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Keggin ion-mediated synthesis of aqueous phase-pure Au@Pd and Au@Pt core-shell nanoparticles[†]

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Development of simple and reliable protocols for the synthesis of phase-pure core-shell metal nanoparticles is an important problem in nanomaterials synthesis; the synthesis of Au core-Pd/Pt shell nanoparticles is described in this paper. This is accomplished by utilizing Keggin ions bound to the surface of gold nanoparticles as UV-switchable reducing agents. Exposure of Keggin ion-capped gold nanoparticles to aqueous solutions of Pd²⁺ and Pt⁴⁺ ions after UV activation of the Keggin ions results in selective reduction of the metal ions only on the surface of the nanoparticles and thus, to phase-pure core-shell nanostructures. The synthesis of the Au@Pd and Au@Pt core-shell nanoparticles was followed by UV-vis spectroscopy, X-ray photoemission spectroscopy and high-resolution transmission electron microscopy measurements.

Introduction

The design, synthesis, and characterization of nanophase materials are subjects of intense research due to the exciting optoelectronic and physicochemical properties of nanoscale matter.¹ Nanomaterials are expected to have potential applications in optoelectronics, semiconductors, catalysis, magnetic devices, drug delivery, and so on.²⁻⁴ Bimetallic nanoparticles, either in the form of an alloy or in core-shell structures, are being investigated in some depth because of their improved catalytic properties⁵ and changes in the electronic/ optical properties⁶ relative to the individual, separate metals. It is postulated that their interesting physicochemical properties result from the combination of two kinds of metals and their fine structures. Insofar as alloy nanoparticles are concerned, the combination of gold and palladium is popular since these metals are miscible at any ratio. Due to the high catalytic activity of Pd and Pt, bimetallic colloids of gold and silver in combination with Pd and Pt (Ag-Pd,7 Ag-Pt,8 Au-Pt,9 and Au-Pd¹⁰) have been studied in great detail. Bimetallic nanoparticles as alloys are conveniently synthesized by simultaneous reduction of two or more metal ions.^{6b,7–10} Many methods have been reported for their preparation by alcohol reduction,¹¹ citrate reduction,^{6b} borohydride reduction,¹² polyol process,¹³ solvent extraction/reduction,¹⁴ thermal decomposition,¹⁵ photolytic reduction,¹⁶ decomposition of organometallic precursors,¹⁷ and electrolysis of bulk metals *etc.*¹⁸ On the other hand, experimental procedures for the

On the other hand, experimental procedures for the formation of core-shell nanostructures are rather cumbersome and involve several steps. Generally, growth of core-shell structures can be accomplished by the successive reduction of one metal ion over the core of another.^{19–22} Often this leads to the formation of fresh nuclei of the second metal in solution, in addition to a shell around the first metal core,²² and is clearly undesirable from the application point of view. We have recently addressed this issue and developed a strategy that involves the immobilization of a reducing agents on the surface of the core metal which, when exposed to the second metal

ions, would selectively reduce them on the surface thereby leading to phase-pure core-shell structures. A desirable feature of this approach for obtaining phase-pure core-shell nanoparticle structures would be a reducing agent bound to the surface of the core nanoparticle that could be selectively activated (i.e., whose reducing capability can be switched off and on at will). We have identified Keggin ions (polyoxometalates) and the amino acid tyrosine as switchable reducing agents that can be bound to gold nanoparticles and thereafter, activated by a stimulus to reduce a second metal ion. Polyoxometalates such as Keggin ions undergo stepwise multielectron redox processes without structural change² and may be reduced electrolytically, photochemically, and with suitable reducing agents. Troupis, Hiskia, and Papaconstantinou have shown that exposure of photochemically reduced [$(SiW_{12}O_{40})^{4-}$] Keggin ions to aqueous Ag⁺, Pd²⁺, AuCl₄⁻, and PtCl₆²⁻ ions resulted in the formation of stable metal nanoparticles capped by the Keggin ions.²⁴ In this laboratory, we have demonstrated that phase-pure Au core-Ag shell nanoparticles can be synthesized using Keggin ions as a UV-switchable reducing agent.²⁵ Phase-pure Au core–Ag shell nanoparticles may also be synthesized using the pH-dependent reducing capability of tyrosine-immobilization of tyrosine molecules on the surface of the Au nanoparticles followed by exposure to Ag⁺ ions at high pH results in the facile formation of such structures.²⁶

In this report, we advance our studies on the use of Keggin ions as UV-switchable reducing agents and demonstrate the formation of Au core–Pt/Pd shell nanostructures. Keggin ions bound to the surface of Au core metal nanoparticles and reduced by exposure to UV radiation when exposed to the second metal ion such as Pt^{4+} and Pd^{2+} , would reduce them, thereby leading to the formation of phase pure Au core–Pt shell and Au core–Pd shell structures. Presented below are details of the investigation.

Experimental details

Chemicals

† Electronic supplementary information (ESI) available: W 4f core level spectra recorded from the PTA-capped Au nanoparticles, Au–Pd and Au–Pt core-shell nanoparticles (PDF, one page, S1). See http:// www.rsc.org/suppdata/jm/b4/b409033k/

Phosphotungstic acid $(H_3PW_{12}O_{40}, PTA)$, chloroauric acid $(HAuCl_4)$, palladium nitrate $(Pd(NO_3)_2)$ and chloroplatinic

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acid (H_2PtCl_6) were obtained from Aldrich Chemicals and used as received.

In a typical experiment 30 mL of 10^{-2} M aqueous deaerated solution of phosphotungstic acid (PTA) was added to 2 mL of propan-2-ol, and the mixture was irradiated by UV light for 4 h (Pyrex filter, >280 nm, 450 W Hanovia medium-pressure lamp (step 1, Scheme 1)). This leads to reduction of $(PW_{12}O_{40})^3$ ions and is seen as a blue color appearing in the solution. To 5 mL of this irradiated PTA solution, 15 mL of 10^{-3} M HAuCl₄ solution was added under continuous stirring for 10 min, and then the solution was allowed to age for 2 h (step 2, Scheme 1). The solution changed color from blue to pink indicating the formation of gold nanoparticles. Uncoordinated PTA ions in solution were removed by thoroughly dialyzing the PTA-gold nanoparticle solution against distilled water for 2 days, using a 12 K cutoff dialysis bag. The dialyzed solution was also extremely stable over time indicating that the Keggin ions are bound to the nanoparticles' surface and stabilize them electrostatically and stereochemically. Following dialysis of the PTA-gold nanoparticle solution, it was UV-irradiated again for 3 h (step 3, Scheme 1) and the solution color changed from pink to a bluish-red. To 15 mL each of this solution, 15 mL of 10^{-4} M aqueous solutions of Pd(NO₃)₂ and chloroplatinic acid (H₂PtCl₆) were added separately under stirring (step 4, Scheme 1).

UV-vis spectroscopic studies

The optical properties of the core-shell nanoparticle solutions at different stages of preparation (steps 1–4, Scheme 1) were monitored on a Shimadzu dual beam spectrometer (model UV-1601 PC) operated at a resolution of 1 nm.

Transmission electron microscopy measurements

TEM measurements were performed on a JEOL model 1200 EX instrument operated at an accelerating voltage of 120 kV. Samples for TEM studies were prepared by placing a drop of the PTA-capped Au core nanoparticles, Au core–Pt shell and Au core–Pd shell nanoparticle solutions on carbon-coated TEM grids. The films on the TEM grids were allowed to dry for 2 min following which the extra solution was removed using a blotting paper. High Resolution Transmission Electron Microscope (HRTEM) measurements were performed on a JEOL model 2010F UHR instrument operated at an accelerating voltage at 200 keV.

X-Ray photoemission spectroscopy (XPS) measurements

X-Ray Photoemission Spectroscopy (XPS) measurements of the PTA-capped Au nanoparticles, Au core–Pt shell and Au core–Pd shell nanoparticle solutions cast in the form of films



Scheme 1 Cartoon illustrating the Keggin ion-mediated synthesis of Au core–Pd/Pt shell nanoparticles. For simplicity, the Keggin ions are shown as octahedral particles.

onto Si (111) substrates were carried out on a VG MicroTech ESCA 3000 instrument at a pressure of better than 1×10^{-9} Torr. The general scan and the C 1s, W 4f, Pt 4f and Pd 3d core level spectra were recorded with un-monochromatized Mg K α radiation (photon energy = 1253.6 eV) at pass energy of 50 eV and electron takes off angle (angle between electron emission direction and surface plane) of 60°. The overall resolution was $\sim 1 \text{ eV}$ for the XPS measurements. The core level spectra were background corrected using the Shirley algorithm²⁷ and the chemically distinct species resolved using a non-linear least squares fitting procedure. The core level binding energies (BE) were aligned with the adventitious carbon binding energy of 285 eV.

Results and discussion

Figs. 1(A) and (B) show the UV-vis spectra of the Au core–Pd shell and Au core–Pt shell nanoparticle solutions at different stages of preparation (steps 1–4, Scheme 1). Curves 1 in Figs. 1(A) and (B) correspond to the spectrum recorded from UV-irradiated PTA solution (step 1, Scheme 1); the presence of an absorption band at 760 nm is seen and is characteristic of one-electron-reduced PTA, $[PW_{12}O_{40}]^{4-.23}$ Curve 2 in Fig. 1(A) and (B) correspond to UV-vis absorption of the UV-irradiated PTA solution to which HAuCl₄ solution was added (step 2, Scheme 1). A strong absorption band at *ca.* 526 nm is observed. This absorption band arises due to excitation of surface plasmon vibrations in the gold nanoparticles.^{6b}

Following dialysis of the PTA-gold nanoparticle solution, it was UV-irradiated again for 4 h (step 3, Scheme 1). The UV-vis spectrum of the PTA-gold nanoparticle solution after irradiation is shown as curves 3 in Fig. 1(A) and (B). At this stage, the solution color changed from pink to a bluish-red, these changes reflected in the UV-vis absorption spectrum as an increase in absorption at 760 nm. This increase in absorption at long wavelengths clearly indicates that the PTA ions bound to the surface of the gold nanoparticles have been reduced. Curves 4 in Fig. 1(A) and (B) correspond to the UV-vis spectra recorded from the UV-irradiated PTA-capped gold nanoparticle solution after addition of palladium nitrate and H₂PtCl₆ solutions respectively (step 4, Scheme 1). The UV-vis spectra from these solutions show a damping and broadening of the gold surface plasmon vibration band relative to the as-prepared PTAcapped gold nanoparticle solution (compare curves 2 and 4 in



Fig. 1 (A) and (B) show the UV-vis spectra of the Au core–Pt/Pd shell nanoparticle solutions at different stages of reaction. Curve 1 in (A) and (B) – 10^{-2} M aqueous solution of PTA after UV irradiation; curve 2 in (A) and (B) – UV-irradiated PTA solution after addition of 10^{-3} M HAuCl₄; curve 3 in (A) and (B) – PTA-capped Au nanoparticle solution after further UV irradiation; curve 4 in (A) and (B) – UV-irradiated PTA-capped Au nanoparticle solution after addition of 10^{-4} M aqueous solutions of Pd(NO₃)₂ and H₂PtCl₆ respectively and curve 5 in (A) and (B) – PTA-capped Au nanoparticle solution after addition of 10^{-4} M Pd(NO₃)₂ and H₂PtCl₆ solutions respectively (without prior UV-irradiation, see text for details).

Fig. 1A and B). The damping of the gold core nanoparticle plasmon band consequent to reaction with Pt and Pd ions is a clear indication of reduction of the ions and formation of a metallic shell of Pt and Pd around the gold core.

To confirm the presence of Pd and Pt in Au-Pd and Au-Pt core-shell nanoparticles, a chemical analysis of these samples was performed using XPS. The Au 4f core level spectra recorded from the Au core-Pt/Pd shell nanoparticles at various stages of preparation are shown in Fig. 2A while the Pd 3d from the Au core-Pd shell sample and Pt 4f core levels from the Au core-Pt shell nanoparticles are shown in Fig. 2B and C respectively. The general scan spectra of the above samples showed the presence of C 1s, P 2p, W 4f, Pt 4f and Pd 3d core levels with no evidence of impurities. As mentioned earlier, charging corrections in all the core level spectra were effected taking the adventitious C 1s binding energy (BE) to be 285 eV. The Au 4f spectrum from the PTA-capped gold nanoparticles (curve 1), Au core-Pd shell (curve 2) and Au core-Pt shell nanoparticles (curve 3) could in all cases be decomposed into a single spin-orbit pair (spin-orbit splitting \sim 3.6 eV). The Au 4f_{7/2} peak had a BE 84.3 eV, characteristic of Au(0).²⁸ The absence of a higher BE Au 4f component clearly shows that all the AuCl₄⁻ ions are fully reduced by the PTA anions after UV irradiation. The reduction in intensity of the Au 4f spectrum after further reduction of Pd and Pt ions (curves 2 and 3) indicate the formation of a concentric shell in both cases. The presence of the Pd/Pt shell would lead to enhanced inelastic scattering of the Au 4f electrons and a consequent reduction in intensity. The Pd 3d core level spectrum recorded from the Au-Pd core-shell nanoparticle sample could be resolved into a single spin-orbit pair (spinorbit splitting ~ 5.4 eV) with a $3d_{5/2}$ binding energy (BE) of 335.8 eV (Fig. 2B, solid lines). This BE is characteristic of Pd in the fully reduced state.²⁹ In this BE window, we also observe the presence of the Au 4d_{5/2} component (Fig. 2B, dashed line) at a BE of 335.5 eV. The fact that the spectrum could be decomposed into a single spin-orbit pair indicates the complete reduction of Pd²⁺ ions by the UV irradiated PTA ions bound to the surface of the gold nanoparticle core. Fig. 2C shows the Pt 4f core level spectrum recorded from the Au-Pt core-shell nanoparticle sample. Unlike in the case of the Pd ion reduction on the surface of PTA-capped gold nanoparticles, the Pt 4f spectrum had to be decomposed into two spin-orbit pairs (spinorbit splitting ~ 3.2 eV) with $4f_{7/2}$ BEs of 71.2 eV (curve 1,



Fig. 2 (A) Au 4f core level spectra recorded from PTA-capped Au nanoparticles (curve 1), Au–Pd (curve 2) and Au–Pt (curve 3) coreshell nanoparticles. The spectra have been shifted vertically for clarity. The spectrum in curve 1 has been decomposed into a spin–orbit pair. (B) Pd 3d and Au 4d core level spectra recorded from Au–Pd core–shell nanoparticles. The solid lines correspond to the Pd 3d spin–orbit pair while the dashed line is due to the Au $4d_{5/2}$ spin–orbit component. (C) Pt 4f core level spectrum recorded from the Au–Pt core–shell nanoparticles. The spectrum has been resolved into two spin–orbit pairs.

Fig. 2C) and 74.2 eV (curve 2, Fig. 2C) respectively. The low BE component corresponds to metallic ${\rm Pt}^{30}$ while the high BE component is assigned to unreduced ${\rm PtCl_6}^{2-}$ ions that are bound to the surface of the Pt metal shell. The presence of phosphotungstic acid in PTA-capped Au nanoparticles, Au–Pd and Au–Pt core–shell nanoparticles is clearly indicated by the presence of the W 4f core level signal in all the samples (ESI, S1†). The W 4f spectrum in all cases could be resolved into a single spin–orbit pair (splitting ~ 2.12 eV) with a 4f_{7/2} binding energy (BE) of 36.36 eV.³¹

Fig. 3A shows a representative low-magnification TEM image of PTA-capped Au nanoparticles. The nanoparticles are polydisperse with sizes ranging from 15 to 50 nm and have an irregular morphology. Fig. 3B shows a HRTEM image of one of the gold nanoparticles. The contrast is uniform throughout the particle, thus indicating that it is a single nanocrystal. A number of multiply twinned gold nanoparticles could also be observed, which at higher magnification clearly showed lattice planes (2.35 Å spacing) corresponding to the (111) planes of fcc gold (Fig. 3B). Fig. 4A and B show representative low and high-resolution TEM images recorded from drop-cast films of Au core-Pd shell nanoparticles. As in the case of the PTA-capped gold nanoparticles core, the particles are quite polydisperse and show a small increase in the particle size (Fig. 4A, now ranging from 20 to 70 nm). At higher resolution (Fig. 4B), a distinct variation in contrast between the dark gold core and the lighter palladium shell is clearly seen. The lattice planes of the Pd shell are clearly imaged (1.95 Å spacing) which corresponds to the (200) planes (Fig. 4B).

Fig. 5A and B show representative low and high-resolution TEM pictures recorded from the Au core–Pt shell nanoparticles. As in the case of Au core–Pd shell nanoparticles, reaction of the PTA-capped gold nanoparticles with $PtCl_6^{2-}$ ions after UV activation results in an increase in the average size of the nanoparticles (sizes ranging from 40 to 85 nm) clearly indicating formation of a Pt concentric shell around the gold core. The presence of a Pt shell is more directly indicated in the high resolution TEM image recorded from one of the particles (Fig. 5B) where the difference in contrast between the gold core and Pt shell is clearly seen. That the Pt layer is crystalline is inferred from the (222) lattice planes imaged in Fig. 5B.

From the above discussion it is clear that after UVirradiation, surface bound PTA molecules on the Au nanoparticle core act as highly localized reducing agents for



Fig. 3 (A) TEM picture of PTA-capped gold nanoparticles. (B) High-resolution TEM image of the gold particles.



Fig. 4 A and B – low and high-resolution TEM images recorded from gold core– palladium shell nanoparticles.



Fig. 5 (A) TEM picture of gold core–platinum shell nanoparticles by sequential reduction of gold and platinum ions by UV-irradiated PTA solution. (B) High-resolution TEM image of one of the Au core–Pt shell nanoparticles.

Pd and Pt metal ions. That the PTA anions are indeed UVswitchable reducing agents is demonstrated by the following control experiment. In this experiment, Pd^{2+} and Pt^{4+} ions were added separately to PTA-capped gold nanoparticle solutions without subjecting the PTA-capped gold nanoparticle solution to UV irradiation. Negligible changes are observed in the UV-vis absorption spectra of the PTA-capped gold nanoparticle solutions before and after addition of the Pd²⁺ and Pt^{4+} ions (compare curves 5 and 2 in Fig. 1A and B respectively). Thus, photochemical charging of PTA molecules bound to the gold nanoparticle surface is the crucial step in protocol that sets it apart from other bimetallic nanoparticle core-shell synthesis protocols that employ reducing agents present uniformly in the reaction medium. That the reducing capability of the Keggin ions can be switched on using UV irradiation is an additional feature that enhances the versatility of the technique.

In conclusion, the formation of Au core–Pd shell and Au core–Pt shell nanoparticles using photochemically reduced phosphotungstate Keggin ions has been described. The use of Au nanoparticle surface-bound switchable reducing agents such as that provided by Keggin ions enables the reduction of Pd^{2+} and Pt^{4+} ions selectively on the surface of the gold particles, thus precluding the possibility of nucleation of fresh Pd and Pt nanoparticles in solution. Using this strategy, it is possible to realize a large combination of core–shell nano-structures using Keggin ions with potential application in engineered nanomaterials and catalysis.

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