The radical scavenging activity of metallic NPs has been an area of interest[25] recently though the mechanism of the radical scavenging has not been understood well yet. To understand the quenching of the DPPH by the NPs, a kinetic study was undertaken. It was found that the reaction between AgNPs and DPPH follows the first- order reaction rate law {ln $[a(a-x)^{-1}] = kt$}. The plot of the term ln $[a(a - x)^{-1}]$ vs. reaction time (t, min) is shown in Figure 5 (Inset), where 'a' denotes the initial DPPH concentration and (a - x) the concentration of DPPH at different reaction times, evaluated from the DPPH standard curve, led to a straight line with a satisfactory correlation of 0.9539. The pseudo-first-order rate constant (k) was evaluated to be 1.79×10^{-2} min^{-1}. However, there was a deviation from linearity beyond 80 min, indicating that the pseudo-first-order reaction condition no longer remains valid beyond this stage i.e., the concentration of AgNPs begins to perceptively decrease beyond a certain stage of the reaction. The pseudo-first-order reaction of DPPH observed in the early stages of the reaction further indicates that multiple sites of each AgNPs reacted with DPPH. Similarly, AuNPs and inverted core-shell bimetallic nanoparticles show radical scavenging properties.

CONCLUSIONS

Spherical, monodispersed silver, gold monometallic nanoparticles and silver-gold, gold-silver inverted core-shell bimetallic nanoparticles can be produced using a soft approach under mild conditions using cyclodextrins, the NPs showing excellent radical scavenging behaviour. This mild reduction activity of cyclodextrin and its protective and stabilizing action on the NPs prevents the galvanic reaction in the formation of Ag_{core}-Au_{shell} bimetallic nanoparticles as reported in literature[26]. Unlike other organic antioxidants, these nanoparticles retain their antioxidant activity for a longer time and are themselves non-toxic and show catalytic behaviour. Higher homologues of the cyclodextrin are better for preparing stable nanoparticles solution due to solubility considerations, which could be useful for the detection and quenching of reactive organic species (ROS) with potential for biomedical applications and for imaging applications.

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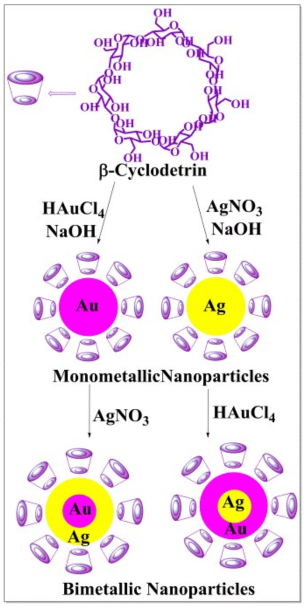

A facile and green route for monometallic and core-shell bimetallic Ag and Au nanoparticles using cyclodextrin as reducing and stabilizing agent for radical scavenging