Polyoxometalate based soft chemical route for preparation of Pt nanorods and self-assemblies

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Abstract. A soft chemical route is described for the preparation of platinum nanorods and self-assemblies over photochemically reduced polyoxometalate (silicotungstate) containing composite films. Transmission electron microscopy shows that the diameters of the platinum nanorods are around 55–60 nm. The formation of platinum nanorods on solid–liquid interface reactions was explained on the basis of single site growth mechanism and diffusion limitation aggregation process.

Keywords. Polyoxometalates; platinum nanorods; diffusion limitation aggregation; sol–gel.

1. Introduction

Metal nanoparticles have received attention in recent years because of their potential applications in microelectronics (Schmid 1992; Andres *et al* 1996), photocatalysis (Kamat 2002), magnetic devices (Thomos 1988) and powder metallurgy (Perenboom *et al* 1981). The intrinsic properties of a metal nanoparticle are mainly determined by size, shape, composition, crystallinity and morphology (Dnruxm *et al* 1999; Dickson and Lyon 2000). In principle, one could control these parameters by adopting various synthetic strategies and in recent years, several approaches have been considered. Typical ones include using channels in macroporous membranes (Martin *et al* 1999), mesoporous materials (Han *et al* 2000), carbon nanotubes (Ugarte *et al* 1996) and DNA chains (Braun *et al* 1998). Although many successful approaches, such as vapour–solid and liquid–solid phase methods exist for the fabrication of 1 D nanomaterials and their arrays, the widely used method is still chemical or electrochemical deposition directed by an appropriate porous "hard" template such as alumina membranes, diblock copolymers, carbon nanotubes and zeolite/mesoporous silica (Sloan *et al* 1999; Zhang *et al* 1999; Huang *et al* 2000, 2002). The hard template approach is an effective route to prepare metal and semiconductor 1 D nanomaterials. However, most of the templates are tedious to prepare and dissolution of the template requires corrosive media.

Soft chemical methods have been employed for the synthesis of noble metal sols (Toshima and Takahashi 1992; Duff *et al* 1995; Attard *et al* 1997; Thurn-Albrecht *et al* 2000; Chen and Kimura 2001; Pol *et al* 2003) which in-

volve the reduction of relevant metal salt in the presence of a suitable stabilizing medium, which is useful to control the particle size and shape. Polyoxometalates (POM) are well-defined metal–oxygen cluster anions. Recently, polyoxometalate has been employed as reducing, stabilizing agent for the preparation of noble metal nanoparticles in homogeneous medium (Troupis *et al* 2002; Mandal *et al* 2003).

In this communication, a method for the preparation of platinum nanorods and self-assemblies of nanorods using reduced silicotungstate-based composite at room temperature is demonstrated. The method consists of solid–liquid interface reaction (heterogenous) where metal ions interact with the active components and get reduced at the interface giving rise to specific shapes.

2. Experimental

UV-visible spectra were obtained by Perkin-Elmer Lamda 17 spectrophotometer. Transmission electron microscopy (TEM) images were taken using Philips CM12/STEM, Scientific and Analytical Equipment. TEM sampling grids were prepared by placing 2 μl of the solution on a carbon-coated copper grid and the solution was evaporated at room temperature.

The organic–inorganic composite was prepared by sol–gel method. For a typical synthesis, 1·5 g of polyvinyl alcohol (PVA 72000) was dissolved in 30 ml distilled water stirred for 30 min and 2·5 ml of tetraethylorthosilicate was added. The mixture was stirred for 10 min, and then 0·5 g of silicotungstic acid was added and refluxed at 343 K for 6 h. The final transparent solution was coated on glass slide by spin coating method. This was dried in oven at 50°C for 10 min and irradiated in sunlight for 60 min.

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3. Results and discussion

The photoreduction of silicotungstic acid was monitored through UV-visible spectroscopy, which has a characteristic band around 750 nm indicating the formation of single electron reduced silicotungstate ion (figure 1). Up to 60 min, with an increase in the irradiation time the intensity at 750 nm increased. After 60 min irradiation, there was no change in the absorption band (750 nm) indicating that all the silicotungstate ions in the composite have been reduced. The ESR spectra of photoreduced composite film exhibited a signal at $g = 1.813$ at 77 K, which is due to the formation of single electron reduced species, $SiW_{12}O_{40}^{5-}$ (Varga *et al* 1970). The photoreduced composite film was stable in air for one week and in inert atmosphere for three months (Viswanathan *et al* 2003). This reduced composite was dipped in beaker containing chloroplatinic acid (5×10^{-3} M) solution. The reduction of metal ions and reoxidation of composite were monitored through UV-visible spectroscopy. The growth and formation of platinum nanorods were monitored through TEM.

The exact mechanism for the formation of platinum nanorods via this reduction technique is still under investigation. The proposed hypothesis is based on the electron microscopic and the absorption spectroscopic studies. Figure 2 shows the transmission micrographs of product obtained at different intervals of time. The formation of nanoparticles in the initial stage is evidenced from the TEM image shown in figure 2a. The metal ions, which are in contact with the surface of the composite film, get reduced to give metal nanoparticles (10–15 nm). The slow

dissolution of small platinum particles into the solution might also play a role to give anisotropic nanocrystals. The obtained nanoparticles aggregate to give anisotropic facets through the Ostwald ripening (Milligan and Morris 1964) (figure 2b). The inset shows the selected area electron diffraction (SAED) pattern for the facets which reveals that only a hexagonal diffraction spot pattern was observed, indicating the formation of single crystal platinum growing along in [111] direction. Beck *et al* (2000) reported a controlled growth of palladium particles at the solid/liquid interface on silica. The formation of anisotropic platinum nanocrystals at the solid–liquid interface indicates that the growth is highly localized, thus leading to considerable growth of the crystals away from the interface forming nanoparticles of triangular, hexagonal, pentagonal, square particles as evidenced from the TEM image (figure 2c). The anisotropic cluster particles grow into bigger particles through cluster–cluster aggregation (Sander 1986) giving rise to flower like morphologies (i.e. scaling is predominant) (figure 2d). The sharp parts of the structure grow faster than the rest of the structure (Witten and Sander 1981); it will catch random walkers more efficiently than the flat portions of the surface, thus giving rise to nanorods having a length of 350 nm and a diameter of 55 nm (figure 2e). Electron diffraction studies reveal that the platinum nanorods are highly single crystalline in nature.

The formation of platinum nanorods could be explained through the diffusion limited aggregation mechanism (DLA). In the present case, the reduction takes place in two-dimensional solid–liquid interface. At the initial stage, the platinum ions interact with the surface of the
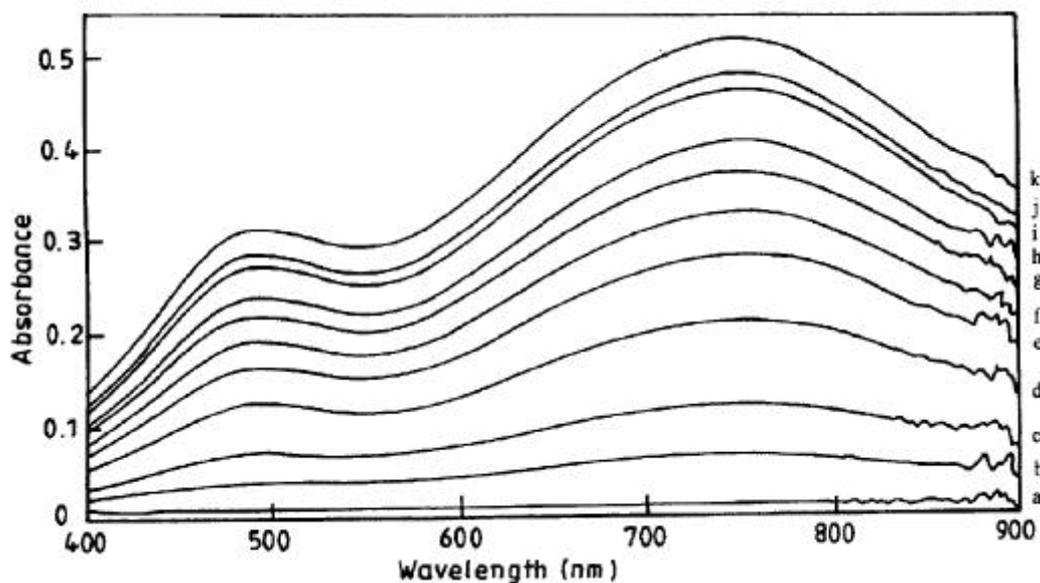
Figure 1. UV-visible absorption spectra of composite film irradiated in sunlight. a. 0, b. 5, c. 10, d. 15, e. 20, f. 25, g. 30, h. 40, i. 50, j. 55 and k. 60 min.
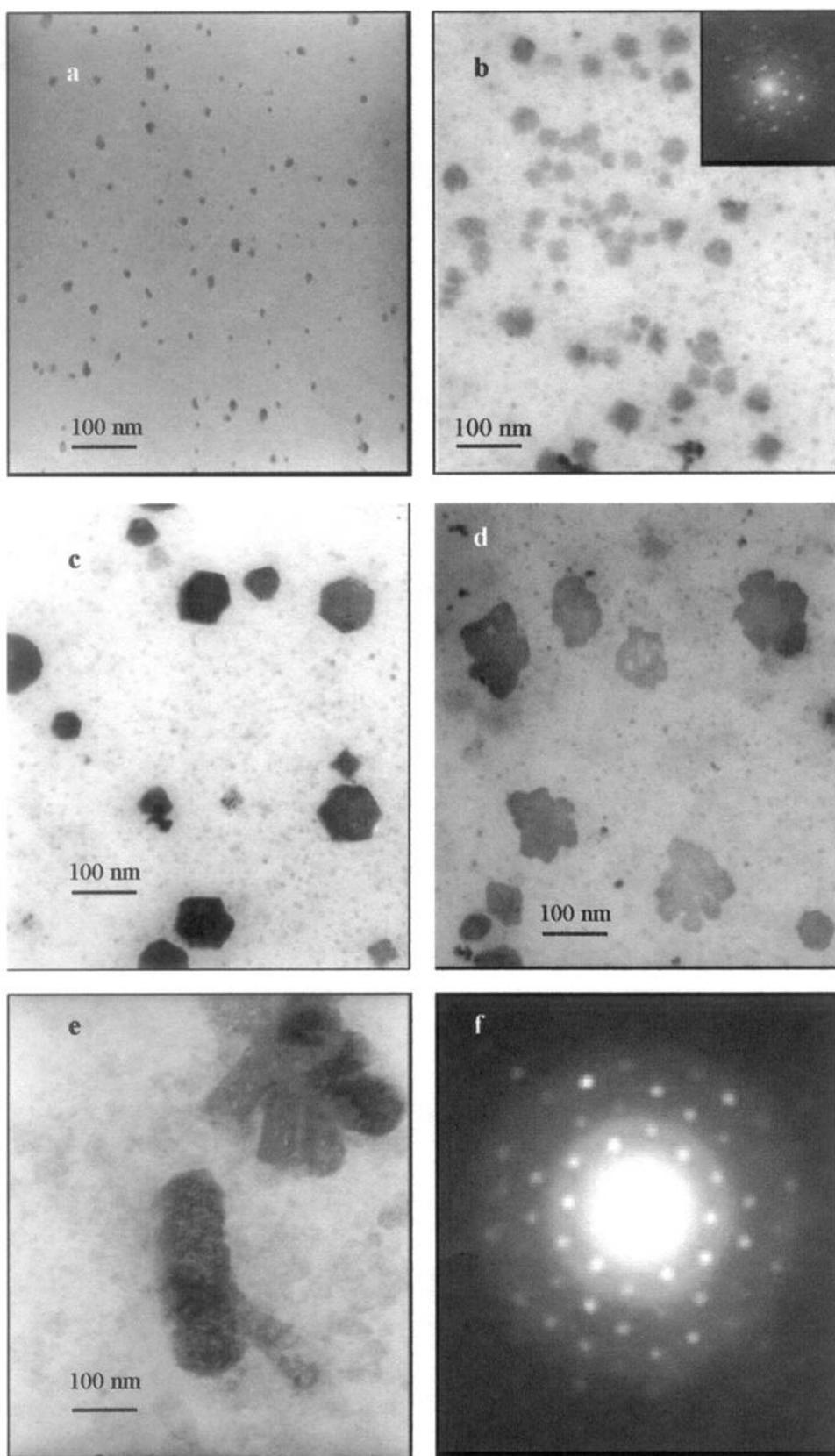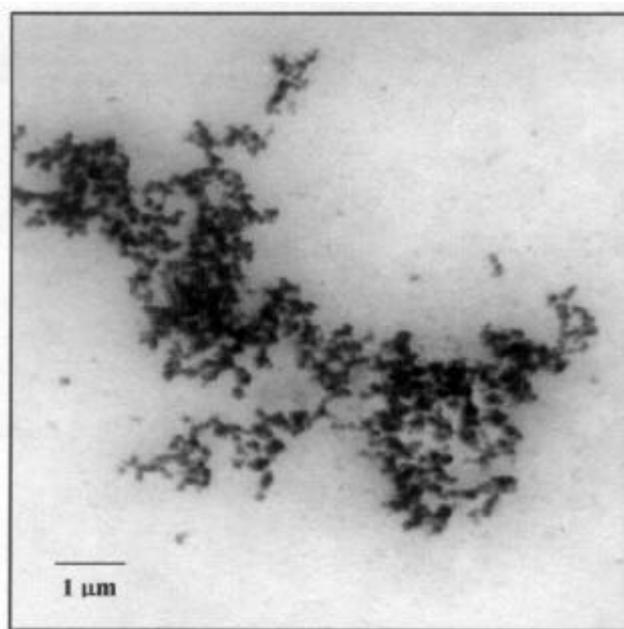
Figure 2. TEM image of reaction mixture at different intervals of time. a. 5, b. 10, c. 15, d. 20, e. 30 min and f. electron diffraction pattern of figure 1e.
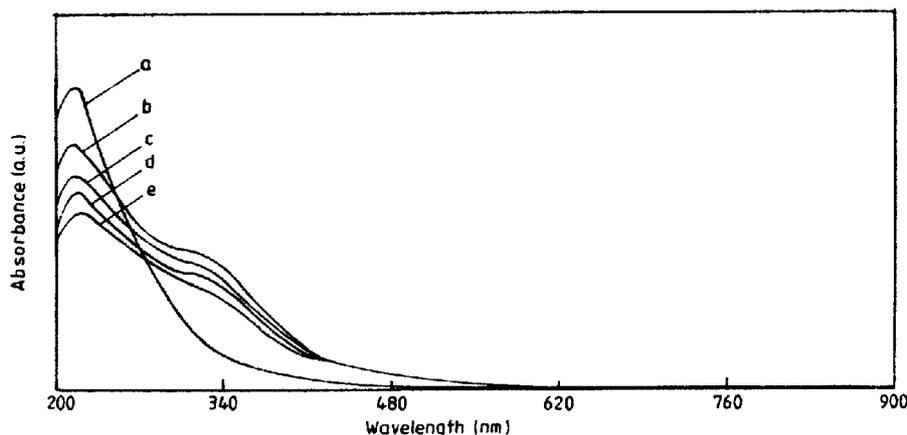
Figure 3. UV-visible absorption spectra of reaction mixtures at different time intervals.
a. 0, b. 5, c. 10, d. 20 and e. 30 min.

composite, get reduced and leave the surface. The new Pt nanoparticles, which are formed at the interface get stuck to the platinum particles and grow into bigger clusters (Zhang and Lagally 1997). In order to understand the formation of platinum nanorods by this method, controlled experiment was carried out. The composite gel (without making film) was irradiated in sunlight for 60 min and chloroplatinic acid was added (homogeneous reaction), which resulted in the disappearance of blue colour. The product obtained was mainly composed of irregular platinum nanoparticles without nanorods. This result indicates that composite film (solid–liquid interface) is vital for the formation of platinum nanorods.

Figure 3 shows the UV-visible absorption spectra of the reaction mixture taken at different time intervals (0, 5, 10, 20, 30 min). Aqueous chloroplatinic acid has an absorption band at 220 nm. It can be seen that the absorption band of $PtCl_6^{2-}$ decreases as the reaction proceeds. At 5th min, the appearance of a weak surface plasmon band at 340 nm indicates the formation of platinum nanoparticles with diameters of 10–20 nm in relatively low concentration. The absorption band of the platinum particles is mainly due to the interband transition from the '*d*' band lying rather close to '*sp*' band in the metal (Henglein *et al* 1995). For silver and gold nanoparticles, the red shift of surface plasmon band have been observed as the particles grow (Satoh *et al* 1994), but for the platinum nanoparticles (Weaver *et al* 1981), the surface plasmon band is weak and blue shifted. The intensity of the surface plasmon band decreases as the platinum particle size increases. When platinum forms clusters, the absorption spectrum becomes more flat which may be due to the dipole–dipole interaction of the aggregated particles (Quinten *et al* 1989). As the reaction proceeds, the intensity of the band at 340 as well as 220 nm further decreased in intensity indicating that the platinum particles are growing and giving rise to anisotropic shapes. This

Figure 4. TEM image of the reaction mixture at 60 min.

observation is well correlated with the TEM studies. As the reaction proceeds the spherical nanoparticles grow into nanorods through the intermediate structures. These experimental results suggest that it would be possible to control the particle morphologies of platinum by varying the experimental conditions (growth time).

Figure 4 shows the TEM image of the reaction mixture at 60 min. Platinum nanorods are aggregated by DLA diffusion limited aggregation mechanism resulting in fractal like structure growth in which one nanorod after the other formed diffuses and sticks to the growing structure. From the TEM and absorption studies it has been speculated that platinum nanorods at the solid–liquid interface formed and the stepwise growth is shown in scheme 1.
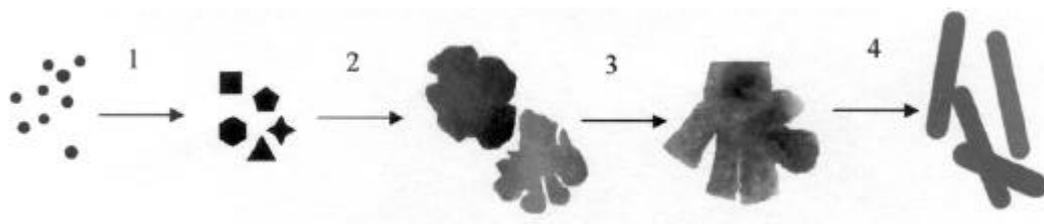
Scheme 1. Stepwise growth and formation of platinum nanorods.

In step 1 the formation of platinum nanoparticles are facile. The formed nanoparticles are reactive and will form facets in order to reduce the surface energy through the Ostwald ripening process (step 2). The cluster–cluster aggregation can be possible between the clusters of similar masses giving rise to three-dimensional growth and fragmentation leads to nanorods (steps 3 and 4).

4. Conclusions

In conclusion, a simple method has been described to prepare platinum nanorods. The adopted method does not require any stabilizing or polymer template to form platinum nanorods. The formation of platinum nanorods and self-assemblies is explained through the diffusion limited aggregation process. The growth and formation of platinum nanoparticles and self-assemblies were proposed based on TEM and absorption studies.

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