A new method for the synthesis of hydrophobized, catalytically active Pt nanoparticles

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A single step method for the synthesis of catalytically active, hydrophobic Pt nanoparticles by the spontaneous reduction of aqueous PtCl₆²⁻ ions by hexadecylamine molecules at a liquid–liquid interface is described.

Development of protocols for the synthesis of metal nanoparticles of variable size and shape constitutes an area of research of considerable topical interest. Exciting application of metal nanoparticles in electronics, magnetic memories, bio-research of considerable topical interest. Exciting application of particles of variable size and shape constitutes an area of liquid–liquid interface is described.

In a typical experiment, 50 ml of a 10⁻³ M aqueous solution of H₂PtCl₆ was taken in a beaker along with 50 ml solution of 3 M HDA in chloroform. The biphasic mixture was stirred vigorously on a magnetic stirrer for 56 h in the dark following which the appearance of brownish colour in the organic phase could clearly be seen. The brown colour in the chloroform phase is a clear indication of the formation of well-dispersed Pt nanoparticles. After completion of the reaction, the chloroform solution was rotovapped yielding a blackish powder of the hydrophobized Pt nanoparticles. This powder was washed purified powder was carried out and the data obtained is shown in Fig. 2A. A weight loss of 30% is observed to occur at 270 °C and is attributed to desorption of surface-bound HDA molecules. The magnitude of weight loss and temperature is almost identical to that observed in our earlier study on HDA complexed with gold nanoparticles indicating similar binding in both cases. The almost 100% weight loss above 450 °C for Pt plasmon vibrations in the Pt nanoparticles. The position of this absorption band and the nature of the absorption tail is similar to that reported by others for solutions of Pt nanoparticles. The inset of Fig. 1A shows the X-ray diffraction (XRD) pattern recorded from a drop-coated film of the hydrophobized Pt nanoparticles. The positions of the Bragg reflections (indexed in the figure) correspond very well with those reported in the literature for face centred cubic (fcc) Pt.13 Fig. 1B shows a representative transmission electron microscopy (TEM) image recorded from the HDA-capped Pt nanoparticles drop-coated onto a TEM grid. A large number of Pt nanoparticles of uniform size are observed in the TEM image. A magnified view of the region defined by the box is also shown in Fig. 1B to get a clearer idea of the average particle size and degree of monodispersity. From an analysis of the Pt nanoparticles in this and other images, an average particle size of 15.5 ± 0.7 nm was determined. Thus, the process of spontaneous reduction of PtCl₆²⁻ ions by HDA leads to very uniform Pt nanoparticles, possibly due to capping of the nanoparticles, which is also carried out by HDA. Another interesting feature of the TEM image is the very regular separation between the Pt nanoparticles. This is clearly due to the HDA molecules capping the nanoparticles and preventing their aggregation after solvent evaporation. An average inter-particle distance of ca. 4.5 nm was determined and is smaller than the separation expected from the size of the HDA molecules (~2 × 2.9 nm). This indicates interdigitation of the hydrocarbon chains from neighbouring nanoparticles.

In order to understand better the nature of interaction of the HDA molecules with the Pt nanoparticle surface, thermogravimetric analysis (TGA) of carefully weighed amount of the purified powder was carried out and the data obtained is shown in Fig. 2A. A weight loss of ca. 30% is observed to occur at 270 °C and is attributed to desorption of surface-bound HDA molecules. The magnitude of weight loss and temperature is almost identical to that observed in our earlier study on HDA complexed with gold nanoparticles indicating similar binding in both cases. The almost 100% weight loss above 450 °C for Pt
nanoparticles is also a feature common to both systems and indicates complete desorption of the nanoparticles at this relatively low temperature.

The changes occurring in the HDA molecules consequent to reduction of the chloroplatinate ions may be conveniently studied by NMR spectroscopy. Fig. 2B shows the results of proton NMR measurements carried out on pure HDA (curve 1) and HDA-reduced platinum nanoparticles (curve 2) dispersed in CDCl₃ after purification in order to understand better changes occurring in HDA during the reduction of aqueous hexachloroplatinate ions. The chemical shifts at 7.1 and 6.75 ppm in curve 1 (pure HDA) are assigned to the two sets of aromatic protons while the chemical shifts at 3.64, 2.56, 1.32 and 0.91 ppm correspond to the NH₂ protons, methylene protons attached to the benzene ring, other methylene protons in the hydrocarbon chain and methyl protons in the pure HDA molecule respectively. In curve 2 (HDA-reduced platinum nanoparticles) there is a complete disappearance of the peaks at 7.1, 6.75 and 3.64 ppm and a broadening of the peak at 2.56 ppm. This indicates that the aniline group in HDA is in close contact with the metal surface with the hydrocarbon chain pointing outwards. We would like to point out that this behaviour is different from alkylamines bound to gold nanoparticles where the peaks for amine-capped Au nanocrystals are all broadened relative to those of the neat amines and a peak at 2.70 ppm, typical of the NCH₂ protons in the neat amines, is not clearly observed in the amine-capped Au nanocrystal spectra. 

To the best of our knowledge, there are no reports on the catalytic activity of hydrophobized Pt nanoparticles in organic media and we were therefore curious to test whether HDA-stabilized Pt nanoparticles retained any catalytic activity. Catalytic activity of the platinum nanoparticles for a hydrogenation reaction involving the conversion of styrene to ethylbenzene (Scheme 1) was studied in a 50 ml reactor (Hastelloy-C, supplied by Parr Instrument Company, USA).

Analysis of the initial and final samples were done using gas chromatography (HP 6890) using an HP-FFAP capillary column (poly(ethylene glycol)–TPA as the stationary phase, 25 m × 0.20 mm × 0.3 μm) having conditions: 403 K for 2 min at 20 K min⁻¹ up to 423 K—hold 2 min—@ 20 K min⁻¹ up to 463 K—hold 1 min; inlet temp: 473 K, inlet pressure: 25 psig; detector temp: 523 K. The GC analysis showed complete conversion of styrene with 99.81% selectivity to ethylbenzene with a TOF of 655 h⁻¹. The HDA-capped Pt nanoparticle catalyst also worked excellently in the hydrogenation of a non-aromatic substrate such as cyclohexene giving complete conversion of cyclohexene to cyclohexane with 100% selectivity (TOF = 2112 h⁻¹).

The use of a multifunctional molecule that accomplishes reduction of aqueous PtCl₄²⁻ ions, caps the Pt nanoparticles thus formed and renders them dispersible in an organic solvent has been described. The Pt nanoparticles capped by the multifunctional molecule, hexadecylamine, are highly active and catalyze the hydrogenation of styrene to ethylbenzene and cyclohexene to cyclohexane with almost 100% selectivity. S. M., PR. S. and D. R. thank the University Grants Commission and the Council of Scientific and Industrial Research (CSIR), respectively, Govt. of India, for financial support. The authors thank Ms Renu Parshica and Ms S.D. Adyanthaya for assistance with the TEM and TGA measurements, respectively.

Notes and references

† UV-vis spectra of the Pt nanoparticle solution in chloroform were measured on a Hewlett-Packard HP 8452 diode array spectrophotometer at a resolution of 2 nm. TEM measurements on the HDA-capped Pt nanoparticle films cast onto carbon-coated TEM grids were carried out on a Jeol model 1200EX instrument at an accelerating voltage of 120 kV. TGA profiles of carefully weighed quantities of purified powders of HDA-capped platinum nanoparticles were recorded on a Seiko Instruments model TG/DTA 32 instrument at a heating rate of 10 °C min⁻¹. XRD measurements on drop-coated HDA-capped Pt nanoparticle films on a glass substrate were carried out on a Philips PW 1830 instrument in the transmission at a voltage of 40 kV and current of 30 mA with Cu Kα radiation. The proton (1H NMR) NMR spectra were recorded on a Bruker AC 200 MHz instrument and scanned in the range 0–15 ppm.