APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 784–787

(www.interscience.wiley.com) DOI:10.1002/aoc.1126

Materials, Nanoscience and Catalysis **AOC**

Short communication

One-pot dual size- and shape selective synthesis of tetrahedral Pt nanoparticles

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Received 12 April 2006; Accepted 13 May 2006

One-pot dual size- and shape-selective synthesis of tetrahedral Pt nanoparticles is achieved using the pre-prepared Pt nanoparticles as the 'external seeds', and controlling the slow diffusional growth under hydrogen reduction in the presence of PVP as the capping agent. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: size and shape selective synthesis; Pt nanoclusters

INTRODUCTION

Size- and shape-controlled nanoparticles offer incentives for their wider applications as electronic, optical and magnetic materials.[1,2] It is well understood that the properties of nanoparticles for these applications are size and shape dependant.[3–5] Further, in catalysis, control of the particle size and their growth kinetics show a direct relation between the catalytic activity and the particle morphology.[5] However, the synthesis of nanoparticles with well-defined geometric confinement remains a challenging task. New synthetic approaches for size- and shape-controlled nanoparticles synthesis are regularly investigated. In this realm the wet chemical synthesis of nanostructures is a very useful and versatile method. Particle size or shape control in wet chemical synthesis can be achieved using *capping agents*,[6–12] e.g. ligands, surfactants, tetralkylammonium salts, dendrimers or *templates*[13–18] like micelles, carbon nanotubes and porous alumina. By using different ratios of precursors and capping agents, nucleation and growth steps are controlled in wet chemical nanoparticle synthesis.[19–21] Nucleation and growth steps during the formation of nanoparticles are sensitive to physical and chemical parameters.[22] The mechanism of Pt nanoparticle formation with different shapes has been discussed previously.[23] The seeding method is also routinely applied to synthesize anisotropic Au nanostructures,[24] but none of the methods developed so far offer a precise control over both the size and the shape together, without drastically altering reaction conditions. One has to either change the amount of surfactants many times or change the temperature to achieve a particular shape. Also one can obtain a particular shape or size and never select both. Or more precisely nanoparticles in similar reaction conditions with same shapes but with different particle sizes are very difficult to achieve.

Here we present a simple and versatile method to control Pt nanoparticle shapes and sizes simultaneously. In our experiments we have combined the seed-mediated synthesis and the buffer action of the polymer-protecting agent as well as the diffusional growth of the nanoparticles by slow reduction as the parameters to control shape and size of Pt nanoparticles. This offers better control over thermodynamic and kinetic parameters. Diffusional growth can be achieved by slow reduction and seeding is applied to vary the particle size. A variety of Pt tetrahedral nanoparticles in different sizes can be prepared using this method. This method is further extended for preparing truncated octahedral particles with different sizes. Using this mode Pd nanoparticles of different sizes and shapes can be prepared.

EXPERIMENTAL

All reagents were obtained from Aldrich Chemicals while REWO (REWOTERIC B 14) was purchased from Degussa and used as received. Ultra-pure de-ionized water (Millipore water) was used to prepare all the aqueous solutions. TEM

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Contract/grant sponsor: Deutsche Forschungsgemeinschaft; Contract/grant number: 1135/2-5.

analysis of each colloidal solution was performed after the complete reduction. TEM analyses were performed using a Hitachi H7500 instrument (magnification up to 1.25 million). For TEM analyses the specimens were prepared by placing a drop of the solution under investigation in water on a carbon film covered with a nickel grid and evaporating the solvent.

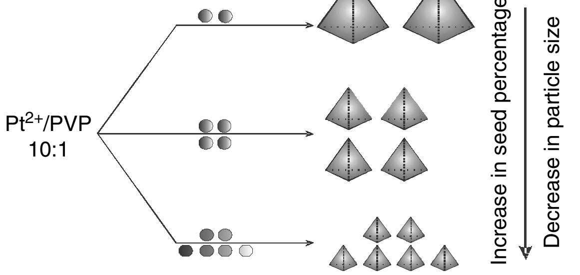
Seed preparation

A 0.18 mmol aliquot of H_2PtCl_6 was dissolved in 50 ml water and REWO (0.54) mmol surfactant and reduced under hydrogen overnight. Solvent from the reaction mixture was pumped out by freeze-drying. The colloid was repeatedly washed with acetonitrile and water (1 : 1) mixture. TEM analysis of the resultant black Pt colloidal powder shows 1 ± 0.2 nm metal nanoparticles.

To prepare tetrahedral Pt nanoparticles with different particle sizes, K_2PtCl_4 precursor solutions (1×10^{-4} M) with Pt^{2+}: PVP in 10 : 1 molar ratio were seeded with 0, 2, 5 and 10% seed nanoparticles (w.r.t. initial Pt^{2+} ion concentrations) and slowly reduced under hydrogen overnight. TEM analysis after complete reductions showed tetrahedral particles with different sizes formed depending upon the concentration of seed particles. If seed concentration was increased from 0 to 2% or from 5 to 10%, particle size decreased accordingly from 8 ± 1, 5 ± 1 and 2.5 ± 0.5 to 1.8 ± 0.3 nm.

RESULTS AND DISCUSSION

In the following experiments tetrahedral Pt nanoparticles were prepared by seeding in different amounts four reaction mixtures of Pt^{2+} salt and the protecting agent (polyvinylpyrrolidone, PVP) with similar reactant concentrations (Scheme 1). The seed particles used were pre-prepared Pt nanoparticles of average size 1 ± 0.2 nm, and narrow particle size distribution was shown by TEM analysis (Fig. 1). Seed particles were prepared by hydrogen reduction method developed in our group. Pt particles of ~1 nm size can be ideally considered as Pt_{55} or two-shell atomic clusters. PVP-stabilized tetrahedral Pt nanoparticles can be prepared in different sizes by varying the amount of these seeds while keeping the amount of surfactant constant.



Scheme 1. Tetrahedral Pt nanoparticles stabilized with PVP prepared by slow reduction under hydrogen. Except for the percentage of seeds, all reaction parameters are kept constant. ● = external Pt seeds.

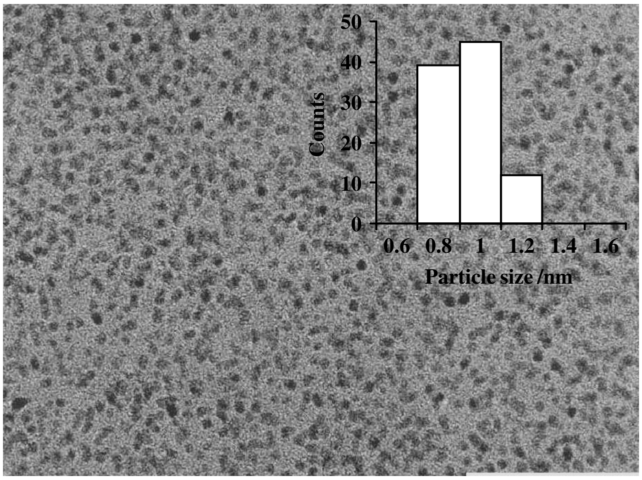


Figure 1. TEM of Pt seed particles. Average particle size ~1 ± 0.2 nm; scale bar, 20 nm.

Dominantly tetrahedral Pt nanoparticles with different particle sizes were obtained by carrying reduction of four different Pt^{2+} ion precursor solutions with Pt^{2+}: PVP as a 10 : 1 molar ratio. These reaction mixtures were seeded with 0, 2, 5 and 10% external Pt seed particles w.r.t. initial Pt^{2+} ion concentration and reduced slowly under hydrogen. In Fig. 2 TEM analyses after complete reductions are shown. Tetrahedral particles with different sizes are formed depending upon the concentrations of seed particles. If the seed concentration was increased from 0 to 2% or 5 to 10%, the nanoparticle size decreased accordingly from 8 ± 1 to 1.8 ± 0.3 nm. Thus the relation between the particle size and the amount of seeding can be correlated as an inverse relationship. It is also clear from TEM that higher seeding leads to smaller particles with size limit tending to particle size of the seeds [Fig. 2(d)]. For very small particles characteristic shapes like tetrahedrals are not easily achievable, but spherical or formless particles are also obtained for higher seeding concentrations. In Fig. 3, this relationship is made clearer.

These results can be interpreted as follows. The final geometric features of the nanocrystals depend upon the kinetic factors, which are the crystal growth conditions. For example, the buffer action of the polymer renders different stable shapes in a particular reaction environment. The strong adsorption of polymer would occupy the growth sites, and thus reduce the growth rate of the nanoparticles. One can simply state that the shape obtained by the nanoparticles is an intrinsic property of the polymer at that concentration, due to the constrained environment during the nanoparticle growth tuning their shapes accordingly.[21] In our case PVP renders the tetrahedral shape to the Pt nanoparticles. Further, the reducing agent strength also affects the shape and the size of the nanoparticles. Here hydrogen as a weak reducing

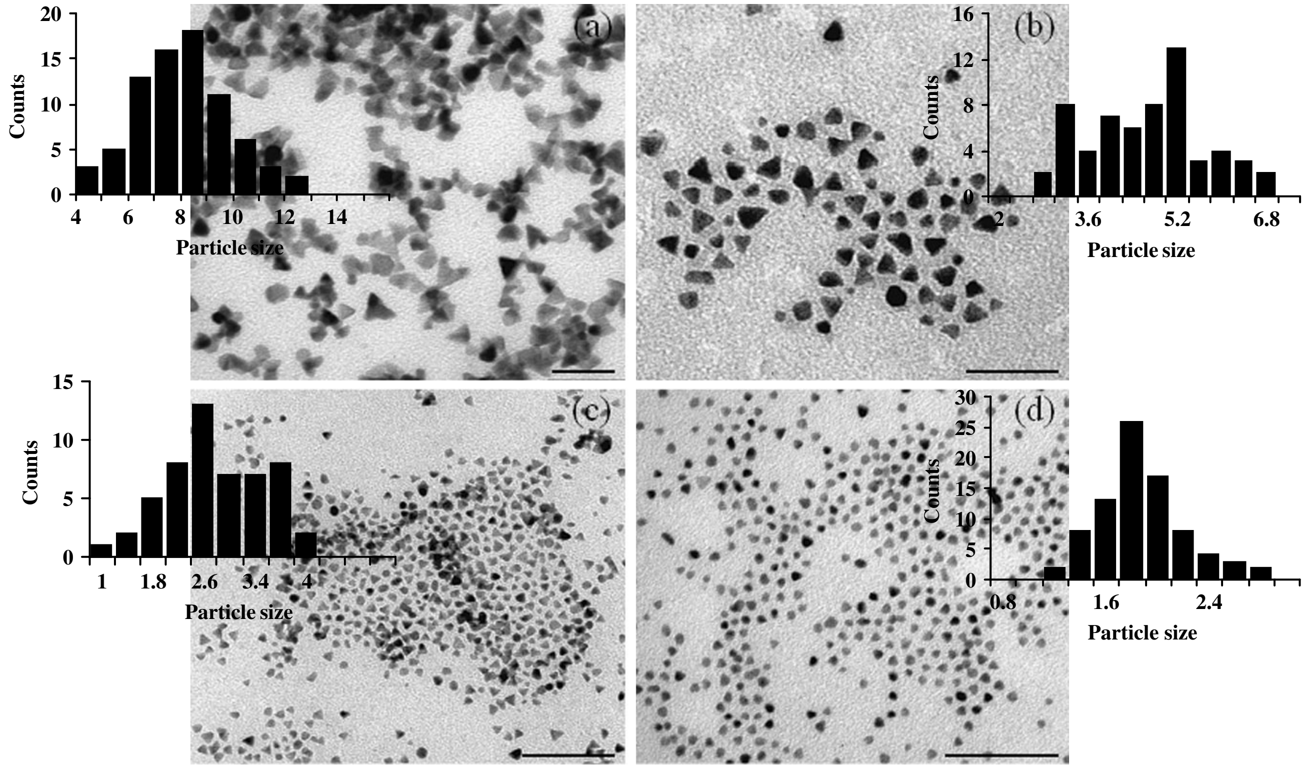


Figure 2. TEM show predominately tetrahedral nanoparticles of (a) 8 nm, (b) 5 nm, (c) 2.5 nm and (d) 1.8 nm average particle size. Scale bar, 20 nm.

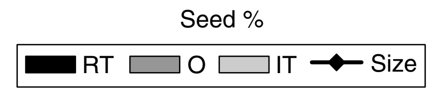


Figure 3. Graphical presentation of the size and the shape distribution of the Pt nanoparticles. As the amount of seed increases average particle size (m,m) decreases (RT, regular tetrahedrons; IT, irregular tetrahedrons; and O, other shapes).

agent causes slow reduction, favoring the slow, diffusional growth of the nanoparticles.[22,23] This, therefore, assures monodipersity of the nanoparticles. Moreover, by keeping the initial metal ion concentration low, uniform distribution of the nanoparticles through diffusional growth is favored. The external seeds act as the nucleation centers and grow further due to the reduction of the bulk metal ions at their surfaces.[24–26] Weak reducing agents like hydrogen inhibit the additional nucleation but promote non-spherical particle formation. Therefore the characteristic tetrahedral shape is preserved in these experiments. Also, different seed-to-metal ions concentration ratios yield different sizes of the faceted nanostructures. Because there are more seeds, the growth is slower and the exhaustion of the seeds is faster. Moreover, the critical size of the nuclei or the seeds in the homo- or heterogeneous nucleation represents the limit of the final nanoparticle size. This is also observed in our experiments, where particles with irregular shapes are also obtained for higher seed concentration (10%).

CONCLUSION

In conclusion, this seed-mediated approach yields different sizes of Pt-tetrahedral nanoparticles in similar reaction conditions when seeded with different amount of pre-prepared Pt seeds. TEM analysis shows that nanoparticle size varies inversely in relation to the added seed amount. Further, Pt (and Pd) nanoparticles with other shapes like truncated octahedrons and sizes could be easily prepared by this approach. This size- and shape-selective synthesis of nanoparticles has a huge significance in catalysis and nanoscience. For example, the shape dependence of the activation energy has been recently studied in the electron transfer reactions.[27,28] We have also shown how this shape selectivity can be exploited for catalysis for real fuel cell systems (S. Kinge, C. Urgeghe, A. De Battisti, H. Bönnemann, manuscript in preparation). Further studies for controlling shapes and sizes of other transition metal nanoparticles and their catalytic studies are under way.

Acknowledgements

Financial support by Deutsche Forschungsgemeinschaft under grant no. 1135/2-5 (Priority Program 1060) is gratefully acknowledged.

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DOI: 10.1002/aoc