RESEARCH PAPER

Synthesis and photo physical properties of Au @ Ag (core @ shell) nanoparticles disperse in poly vinyl alcohol matrix

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Abstract Synthesis of core @ shell (Au @ Ag) nanoparticle with varying silver composition has been carried out in aqueous poly vinyl alcohol (PVA) matrix. Core gold nanoparticle (~ 15 nm) has been synthesized through seed-mediated growth process. Synthesis of silver shell with increasing thickness (~ 1–5 nm) has been done by reducing Ag^+ over the gold sol in the presence of mild reducing ascorbic acid. Characterization of Au @ Ag nanoparticles has been done by UV–Vis, High resolution transmission electron microscope (HRTEM) and energy dispersive X-ray (EDX) spectroscopic study. The blue shift of surface plasmon resonance (SPR) band with increasing mole fraction of silver has been interpreted due to dampening of core, i.e. Au SPR by Ag. The dependence of nonlinear optical response of spherical core @ shell nanoparticles has been investigated as a function of relative composition of each metal. Simulation of SPR extinction spectra based on quasi-static theory is done. A comparison of our experimental and the simulated extinction spectra using quasi-static theory of nanoshell suggests that our synthesized bimetallic particles have core @ shell structure rather than bimetallic alloy particles.

Introduction

In recent years, considerable efforts have been devoted to synthesize bimetallic nanoparticles for their different optical (Henglein and Brancewicz 1997), catalytic (Toshima and Wang 1994; Harada et al. 1993; Wang and Toshima 1997), surface plasmon resonance (SPR) band energies (Han et al. 1998; Link et al. 1999), magnetic properties (Link et al. 1999; Sun et al. 2000) relative to their individual metal nanoparticles. Noble metal nanoparticles have mainly been studied because of their unique optical properties, especially gold and silver have a broad absorption band in the visible region of electromagnetic spectrum (Kreibig and Vollmer 1995; Kerker 1969; Bohren and Huffman 1983; Mulvaney 1996). Solutions of these noble metals have intense colour, because of the collective oscillation of the free conduction electrons induced by the interacting electromagnetic field and this is termed as SPR. Core @ shell nanoparticles form an important class of nanostructures from fundamental, scientific and technological points of view, since one of the

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metals forming the outer shell determines the surface properties of the particles, whilst the other present in the core is responsible for optical, catalytic and magnetic properties of the system.

Methodologies for synthesis of bimetallic nanoparticles can be divided into two categories: one is co-reduction and the other is successive reduction of the metal salts. Generally co-reductions of the two metal salts give alloy particles, whereas successive reduction gives the core @ shell nanoparticles. Recently Chiu et al. (2009) and Chen and Chen (2002) synthesize core @ shell nanoparticles using micro-emulsion techniques. Synthesis and optical properties of Ag @ TiO_2 nanocomposite with the increasing thickness of shell layer have been studied by Ganguli et al. (Vaidya et al. 2010). There is a variety of synthetic techniques for the preparation of noble metal core @ shell (Au @ Ag and Ag @ Au) nanoparticles such as in aqueous media (Douglas et al. 2008; Mallik et al. 2001; Srnova-Sloufova et al. 2004) and nonaqueous media (Nath et al. 2005). Recently Pal et al. (Pande et al. 2007) synthesized Ag @ Au and Au @ Ag nanoparticles, and it has been substantiated by their enhanced surface enhanced Raman scattering (SERS) properties. Teo et al. synthesized Au–Ag cluster ($Au_{18}Ag_{20}$) with SPR band maxima at 495 nm (Teo et al. 1987). Mulvaney (1996) and Sinzig et al. (1993) prepared Ag @ Au nanoparticles, having two distinct SPR bands and their relative intensity depends on the thickness of the shell. It has already been established that spherical silver nanoparticles exhibit SPR peak around 400 nm where as for gold the SPR peak appears at 520 nm. But the optical properties of bimetallic nanoparticles depend on the structure and composition of individual particles. For Au @ Ag (core @ shell) nanoparticles, there is only one SPR band with maxima in between that of the pure silver and pure gold, and the optical absorbance depends on the alloy compositions (Pande et al. 2007; Pal et al. 2007). Roy et al. theoretically shows that there is red shift of the SPR band with the increase in the gold concentration based on quasi-static limit (Roy et al. 2003).

In this article we report Au @ Ag nanoparticle using seed-mediated growth approach in polyvinyl alcohol (PVA) matrix. Thickness of the shell has been monitored by increasing concentration of Ag^+ ions and its subsequent reduction to Ag by mild reducing ascorbic acid. SPR extinction spectra show gradual damping of core SPR band with increasing thickness of shell, and the band gradually shifted towards the shell SPR position. The increase of shell thickness has nicely been reflected on the high resolution transmission electron microscope (HRTEM) micrograph and energy dispersive X-ray (EDX) spectra of the core @ shell (Au @ Ag) nanoparticles. We also simulate the SPR spectra using quasi-static model for bimetallic particles. Our calculated spectra nicely demonstrate that our synthesized bimetallic particles have core–shell structure rather than bimetallic alloy.

Experimental section

Reagents and instruments

All chemicals used in the experiment were analytic reagent (AR) grade. Silver nitrate ($AgNO_3$, >99.8%), $HAuCl_4 \cdot 2H_2O$ was purchased from RFCL Ltd. (India). Sodium borohydride ($NaBH_4$, >99%) was purchased from S.D. Fine-Chem. Ltd. Ascorbic acid ($C_6H_8O_6$, >99%) and sodium hydroxide (NaOH, >97%) were provided by E. Merck Ltd. Poly vinyl alcohol (PVA) (25–30 cps, degree of polymerization 1700–1800, pH 5–7) was purchased from LOBA chemie. CTAB was purchased from E. Merck Ltd. and recrystallised from 1:1 ethanol water mixture before use. All solutions were prepared using triple distilled de-ionized water.

Characterization of core @ shell nanoparticles was made by UV–Vis spectroscopy, HRTEM, and EDX study. UV–Vis spectroscopic measurements were carried out using a 'SHIMADZU' UV-1601 spectrophotometer. HRTEM study of nanoparticles has been done using JEOL-JEM-2100 HRTEM.

Preparation of gold seed

Aqueous 2.5 mL, 5×10^{-4} M $HAuCl_4$ solution was mixed with 2.5 mL, 0.2 M aqueous CTAB solution in a two-necked round-bottom flask and the solution was placed over freezing mixture (-10 °C) for 15 min. Ice-cold aqueous 0.3 mL, 0.1 M $NaBH_4$ was added to the above mixture with vigorous stirring for 15 min. Solution turned pink indicating the formation of gold hydrosol. This pink coloured gold hydrosol was kept at room temperature for 2 h and was used as seed in the subsequent synthesis of larger spherical-shaped gold nanoparticles.

Preparation of spherical-shaped gold nanoparticles through seed-mediated growth process

Aqueous growth solution was prepared by mixing 5 mL 0.2 M CTAB, 5 mL 1 mM $HAuCl_4 \cdot 2H_2O$ in a round-bottom flask at room temperature. Colour of the solution became deep yellow due to complexation between CTAB and gold solution (Au^{3+}). Aqueous 0.07 mL, 0.01 M mild reducing, ascorbic acid was added to the growth solution and the yellow colour solution became colourless due to reduction of Au^{3+} to Au^{+}. Next 0.05 mL of aged gold seed was added to the above colourless growth solution and solution was kept undisturbed at room temperature for 12 h. Colour of growth solution turned red indicating the formation of larger gold nanoparticles.

Preparation of Au @ Ag nanoparticles

Aqueous 0.8 mL of gold hydrosol was mixed with 4 mL PVA (1% by weight) solution in a two-necked round-bottom flask. Different amounts (0.1, 0.25, 0.5, 0.75 mL) of 1 mM $AgNO_3$ were added to the above solution with constant stirring at 25 °C. Again 0.2 mL, 0.1 M NaOH was added to the above solutions to maintain basicity and then 0.1 mL, 0.1 M ascorbic acid to reduce Ag^{+} to Ag. Colour of the hydrosol changes from pink to orange to yellow with the increasing concentration of $AgNO_3$. This colour change indicates the formation of silver shell over the gold core and it has been substantiated by UV–Vis extinction spectroscopy which is shifted towards silver SPR band with increasing concentration of $AgNO_3$.

Results and discussion

UV–Vis spectra

It has been observed that nanosize silver and gold particles interact with visible light more effectively than any known organic or inorganic chromophore. This interaction is a consequence of the large density of conducting electrons, their size confinement dimensions smaller than the mean free path and the unique frequency dependence of the real and imaginary parts of the dielectric function in the metal, collectively resulting in the existence of SPR. Size

and shape of the particles as well as the dielectric function of the surrounding medium determine the frequency and strength of the resonance (Burda et al. 2005). SPR band of pure gold and pure silver appears at 520–530 and 400–420 nm, respectively.

Figure 1 shows the UV–Vis extinction spectra of gold, and a series of Au @ Ag hydrosol with varying silver concentration. The absorption bands with peaks at 520 and 410 nm are due to SPR band of gold and silver nanoparticles, respectively. As the metal of shell layer forms a thin uniform film (3–4 nm) on the core particles, the SPR extinction band shows only one peak which results from the metal of shell layer (Pande et al. 2007). It has been observed that the colour of Au @ Ag hydrosol changes with the increasing thickness of Ag layer. In this study, the colour of the reaction solution changes from colourless to pink during the formation of the Au nanoparticles. After the addition of silver salt solution along with ascorbic acid to the above gold sol, the colours of the solution change from pink to light red to golden yellow with the increasing concentration of silver salt (Fig. 2). The formation of Au @ Ag leads to the disappearance of SPR peak of gold nanoparticles. From the UV–Vis extinction spectra we can reasonably infer that the reduction of silver salt alone occurs on the preformed gold core surface rather than forming more nucleation sites. With the increase in concentration of silver, i.e. Au:Ag = 4:1 and 4:2 (assuming all the gold and silver ions are being reduced during the course of reaction), the plasmon absorption band of gold slightly blue-shifted whilst the plasmon peak of gold still existed.
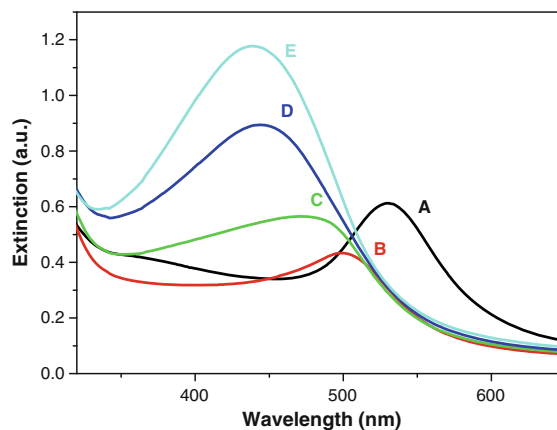

Fig. 1 UV–Vis extinction spectra of Au core (*A*) and Au @ Ag nanoparticles with increasing concentration (*B → E*) of Ag
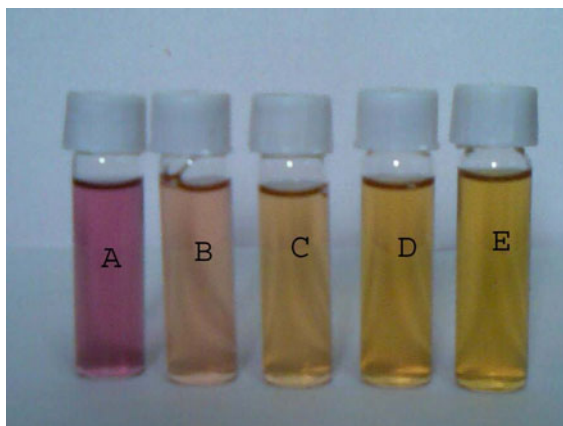
We believe that the concentration of silver under the above composition is small enough to form a thick layer (3–4 nm) on the surface of gold core. Since the atomic size of Ag is similar to that of Au, the inter diffusion between Au atoms and Ag atoms is easy and thus the surface layer of core becomes alloy of silver and gold rather than the pure silver. The alloy formation on the surface layer of core nanoparticles shows the SPR band which is slightly blue-shifted from the pure gold SPR band.

If gold and silver ions are reduced simultaneously by sodium borohydride in the same solution, then gold–silver alloy particles are formed. The alloy formation is excluded from the fact that the optical extinction spectrum shows only one SPR band and the wavelength at which maximum extinction occurred varies in a nonlinear fashion with respect to the increasing mole fraction of the shell layer. The divergence of SPR band maxima between Au, Ag, and Au @ Ag is due to the difference of extinction coefficients at the plasmon maximum.

We believe that in our present UV–Vis study the decrease in gold SPR intensity and the gradual blue shift of SPR band is due to the damping of gold SPR by the surface silver atoms. This dampening of gold SPR with increasing concentration of silver also confirms the formation of Au @ Ag nanoparticles.

HRTEM and EDX study

Figure 3A shows the HRTEM micrograph of gold particles which are being used as core particle in the

present core @ shell nanoparticle synthesis. Particles are mostly spherical in shape with an average diameter ~ 15 nm. Selected area electron diffraction (SAED) pattern of gold core nanoparticles is shown in Fig. 3B and it illustrates the crystalline nature of gold particle.

High resolution transmission electron microscopy images in Figs. 4 and 5 illustrate the formation of Au @ Ag nanoparticles of different shell thickness. HRTEM images show the core, i.e. gold particles
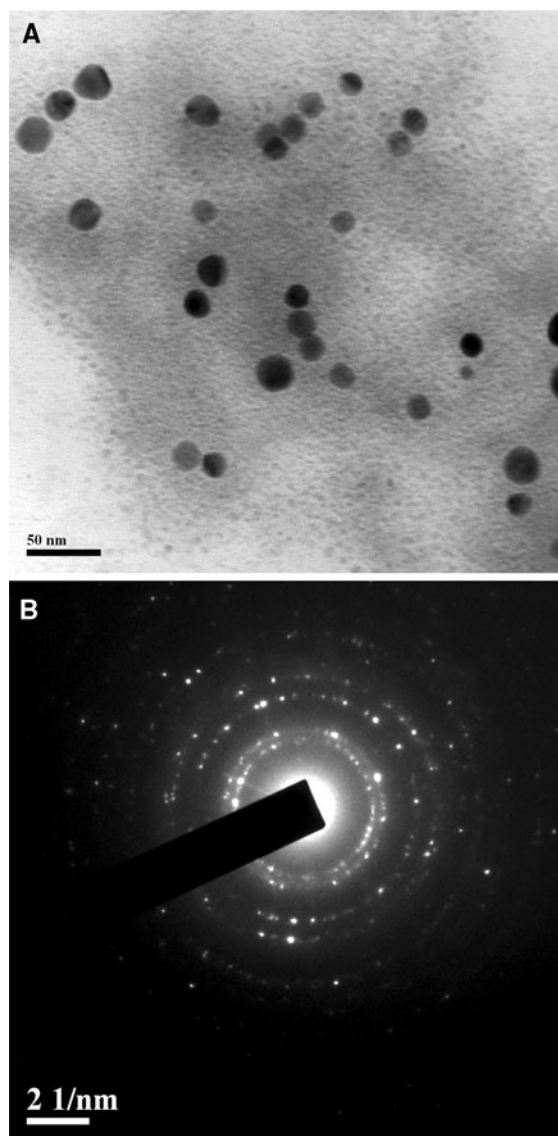

Fig. 3 HRTEM images of core Au nanoparticles obtained through seed-mediated growth processes (**A**) and its SAED images (**B**)
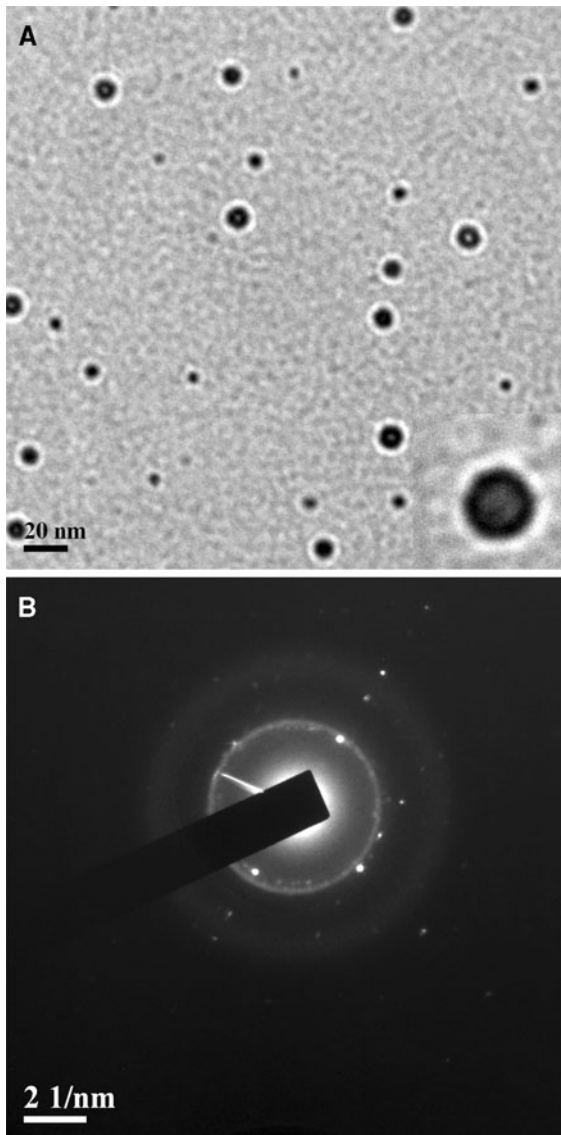
Fig. 4 HRTEM image (**A**) and SAED (**B**) of Au @ Ag nanoparticles with lower silver content (*inset* shows the clear picture of one core @ shell nanoparticles)

Fig. 5 HRTEM image (**A**) and SAED (**B**) of Au @ Ag nanoparticles with higher silver content

with high density and the core is surrounded by the shell of silver with thinner density. Similar to the observation of other research groups (Pande et al. 2007; Mulvaney et al. 1993; Tsuji et al. 2008; Hodak et al. 2000; Shibata et al. 2002), a clear boundary between Au and Ag elements can be distinguished by bright and dark contrast in our HRTEM images. In order to understand growth mechanisms of these Au @ Ag nanospheres, Au @ Ag nanocrystals have been prepared at different $AgNO_3/HAuCl_4$ molar ratios.

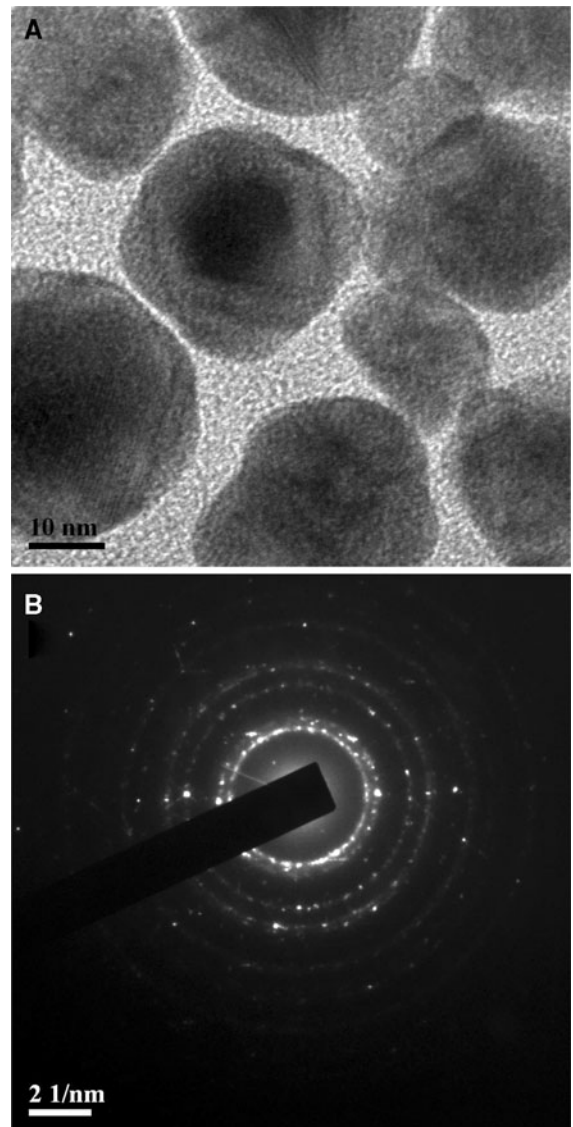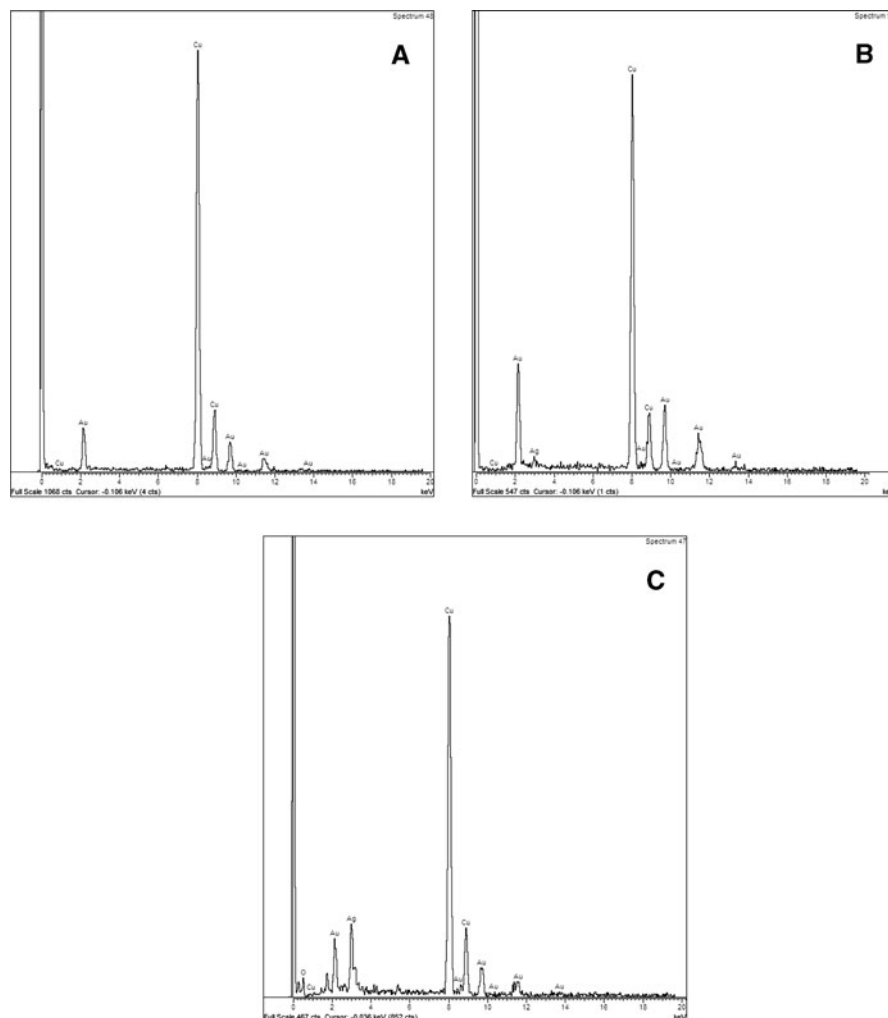At low silver content (Fig. 4), the Au @ Ag nanocrystals have core diameter 15 nm, similar to average diameter of Au core (Fig. 3) and its shell thickness is ~ 1 nm. The thickness of silver shells enlarges when silver content is increased (Fig. 5). Here thickness of silver shell using maximum concentration of Ag^+ (0.128 mM $AgNO_3$) achieves about five times thicker than the Au @ Ag nanocrystals with lesser silver (0.0192 mM $AgNO_3$) content. On the other hand thickness of gold core particle remains same as that of gold seed particle

(∼15 nm). Thus, Figs. 4 and 5 illustrate that silver atoms are deposited on the surface of core gold particle to form spherical Au @ Ag nanoparticles.

Relative composition of gold and silver in the Au @ Ag nanoparticles synthesized from different molar ratio of gold and silver has been determined using EDX study. For each molar ratio of Au:Ag about 20 particles on the Cu grid were chosen to analyse their average composition by EDX. The elemental ratio of core Au (Fig. 6A) is similar to the [HAuCl₄]. The elemental ratio of Au @ Ag particle with lower silver content (Au:Ag = 39.2:1.76) and higher silver content (Au:Ag = 18.08:16.21) are shown in Fig. 6B and C, respectively. This reveals that the concentration silver within the shell increases with increasing concentration of silver ions and thereby increases the thickness of silver shell.

Quasi-static model of nanoshell and the SPR spectra

The observed plasmon resonance shift shown in Fig. 1 can be understood with Mie scattering theory (Mie 1908). Mie theory is the solution of Maxwell's equations in spherical coordinates with boundary conditions appropriate for a sphere. In the modern approach to this problem the solutions to Maxwell's equations for the fields are expressed in a series expansion of vector eigen functions that form a complete set (Kerker 1969; Bohren and Huffman 1983; Stratton 1941; Sarkar 1996; Sarkar and Halas 1997). Nanoparticles have SPR maximum due to the collective excitation of electrons that are coupled to the transverse electromagnetic field. The electrons oscillate with respect to the positive ionic cores, and

Fig. 6 A EDX spectra of Au core. B EDX spectra of Au @ Ag nanoparticles with lower silver content. C EDX spectra of Au @ Ag (core @ shell) nanoparticles with higher silver content

it is the surface polarization that provides a restoring force. Mie theory requires that the dielectric function of the particle and the embedding medium be specified. This theory is phenomenological in character since it provides no physical insight into material properties other than what is specified by the input dielectric function.

Quasi-static model is an extension of Mie theory. In quasi-static model spatial variation of the electromagnetic field is neglected whilst the temporal dependence is preserved, considerably simplifying the calculations. Conceptually, the extension of Mie theory to a metallic shell is quite simple. The core @ shell system shown in Scheme 1B has been studied with Mie scattering theory, and expressions for the polarizability and the extinction cross-section of shell–core particles have been used to calculate the extinction spectra (Kreibig and Vollmer 1995; Sarkar 1996; Aden and Kerker 1951). Two assumptions are used in our analysis. The nanoshells are not perfectly spherical, but for calculation it is assumed that they

A

19 μM AgNO3 | Vit-C + NaOH

47 μM AgNO3 | 128 μM AgNO3
Vit-C + NaOH | Vit-C + NaOH

89 μM AgNO3 | Vit-C + NaOH

B

r_1

ε_3　ε_2　ε_1

r_2

Scheme 1 Schematic representation of Au @ Ag (core @ shell) nanoparticles. **A** Formation of Au @ Ag nanoparticles with increasing thickness of silver shell. **B** Quasi-static model of Au @ Ag nanoparticles

are spherical. It is also further assumed that the interactions between nanoparticles (e.g. dipole–dipole) will not be considered, since the nanoshell concentration is in the nanomolar range.

A schematic presentation of Au @ Ag nanosphere with increasing thickness of silver shell is shown in Scheme 1A. The core has a radius r_1 with dielectric function ε_1; the shell has a thickness $(r_2 - r_1)$ with dielectric function ε_2; and the embedding medium has dielectric function ε_3. It is important to note that ε_1 and ε_2 can have real and imaginary frequency-dependent components. According to the quasi-static theory of nanoshells, the absorption cross-section is given by the following expression (Averitt et al. 1999).

$$C_{abs} = \frac{8\pi^2 r_2^3 \sqrt{\varepsilon_3}}{\lambda} \text{Im}\left(\frac{\varepsilon_2\varepsilon_a - \varepsilon_3\varepsilon_b}{\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b}\right) \quad (1)$$

where $\varepsilon_a = \varepsilon_1(3 - 2p) + 2\varepsilon_2 p$, $\varepsilon_b = \varepsilon_1 p + \varepsilon_2(3 - p)$, $\varepsilon_1(\omega) = \varepsilon_1'(\omega) + i\varepsilon_1''(\omega)$, $\varepsilon_2(\omega) = \varepsilon_2'(\omega) + i\varepsilon_2''(\omega)$, $p = 1 - \left(\frac{r_1}{r_2}\right)^3$

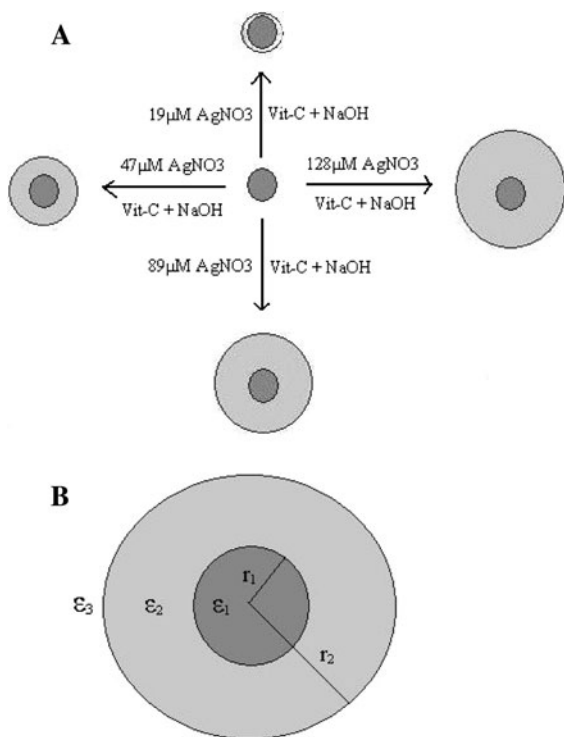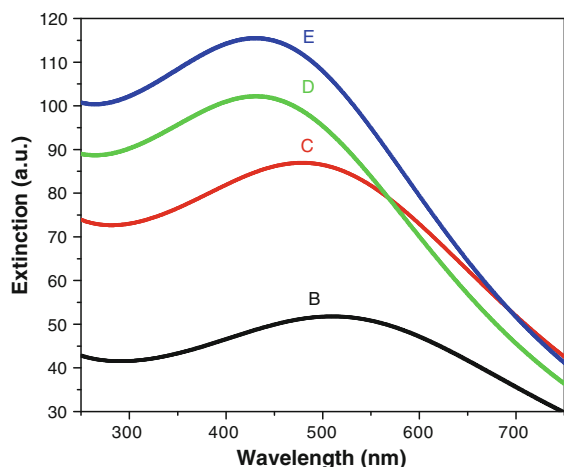$$C_{abs} = \frac{8\pi^2 r_2^3 \sqrt{\varepsilon_3}}{\lambda}\left(\frac{BC - AD}{C^2 + D^2}\right)$$

$$A = (3 - 2p)\left(\varepsilon_1'\varepsilon_2' - \varepsilon_1''\varepsilon_2''\right) + 2p\left(\varepsilon_2'^2 - \varepsilon_2''^2\right) - (3 - p)\varepsilon_3\varepsilon_2' - p\varepsilon_3\varepsilon_1',$$

$$B = (3 - 2p)\left(\varepsilon_1''\varepsilon_2' + \varepsilon_1'\varepsilon_2''\right) + 4p\varepsilon_2'\varepsilon_2'' - (3 - p)\varepsilon_3\varepsilon_2'' - p\varepsilon_3\varepsilon_1'',$$

$$C = (3 - 2p)\left(\varepsilon_1'\varepsilon_2' - \varepsilon_1''\varepsilon_2''\right) + 2p\left(\varepsilon_2'^2 - \varepsilon_2''^2\right) + (3 - p)\varepsilon_3\varepsilon_2' + p\varepsilon_3\varepsilon_1',$$

$$D = (3 - 2p)\left(\varepsilon_1''\varepsilon_2' + \varepsilon_1'\varepsilon_2''\right) + 4p\varepsilon_2'\varepsilon_2'' + 2(3 - p)\varepsilon_3\varepsilon_2'' + 2p\varepsilon_3\varepsilon_1''$$

We simulate the UV–Vis extinction spectra for Au @ Ag nanoparticles using a constant value of core radius (r_1) and different shell thickness $(r_2 - r_1)$. Keeping in mind the radius of our synthesized core @ shell particles, we use 15 nm for r_1 and the thickness of shell has been chosen from the HRTEM photograph of Au @ Ag nanoparticles (Figs. 4, 5). Our simulated SRP band (Fig. 7) suggests that the SPR maxima shifted towards the silver SPR band maxima with the increasing thickness of silver shell. This is in conformity with our experimental results, where we

Fig. 7 Simulated extinction spectra of Au @ Ag nanoparticles using Quasi-static model of core @ shell nanoparticle
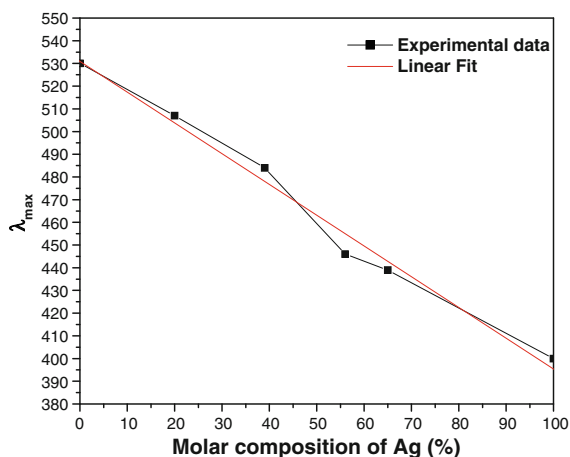

Fig. 8 Variation of extinction maxima (expt. curve) with increasing mole fraction of silver

observe that with the increasing thickness of silver shell layer core @ shell SPR band maxima shifted towards the silver SPR band position. Figure 8 shows the plot of SPR band maxima with the increasing mole fraction of silver and it shows nonlinear behaviour as that of our experimental plot. Similar nonlinear shift of SPR band using quasi-static model for core @ shell nanoparticle is observed by Zhu (2005). On the other hand for alloy nanoparticles, they observe a linear behaviour for the same plot. Thus, the above theoretical model suggests that our synthesized particles are core @ shell nanoparticles rather than alloy of gold and silver.

Conclusions

In this article we report core–shell nanoparticles, where core particles have been synthesized using seed-mediated growth approach. Since the growth process is a slower one, equilibrium size distribution of particles obtained through seeding growth approach shows uniform distribution of particle size. Important feature of a useful synthetic procedure is that the particles should be stable, and secondly, it is desirable for processes such as biofunctionalization, i.e. preparation should be carried out in aqueous environment. The present synthetic method has made considerable progresses in overcoming these issues. The nonlinear shift of the SPR band maxima with increasing concentration of silver has been explained in terms of dampening of core SPR by the shell SPR and it has been further substantiated theoretically using quasi-static theory of nanoshell.

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