Synthesis and characterization of lower size, laurylamine protected palladium nanoparticles

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Abstract

A procedure to synthesize lower size mono dispersed palladium nanoparticles is described. The nanoparticles are stabilized by lauryl amine and are isolable as dispersible solids. The particles are characterized by UV–Vis, FT-IR, XRD, STM and TEM techniques.

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1. Introduction

Transition metal nanoparticles have attracted the attention of scientific community in recent years. Synthesis, structural determination and exploration for diverse applications of these nano systems are topics of current research. Fine metal particles have applications in the area of catalysis, opto-electronics due to their size dependent optical, electrical and electronic properties [1–4]. A quantum confinement sets in when the particle size is less than 5 nm [1]. The smaller the cluster of atoms, the higher the percentage of atoms on the surface and this property makes nanoparticles very interesting in catalysis [5–8]. Thus a nanoparticle of 10 nm diameter has about 10% of its atoms on the surface and a particle [9] with 1 nm has 100%.

However nanoparticles tend to aggregate to form larger particles as they have a very large surface area. In order to synthesize well-defined mono dispere nanoparticles, control over the nucleation and growth process is essential. There are several different methods for making nanoparticles. The most common approach is based on the use of a suitable capping agent, that passivates growth at an early stage. The use of capping agents enable the isolation of metal nanoparticles in dispersible solid form.

Palladium is a versatile catalyst for many organic transformations [5] such as Mizoraki-Heck [10,11], Suzuki-cross coupling [12,13], Stille [14–16] and Sonogashira [16] coupling reactions. Formation, stabilization and the size of the palladium nanoparticles has a critical role in all these reactions. Preparation of palladium nanoparticles has been reported using hydrazine [5], hydrogen [6] and sodium borohydride [7]. Electrochemically, tetraalkylammonium salt stabilized palladium nanoparticles with 3–5 nm diameter were synthesized [17]. Stronger reducing agents favor smaller nanocluster formation. To the best of our knowledge, there are no reports on the synthesis of palladium nanoparticles passivated by shorter chain length stabilizer such as laurylamine which is a low cost stabilizer. In the present communication we describe, for the first time, the biphasic synthesis of lauryl amine stabilized palladium nanoparticles, using sodium borohydride as reducing agent.

2. Experimental

All chemicals used were of analytical grade. Palladium chloride was purchased from Arora Matthey Ltd. (India). Sodium borohydride and laurylamine were purchased from Aldrich chemical company. Cyclic voltammetry was carried out in 0.5 M sulfuric acid solution at a scan rate of 100 mV/s using three electrode assembly on BAS system. Pt wire was used as an
auxiliary and S.C.E was used as reference electrode. Pd–LA nanoparticles were concentrated on to the Pt working electrode (0.25 cm²) using toluene solution and dried prior to the experiment. XRD experiments were carried out on JEOL JDX-8030 instrument. UV–Vis spectra were recorded on CARY 506 SCAN UV–Vis-Spectrophotometer. FT-IR spectra were recorded on model no. Paragon-500 from Perkin-Elmer. TEM experiments were performed on JEOL JEM-200FXII instrument operating at an accelerating voltage of 200 kV. Drop of toluene solution of the samples were placed on the TEM carbon grids. The films on the TEM grids were allowed to dry for two minutes following which the extra solution was removed using blotting paper. Thermo gravimetric analyses were performed under air on model no. STA 1500 of PL Thermal Sciences.

Palladium nanoparticles were synthesized in biphasic mixture of water and toluene. In a typical synthesis, to PdCl₂ (0.08 g, 0.45 mM) in 60 ml distilled water was added 60 ml of toluene containing lauryl amine (1.1 ml, 5 mM) and stirred vigorously for half an hour to get white turbid dispersion. All palladium chloride went into solution. While the mixture is being stirred, an aqueous solution (10 ml) of sodium borohydride (0.03 g, 0.79 mM) was added drop wise. Stirring was continued for two more hours by which time the white solids slowly turned into clear black solution. The black toluene layer was separated and the solvent removed at room temperature to obtain brown solid powder. Careful washing of the product with acetone or methanol three times effected in purification. The nanoparticles are dispersible in non-polar solvents such as toluene, benzene and hexane.

3. Results and discussion

Lauryl amine adsorbed palladium nanoparticles (Pd–LA) are obtained by reducing palladium chloride in presence of laurylamine
(1:10) in water–toluene biphasic reaction mixture using sodium borohydride as reducing agent. A white dispersion is formed when palladium chloride and lauryl amine are vigorously stirred in water–toluene mixture. At this stage aqueous solution of sodium borohydride is added drop wise and instant formation of black colour is noticed for the toluene layer, indicating the formations Pd–LAs. The final colour

Fig. 4. Cyclic voltammogram of Pd–LA nanoparticles concentrated on Pt electrode in 0.5 M sulphuric acid. The scan rate is 50 mV/s.

Fig. 5. STM image of the Pd–LA nanoparticles. The images show 3 particles. (A and B are the same but in 2D and 3D perspectives). Lower one (C) shows an individual particle zoomed. The graphs (D and E) show the line scan size (the particle height and width).
of the solid Pd–LA obtained after removal of toluene was black-brown. Stable Pd–LA nanoparticles are also formed when the concentration of the LA reduced from 1:10 to 1:8. The yield and the dispersing property of the nanoparticles is greatly reduced when the ratio decreased to 1:5. The formation of nanoparticles is confirmed by observation of broad peaks in the XRD spectrum (Fig. 1). The figure shows reflections due to (111), (200) and (220) planes at $2\theta = 39.64, 45.62$ and $68.3\degree$ respectively. This indicates that the palladium nanoparticles form face-centered cubic crystalline structures similar to Pd in the bulk phase.

The FT-IR spectra showed bands due to the adsorbed protecting agent lauryl amine. The methylene antisymmetric and symmetric vibration modes at 2920 and 2850 cm$^{-1}$, respectively, are clearly seen in Fig. 2 and indicate that the hydrocarbon chains capping the palladium nanoparticles are closely packed without a significant density of defects in the chains [18]. A broad peak centered at 3370 cm$^{-1}$ is observed and is assigned to the N–H stretch modes of vibration from the traces of uncoordinated laurylamine molecules remained [18]. In the lower spectral region, the feature at 1460 cm$^{-1}$ arises due to methylene scissoring modes of vibration, the splitting of which is a sensitive indicator of the crystalline packing of hydrocarbon chains [19]. The fact that this feature is sharp without discernible splitting indicates that the chains, are close packed which are in a crystalline environment. Another absorption due to N–H bending vibration of amino group at 3370 cm$^{-1}$ is also observed.

Surface plasmon resonance (SPR) is an important optical property of colloidal particles of ‘free-electron’ metals such as Ag, Au, Al and are very useful in characterizing these nanoparticles systems. The UV–Vis spectrum of aqueous palladium chloride shows a clear absorption at 420 nm (Fig. 3) originating from d–d transition [20]. This band totally disappears when palladium chloride is reduced with borohydride. The UV–Vis absorption profile in the range of 300 to 600 nm (shown in Fig. 3) shown by the palladium nanoparticle toluene solution does not show any surface plasmon band as expected above. This is consistent with most reports about the solution of thiolated Pd nanoparticles in toluene [21] or in water [22] and with theoretical calculations [23]. A nearly identical UV–Vis absorption spectra of the toluene solutions, measured shortly after preparation and few months later, indicated that the Pd solution is very stable against oxidation.

The electrochemical property of the nanoparticles has been investigated by cyclic voltammetry. Fig. 4 shows cyclic voltammetry of the particles in 0.5 N sulfuric acid solution. It suggests that the palladium metallic core undergoes oxidation at $E_{pa} = 1.15$ V and gets
reduced at $E_{pc} = +0.2$ V. This implies that the stabilizing shell of laurylamine formed on the surface of the palladium is thin enough to allow electron tunneling through it. This observation is similar to the behavior of palladium nanoparticles stabilized by tetraalkylamine salts in organic solvents [17b].

Pd–LA system is characterized STM. The sample is dispersed in toluene and spread onto HOPG (highly oriented pyrolytic graphite). The specimen was imaged under constant current mode in STM. Individual particles are clearly visible. The particle sizes are quite uniform and are typically 3 to 4 nm. The image in Fig. 5 shows 3 particles. A and B are the same but are shown in 2D and 3D perspectives. Lower one (C) shows an individual particle zoomed. The particles size and their distribution is also analyzed by tunneling electron microscopy (Fig. 6A). TEM investigations showed that the particles are almost mono disperse with sizes ranging between 3 and 4 nm as probed by STM. Analysis [Fig. 6B] showed that 80% of the particles fall in 3–4 nm size.

The palladium nanoparticles are capped with amine molecules that provided sufficient hydrophobicity to the nanoparticles to accomplish their phase transfer to toluene layer. The toluene dispersions of the nanoparticles are stable up to few months at room temperature. To understand the stability of these systems at higher temperatures, thermo gravimetric analysis were performed on purified samples. The TGA profile for Pd–LA (1:8) system is shown in Fig. 7. Two prominent losses occur at 218 and 388 °C, accounting for a total loss 30% which is due to desorption of laurylamine from the surface of the nanoparticles. However the weight loss found (30%) seems to be large for decomposition of laurylamine monolayer formed at Pd nanoparticle surface [19]. This indicates that the observed weight loss would include loss of not only laurylamine bound to Pd particles, but also unbound amine molecules and traces of solvent molecules. The presence of two distinct temperatures at which weight loss occurs indicates the possibility of two different modes of binding of the alkylamine molecules with the palladium nanoparticle surface. This observation is similar to Au–LA system reported in literature [19]. The sharp exothermic feature at 420 °C observed in the DTA curve may attributed to sintering of the palladium nanoparticles consequent to complete decomposition of the protective LA monolayer.

4. Conclusion

In conclusion, it is shown that stable palladium nanoparticles are formed when laurylamine is used as stabilizer (Pd:LA = 1:8 to 1:10). The particles show narrow range distribution and the size ranged from 3 to 4 nm. The nanoparticles are susceptible for oxidation and reduction as evident from cyclic voltammetry.

References