

Hollow gold and platinum nanoparticles by a transmetallation reaction in an organic solution†

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Transmetallation reaction between hydrophobized silver nanoparticles with hydrophobized chloroaurate and chloroplatinate ions in chloroform results in the formation of hollow gold and platinum shell nanoparticles respectively.

Metal nanoparticles are being investigated in considerable detail due to their exciting potential applications in catalysis,¹ biological and chemical sensing,^{2,3} and optoelectronics.⁴ One of the important current challenges is to develop experimental recipes that would enable nanoparticle shape control in addition to size and polydispersity. A number of nanoparticle morphologies such as wires,⁵ rods,⁶ cubes⁷ and nanotriangles/prisms⁸ can now be routinely synthesized by wet chemical methods. Often, the shape-modulated nanostructures exhibit interesting catalytic⁹ and optoelectronic properties.

Of late, hollow metal nanoparticles have captured the attention of researchers. The increased surface area, low density, saving of material and concomitant reduction in cost coupled with the interesting optical properties of such structures has potential application in catalysis¹⁰ and cancer hyperthermia. Hollow metallic nanoparticles may be prepared by coating the surface of latex particles, silica beads, gold and silver nanoparticles by the desired material and then etching away the core¹¹ while retention of the core leads to the formation of thin metallic shells with interesting optical properties.¹² The Xia and Bai groups have recently demonstrated a promising alternative route to obtaining water dispersible hollow metal nanostructures of various shapes by a simple transmetallation reaction.^{10,13} This elegant method employs a sacrificial nanoparticle that by a galvanic replacement reaction with another suitable metal ion (transmetallation reaction) results in the formation of excellent hollow particles that take on the morphology of the sacrificial partner.^{10,13} In this communication, we demonstrate that a similar transmetallation reaction involving hydrophobic spherical silver nanoparticles and hydrophobized AuCl_4^- and PtCl_6^{2-} ions may be carried out in an equally facile manner in organic solvents resulting in excellent hollow Au and Pt nano shells that are organically dispersible. This adds significantly to this as yet little studied method; the synthesis of hollow metal nanoparticles such as Pt in an organic environment would be of much greater value in catalytic applications than a water-based process.¹⁰ Furthermore, organically soluble hollow nanoparticles would be a better option for optical coatings by spray-deposition than water-based formulations.

Silver nanoparticles synthesized in the aqueous phase by the sodium borohydride reduction of silver ions were immediately transferred into chloroform by stirring with 10^{-3} M chloroform solution of octadecylamine (ODA).¹⁴ After complete transfer of silver nanoparticles into the organic medium, it was separated from the aqueous phase and purified as described elsewhere.¹⁴ Phase transfer of aqueous chloroaurate ions was achieved by the vigorous stirring of aqueous chloroauric acid with 10^{-3} M chloroform solution of octadecylamine (ODA).¹⁵ Aqueous chloroplatinate ions (PtCl_6^{2-}) ions were phase transferred into chloroform in a similar manner but benzyldimethylstearylammonium chloride (BDSAC) was used as the metal ion phase transfer molecule instead of ODA. The appearance of a yellow color in the chloroform phase indicated the transfer of chloroaurate and chloroplatinate ions. Estimating that complete transfer of these ions to chloroform had occurred,¹⁵ the concentration of the ions in the organic phase is 10^{-3} M. The hydrophobized chloroaurate and chloroplatinate ions synthesized by the above procedure were separated from the aqueous phase and used as such for further experiments. Different volumes of 10^{-3} M hydrophobized AuCl_4^- ions in chloroform were added to 19 ml of the ODA-capped Ag nanoparticles in chloroform to yield 3×10^{-5} , 5×10^{-5} , 10^{-4} and 5×10^{-4} M of AuCl_4^- ions in the reaction medium. In almost all cases, the solution rapidly changed color from yellow (test tube 1, inset of Fig. 1A) to different shades of red/pink (test tube 2, Fig. 1A) indicating reduction of gold ions and oxidation of silver atoms.

Curve 1 in Fig. 1A corresponds to the UV-Vis absorption spectrum of the ODA-capped Ag nanoparticles in chloroform; the strong absorption at 410 nm is due to excitation of surface plasmon vibrations in the nanoparticles. Fig. 2A shows a transmission electron microscopy (TEM) picture of the ODA-capped silver nanoparticles drop-coated from chloroform onto carbon-coated TEM grids. The particles are clearly spherical in morphology and often are multiply twinned. An analysis of a large number of Ag nanoparticles yielded an average diameter of 17.5 ± 5.4 nm. Upon addition of different amounts of hydrophobized AuCl_4^- ions to the ODA-capped Ag nanoparticle solution, it is observed that the Ag surface plasmon resonance band is reduced in intensity (Fig. 1A, curves 2 and 3) and in conditions where the gold ion concentration is high (curves 4 and 5), a new absorption band appears at ca. 570 nm. The new absorption band arises due to reduction of AuCl_4^- ions and formation of metallic gold while the concomitant loss in intensity of the Ag nanoparticle surface plasmon absorption at 410 nm is due to oxidation of silver atoms during the transmetallation reaction and deposition of the gold in the form of a shell around the silver core.^{13a} The fact that the

† Electronic supplementary information (ESI) available: FTIR spectral details. See <http://www.rsc.org/suppdata/cc/b4/b418566h> *sastry@ems.ncl.res.in

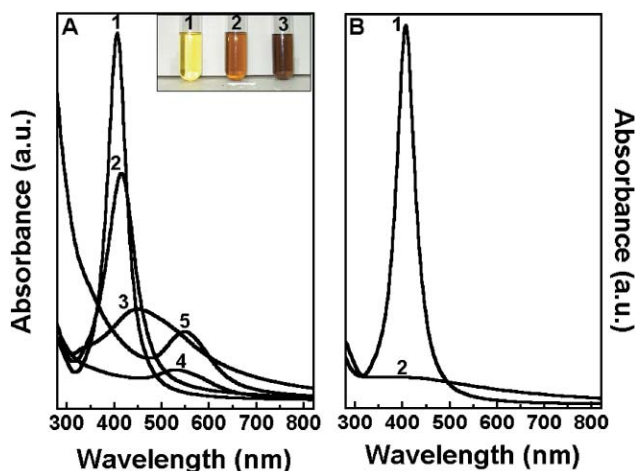


Fig. 1 (A) UV-Vis absorption spectra recorded from ODA-capped Ag nanoparticles in chloroform at various stages of reaction: 1—as-prepared ODA-capped silver nanoparticles; 2 to 5—after addition of 3×10^{-5} , 5×10^{-5} , 10^{-4} and 4×10^{-4} M of hydrophobized AuCl_4^- ions respectively. The inset shows pictures of the ODA-capped silver nanoparticles in chloroform before (1) and after addition of hydrophobized AuCl_4^- (2) and PtCl_6^{2-} ions (3). (B) UV-Vis absorption spectra recorded from ODA-capped silver nanoparticles in chloroform before (1) and after addition of 5×10^{-5} M of hydrophobized PtCl_6^{2-} ions (2).

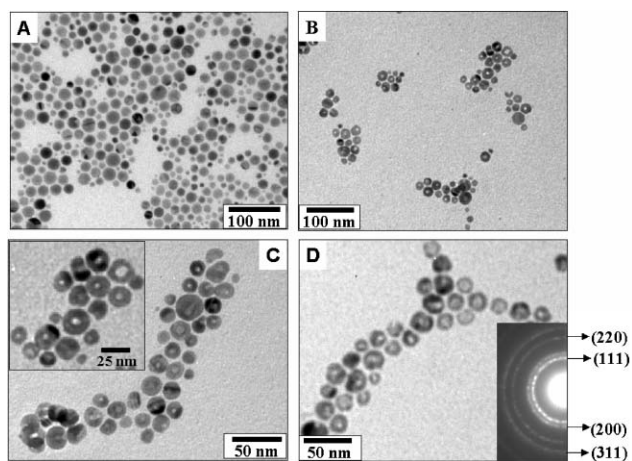


Fig. 2 Representative TEM images of (A) ODA-capped Ag nanoparticles; (B & C, inset) hollow Au nanoparticles and (D) hollow Pt nanoparticles obtained by reaction of ODA-capped Ag nanoparticles with hydrophobized AuCl_4^- ions and hydrophobized PtCl_6^{2-} ions in chloroform. The inset corresponds to the SAED pattern from the hollow nanoparticles in the main image.

surface plasmon resonance of gold in the transmetallation reaction occurs at wavelengths slightly higher than that reported for spherical gold nanoparticles (*ca.* 520 nm) suggests the formation of shells of gold.¹² The transmetallation process described above works equally well in the reaction between ODA-capped Ag nanoparticles in chloroform and hydrophobized PtCl_6^{2-} ions. Curves 1 and 2 in Fig. 1B correspond to the UV-Vis absorption spectra recorded from the ODA-capped Ag nanoparticles before and after reaction with 5×10^{-5} M PtCl_6^{2-} ions respectively. As in the former reaction, the silver plasmon resonance band is significantly reduced in intensity and is accompanied by a broad

band in the visible region of the spectrum. Unlike in the case of formation of gold nanoparticles that exhibit a pronounced absorption in the visible region of the spectrum, Pt particles do not show such an absorption. However, that the transmetallation reaction was successful is indicated by a change in color of the ODA-capped Ag nanoparticle solution from yellow (test tube 1 in inset of Fig. 1A) to brown (test tube 3, inset of Fig. 1A) after addition of hydrophobized PtCl_6^{2-} ions.

Fig. 2B and C show representative TEM images recorded from ODA-capped Ag nanoparticles after reaction with 0.5×10^{-3} M hydrophobized AuCl_4^- ions at different magnifications. At low magnification (Fig. 2B), it is observed that almost all the Ag nanoparticles have participated in the reaction, including particles smaller in dimension than 20 nm. The oxidation of the silver and reduction of the gold ions manifests itself in the formation of a fairly uniform Au shell and an apparent hollow core due to leaching out of the Ag atoms as Ag^+ ions. At higher magnifications (Fig. 2C and inset), the nanoparticles are seen in much greater detail and the hollow cores in all the particles are quite prominent. The reaction of ODA-capped silver nanoparticles with hydrophobized PtCl_6^- ions is equally facile and very uniform hollow Pt nanoparticles are seen at the end of this transmetallation reaction (Fig. 2D). In the absence of other tools in this study, it is not possible to make a statement on whether the structures observed in Fig. 2B–D are three dimensional in nature (hollow spherical particles) or two dimensional (annular rings, donuts). We speculate that given the isotropic nature of the reaction in chloroform, the structures obtained are hollow spheres, an interpretation consistent with that of Sun and Xia who observed similar structures in studies related to transmetallation reactions of aqueous silver nanospheres with gold ions.^{13b} The inset of Fig. 2D shows the selected area electron diffraction (SAED) pattern recorded from the hollow Pt nanoparticles. The particles are clearly polycrystalline and the rings could be indexed based on the fcc structure of Pt alone. Thus, it is clear that under these reaction conditions, all the silver ions are consumed in the transmetallation reaction. The hollow Au and Pt nanoparticles are extremely stable in solution and may be readily stored as a dry powder and redispersed in a range of organic solvents. This indicates that the hollow particles are capped with ODA and, thereby, rendered hydrophobic. This is corroborated by Fourier transform infrared (FTIR) spectroscopy analysis of the ODA-capped silver nanoparticles before (ESI, curve 1 in S1†) and after reaction with 5×10^{-4} M hydrophobized gold ions (ESI, curve 2 in S1). No detectable changes could be observed in the region of the $-\text{N}-\text{H}$ stretch (*ca.* 3300 cm^{-1}) suggesting strong complexation of ODA with the gold shell.

The above studies clearly indicate that even in an organic environment, the transmetallation reaction occurs quite readily and as observed in aqueous environments in previous studies,^{10,13} hollow nanoparticles are formed. In earlier studies on the formation of hollow Au nanoparticles in water with sacrificial silver nanospheres, uniform shells were formed only in transmetallation reactions carried out under refluxing conditions ($100 \text{ }^\circ\text{C}$).^{13a,b} We observe the formation of highly uniform Au and Pt shells even under room temperature reaction conditions (Fig. 2B–D) suggesting that the solvent plays an important role. This could possibly be due to ionic effects mediated by the low dielectric constant of the organic environment. The evolution of such hollow structures from the spherical silver nanoparticles

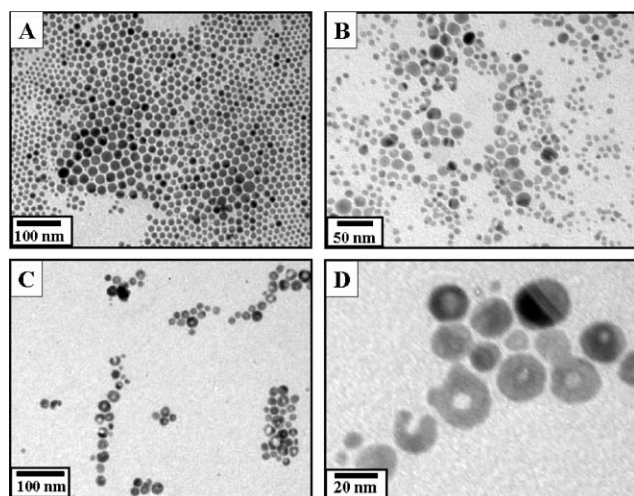


Fig. 3 Representative TEM images showing the evolution of hollow nanostructures from the spherical hydrophobic silver nanoparticles (A) after: (B) 2 minutes, (C) 10 minutes and (D) 1 hour of reaction with hydrophobized chloroaurate ions.

during reaction with hydrophobized chloroaurate ions was followed by TEM in order to shed some light on the mechanism of formation such structures (Fig. 3). Fig. 3B shows that after two minutes of reaction, the spherical silver particles become more irregular in morphology with a very small percentage already showing evidence of a hollow interior. After 10 minutes of reaction, these differences are amplified and an increase in the density of hollow particles is observed (Fig. 3C). After 1 h of reaction, almost all particles show evidence of completion of the transmetallation reaction in the form of hollow cores of varying sizes (Fig. 3D). Indeed, some of the particles indicated preferential reaction along certain directions resulting in hollow cores opening up completely (Fig. 3D).

While the exact process is still to be elucidated, we believe the formation of hollow nanoparticles occurs by reaction of the $\text{ODA}^+ - \text{AuCl}_4^-$ and $(\text{BDSAC}^+)_2 - \text{PtCl}_6^{2-}$ ion pairs in chloroform with the surface of the ODA-capped Ag nanoparticles in an isotropic manner. The leaching out of the core in this reaction during creation of Ag^+ ions suggests that the Ag nanoparticles possess defects that facilitate reaction of the gold/platinum ions with the silver core as well as outward diffusion of the Ag^+ ions. Such pathways could be provided by twin boundaries in multiply twinned silver particles (MTP) that are observed in this study. Twin boundaries have been previously implicated in the growth of gold nanorods with gold MTPs as seeds.¹⁶ High resolution TEM studies are currently in progress and will lead to a better understanding of the mechanistic aspects of hollow structure formation *via* transmetallation reactions.

In conclusion, the formation of organically redispersible hollow nanoparticles with compact and uniform shells of Au and Pt by a transmetallation reaction in one step in an organic phase has been demonstrated. Such a synthesis process is expected to be important in catalysis, biomedical and optical coating applications.‡

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Notes and references

‡ The UV-Vis spectra were recorded on a JASCO dual-beam spectrophotometer (V-570) operated at a resolution of 2 nm. TEM samples of the silver nanoparticles and silver nanoparticles after the addition of hydrophobized chloroaurate ions in the organic phases were prepared by placing a drop over carbon coated copper grids and allowing the solvent to evaporate. TEM measurements were performed on a JEOL model 1200EX instrument operated at an accelerating voltage at 120 kV. FTIR measurements of ODA, ODA-capped silver nanoparticles, ODA-phase transferred chloroaurate ions and the ODA-capped hollow gold nanoparticles were carried out on a Perkin-Elmer FTIR Spectrum One spectrophotometer in the diffuse reflectance mode operating at a resolution of 4 cm^{-1} . FTIR spectral data are given in the ESI.

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