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Room temperature synthesis of colloidal platinum nanoparticles†

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Abstract. Efficient preparation of stable dispersions of platinum nanoparticles from platinous chloride (K_2PtCl_4) was achieved by simultaneous addition of capping polymer material. The size of platinum nanoparticles was controlled by changing the ratio of concentration of capping polymer material to the concentration of platinum cation used. The morphology of colloidal particles were studied by means of UV-visible spectrophotometry and transmission electron microscopy (TEM). Particle size increased with low reagent concentration. The change in absorption spectra with the particle size was observed, i.e. blue shift attributed to decrease in particle size.

Keywords. Platinous chloride (K_2PtCl_4); sodium polyacrylic acid; platinum nanoparticles; UV-visible; TEM.

1. Introduction

Interest in nanoscale materials increased in recent years with the realization that unique properties may be obtained from otherwise ordinary materials (Gleiter 1989). Colloidal metal particles are of interest because of their use as catalysts (Hirai *et al* 1983), photocatalysts (Brugger *et al* 1981), adsorbent and sensors (Thomas 1988) and application also in optical, electronic and magnetic devices (Schon and Simon 1995). The catalytic reactivity depend on size and shape of nanoparticles and therefore synthesis of controlled shapes and size of colloidal platinum particles could be critical for these applications. Nanostructured materials promise unique properties with potential applications in a wide range of technologies including advanced ceramics, electronics, catalysis, sensors etc. Colloidal platinum in aqueous solution has been known for many decades. In most methods of preparation two or four valent platinum are reduced. The most popular procedure being the reduction of $PtCl_6^{2-}$ by citrate as described by Aika *et al* (1976). Ionizing radiation has also been applied to initiate the reduction, making use of the reducing properties of the hydrated electrons and organic radicals which are formed in the radiolysis of the solvent and added organic compound polyvinyl alcohol used as stabilizer.

In this paper we report the synthesis of colloidal platinum nanoparticles in an aqueous medium at room temperature and its characterization by UV-vis and TEM studies.

2. Experimental

2.1 *Colloid preparation by hydrogen reduction*

The colloidal platinum nanoparticles were synthesized by Rampino and Nord (1942) method. The platinum was incorporated in the form of potassium platinous chloride (K_2PtCl_4) solution. A solution of 1×10^{-4} M K_2PtCl_4 was prepared in 250 ml water to which 0·2 ml and 0·5 ml of 0·1 M sodium polyacrylic acid (average m.wt. 2,100) was added separately to the starting solution. Argon gas was bubbled in the solution for 20 min. Later, reduction of platinum ions was carried out by bubbling hydrogen gas vigorously into the solution for 10 min. Then the reaction vessel was tightly sealed and left overnight. After 12 h, the solution turned light golden. In another experiment the amount of polymer material was kept constant as 0·2 ml of 0·1 M solution and varied the K_2PtCl_4 concentration from 1×10^{-3} to 1×10^{-7} and rest of the procedure remained the same.

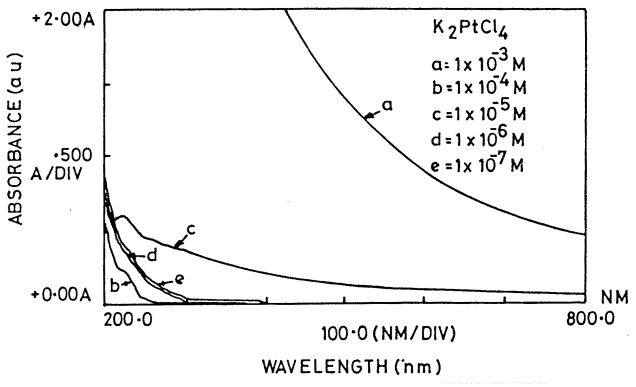

Figure 1. a–e. Absorption spectra of platinum particles containing varying concentrations of K_2PtCl_4 (1×10^{-3} to 1×10^{-7}) and polyacrylic acid (0·2 ml of 0·1 M).

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Yet in another experiment instead of hydrolyzing $PtCl_4^{2-}$ before the treatment with hydrogen, the solution was aged (for 1 day before exposure to hydrogen) to allow the complex to aquate ($Cl^- \rightarrow H_2O$ ligand exchange). 1×10^{-4} M of the aged K_2PtCl_4 solution was taken in R.B. flask containing 0·2 ml of 0·1 M sodium polyacrylic acid solution and then bubbled argon gas for 20 min and 10 min with hydrogen. These platinum particles were characterized by UV absorption and TEM studies, which showed the formation of platinum particles.

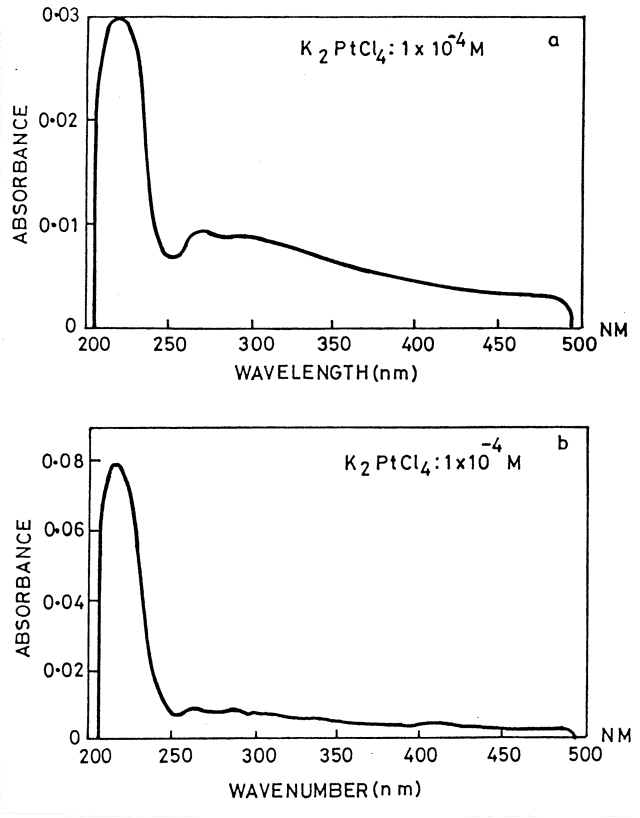

Figure 2. Absorption spectra containing 1×10^{-4} M K_2PtCl_4 and varying the amount of polymer **a.** 0·2 ml of 0·1 M and **b.** 0·5 ml of 0·1 M.

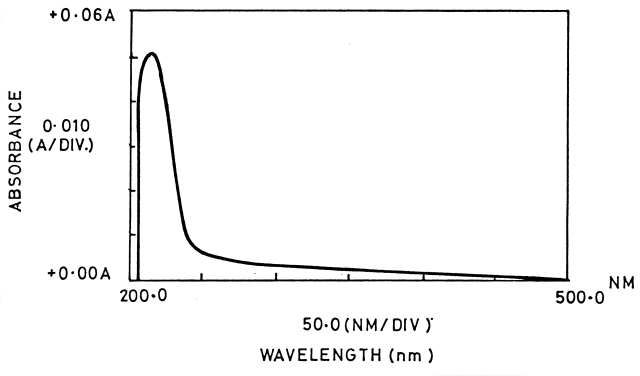

Figure 3. Absorption spectrum of platinum particles of aged samples (1×10^{-4} M K_2PtCl_4 and 0·2 ml of 0·1 M polymer).

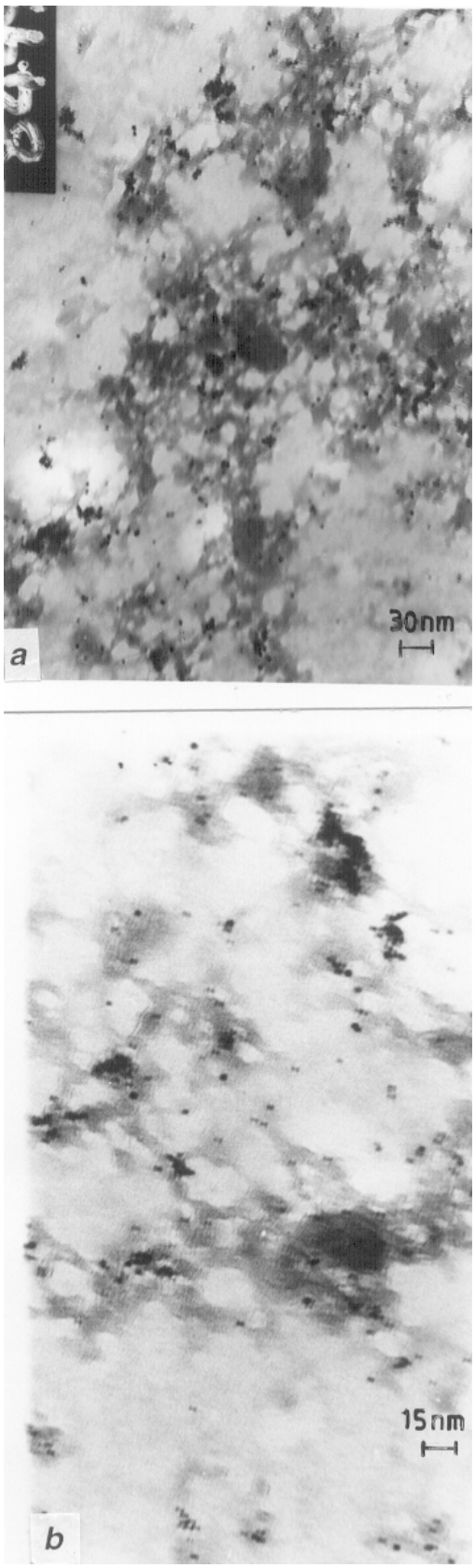

Figure 4. TEM image of platinum particles with 1×10^{-4} M K_2PtCl_4 and 0·2 ml of 0·1 M sodium polyacrylic acid **a.** low magnification and **b.** high magnification.

3. Results and discussion

Synthesized colloidal platinum particles were characterized by UV absorption and crystal structure determined using transmission electron microscope. The TEM specimen were prepared by dispersing the platinum particles on copper grid.

3.1 *Reduction of Pt(II) complex by hydrogen*

When a freshly prepared K_2PtCl_4 solution containing polyacrylic acid was kept under hydrogen, the reduction occurred slowly. The reduction was faster when K_2PtCl_4 solution was aged for 1 day before exposure to hydrogen. $PtCl_4^{2-}$ in dilute aqueous solution was known to be converted into aquated complexes within few hours at ambient temperature (Cotton and Wilkinson 1972)

$$PtCl_4^{2-} + H_2O \rightarrow PtCl_3(H_2O)^- + Cl^-,$$

$$PtCl_3(H_2O)^- + H_2O \rightarrow PtCl_2(H_2O)_2 + Cl^-.$$

The rate of reduction of the aquated complexes by hydrogen was faster than that of freshly prepared K_2PtCl_4 solution.

3.2 *UV absorption spectra*

Figures 1a–e show the absorption spectra of platinum particles wherein the concentration of polymer material remains constant (0·2 ml of 0·1 M polymer) and varying the K_2PtCl_4 concentration from 1×10^{-3} to 1×10^{-7} M. The spectra clearly showed a decrease in wavelength with decrease in concentration of platinous chloride (399 nm for 1×10^{-3} and 234 nm for 1×10^{-7} concentration) which in turn relates to decrease in particle size. The spectrum was obtained when solutions containing $PtCl_4^{-2}$ in different concentrations were completely reduced and when the colloidal solutions were diluted.

Figures 2a,b show the absorption spectrum of the platinum colloids when the amount of sodium polyacrylic acid stabilizer was varied (0·2 and 0·5 ml of 0·1 M polymer) and keeping K_2PtCl_4 concentration constant (1×10^{-4}). It was seen that with increase in amount of polymer there was a gradual decrease in wavelength of absorption spectrum. Figure 3 is the absorption spectrum of platinum particles of aged samples. Practically there was no change in absorption spectrum of the aged samples except that the

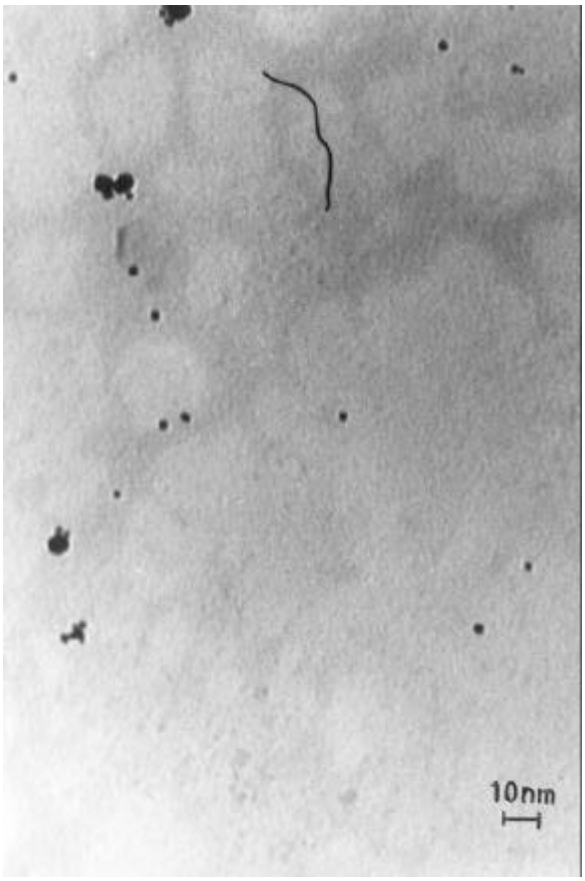

Figure 5. TEM image of platinum particles with 0·5 ml of 0·1 M polymer material.

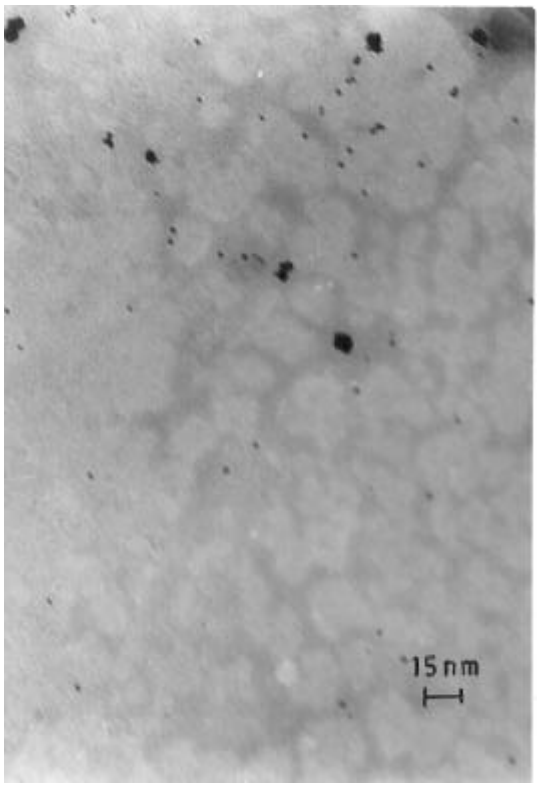

Figure 6. TEM image of platinum particles of aged sample (1×10^{-4} M K_2PtCl_4 and 0·2 ml of 0·1 M polymer).

reduction was faster compared to freshly prepared solutions. The spectrum was identically the same.

3.3 *Transmission electron microscope*

Figure 4a is the low magnification TEM image of platinum nanoparticles containing 0·2 ml of 0·1 M polymer and 1×10^{-4} M K_2PtCl_4 solution. The sample predominantly contains particles with a square outline with a particle size of 12 nm. The particles are well separated whereas figure 4b is high magnification image of typical platinum nanoparticles. These particles show square surface clearly. However with increase in capping polymer material to 0·5 ml of 0·1 M and 1×10^{-4} M K_2PtCl_4 solution the platinum particles showed rounded shapes with particle size of 8 nm as seen in figure 5 whereas samples kept for ageing before reduction also showed square shaped particles with size of 11 nm as seen in figure 6. Hence shape depends on the amount of polymer material.

4. Conclusions

To summarize the various findings on chemical reactivity, it is seen that using same capping material, same salt, solvent and temperature but changing the ratio of the concentration of capping material (sodium polyacrylic acid) to that of platinum ions produces different shapes of platinum nanoparticles. A blue shift observed in UV absorption due to quantum size effect attributed to decrease in particle size successfully synthesized platinum nanoparticles at room temperature.

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