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Morphology and crystalline structure of polymer stabilized Pd nanoparticles†

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Five types of crystal morphologies, including triangular, hexagonal, pentagonal, square and rhombohedral, have been observed for polymer stabilized Pd nanoparticles.

Nanometer sized particles have unique electrical, optical and catalytic properties:[1] research into metallic and alloy nanoparticles has blossomed and become a major force in science in recent years, although these materials have at least a 100-year old history. Various preparative methods have been found, including chemical and electrochemical reduction,[2,3] sonochemical,[4] vapor deposition[5] and microwave irradiation[6] in the presence of polymers,[2] microemulsions,[7] ligands[8] or appropriate solvents[9] as stabilizing matrices in order to prevent aggregation and growth into larger particles. Many scientists are enthusiastic about the control of the size of such materials as it is well known that the catalytic reactivity and selectivity are strongly dependent on the particles size. It is also believed that the shape of the particles has an effect on the catalytic reactions due to the changing of the surface-to-volume ratio. However the shape control of nanoparticles without any supporting material or surface deposit has still rarely been reported, especially for Pd nanoparticles. Moreover, according to Teranishi *et al.*[10] and Natan *et al.*,[11] larger metal particles with narrow size distributions can not be obtained in a one-step reaction; they should instead be generated through the stepwise growth method. Therefore an effective preparation method for particles with well-controlled shapes and sizes in a one-step reaction has yet to be developed. Nearly monodispersed nanoparticles with sizes ranging from 1 to 20 nm have been reported, with most of them assuming near spherical shapes. For protected noble metal nanoparticles without solid support, only sponge-like Rh,[12] Pd and Au particles,[13] cubic, tetrahedral and truncated octahedral Pt,[14] decahedral Ag[15] and rod-like and plate-like Au[16] have been described. An earlier paper[17] reported the TEM micrograph of large Pd particles with average diameter of 45 nm stabilized by sodium polyacrylate prepared by reduction of palladium chloride solution with sodium formate. The formed particles showed defined geometry but no description and control of their morphologies and structures was reported. As far as we can ascertain, no other nanocrystalline modification for unsupported Pd clusters has been reported. Such materials may be viable alternatives for the study of the effect of morphology and crystal facets on catalytic reactivity. In this communication we report, for the first time, the preparation and characterization of four nanocrystalline modifications of Pd colloids with average sizes ranging from 4 to 14 nm prepared *via* methanol reduction in an aqueous environment by using polyvinylpyrrolidone (PVP) as the stabilizing matrix.

The PVP stabilized Pd colloids were prepared by modification of a reported method[18] as follows: appropriate amounts of PVP (as monomeric residue) and Pd precursor (H_2PdCl_4, prepared by addition of HCl to $PdCl_2$) were dissolved in a mixture of methanol (65 ml)–water (75 ml) as solvent. The solution was refluxed under vigorous stirring for 180 min to obtain a black homogeneous dispersion. During the reaction, 10 ml of 0.1 M methanolic NaOH solution was added dropwise. The particle size distribution, morphology and crystalline structure of the Pd nanoparticles were determined by TEM (Philips CM120 at 80 kV), HRTEM and electron diffraction (JEOL-1020 at 200 kV).

A typical TEM micrograph with different morphologies of Pd nanoparticles after refluxing for 3 h is shown in Fig. 1a. As shown in Table 1, the average particle sizes increase with increasing amounts of Pd precursor when the PVP concentration is kept constant. Meanwhile, the average particle size increases slightly with decreasing PVP concentration and without addition of NaOH during the synthesis, as shown in runs 4, 5 and 6 in Table 1. Their relative standard deviations are generally between 0.3–0.5 except for the 40 : 2 sample (∼0.9). No geometric shape other than spherical or near spherical was observed for the smaller nanoparticles with a PVP : Pd ratio of 40 : 1; for PVP : Pd = 40 : 2 ∼20% of the particles have geometrical shapes, the majority of which are hexagonal faced. For the samples prepared with higher PVP : Pd ratios, most of the particles have definite geometric shapes. Truncated triangular, four-sided, pentagonal and hexagonal are the most frequently observed particle face shapes, which are shown in Fig. 1a–c. Thus, the polydispersity of PVP : Pd = 40 : 2 may be explained by the transformation from spherical to other geometric shapes. On higher magnification, both the triangular and some of the hexagonal faced particles do not show more features indicating that these are plane surfaces of the particles. However the other hexagonal faced particles are twinned as some of them showed a ridge across the opposite angles. The four-sided face particles are either square or rhombohedral. The pentagonal particles are made up of five triangles with the vertex in the center protruding out of the plane of the micrograph. These polyhedral particles are either pentagonal bipyramids or decahedra of distorted cubes or twinned tetrahedra derived from the triangular single crystallites. The HRTEM micrograph and electron diffractogram (Fig. 2) of the triangular face shaped particle shows that these particles are single prismatic crystals along the (011) plane. The atom arrangement showed a non-distorted face centered cubic (FCC) packing with a unit cell

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†Electronic supplementary information (ESI) available: particle size distributions for various molar ratios of PVP : Pd. See http://www.rsc.org/suppdata/jm/b1/b106578p/

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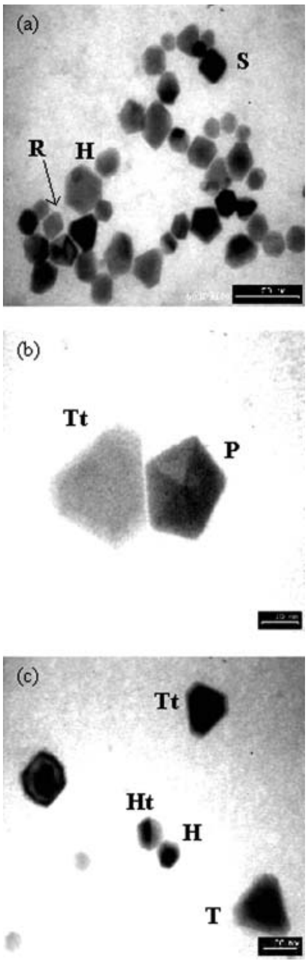

Fig. 1 TEM micrographs of PVP stabilized Pd nanoparticles (PVP : Pd = 60 : 4). S: square, R: rhombohedral, H: hexagonal, Ht: twinned hexagonal, T: triangular, Tt: truncated triangular and P: pentagonal [scale bar: (a) 50 nm; (b) 10 nm; (c) 20 nm].

dimension of ~0.39 nm. The {200} and {111} *d*-spacings of the particles are respectively 0.216 nm and 0.248 nm, which are about 10% larger than the unit cell dimensions of bulk Pd metal, in contrast to the expansion of 9% and 4% of smaller Pd particles deposited on TiO_2.[19]

Table 1 Synthesis conditions, mean diameter ($\bar{d}$), standard deviation (σ) and relative standard deviation (σ_r) for PVP–Pd nanoparticles which were refluxed in $CH_3OH–H_2O$ solution for 3 h

No.	PVP : Pd (molar ratio)	n_{Pd}/mmol	$\bar{d}$/nm	σ/nm	$\sigma_r{}^a$
1	40 : 1	0.125	1.5	0.42	0.28
2	40 : 2	0.250	5.7	5.12	0.89
3	40 : 3	0.375	7.4	2.84	0.38
4	40 : 4	0.500	13.7	6.43	0.47
5	60 : 4	0.500	12.6	4.35	0.34
6	60 : 4^b	0.500	14.4	6.09	0.42

[a] Relative standard deviation ($\sigma_r = \sigma/\bar{d}$). [b] Without 0.1 M NaOH–CH_3OH.

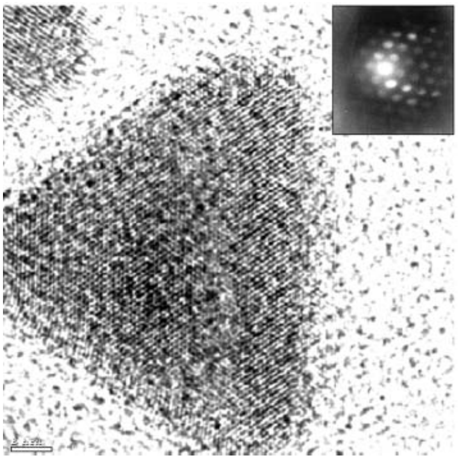

Fig. 2 HRTEM micrograph [scale bar: 2 nm] and (insert) electron diffractogram of the triangular faced particles. The spacings indexed to the FCC lattice.

The relative percentages of the various modifications of these particles in different colloids are shown in Fig. 3. It is observed that the morphology of the particles formed depends on the concentration of the Pd precursor. When the PVP : Pd ratio is smaller than 40 : 2 the predominant morphology of the particles is spherical or near spherical with no definite geometric shape. This may however be due to the low resolution of the instrument. The proportion of these rather shapeless particles decreases to less than 10% of the total observed at higher Pd precursor concentrations. The proportion of triangular or truncated triangular face shaped particles increases, reaching more than 30% when the PVP : Pd ratio is 40 : 4. For the ratio of 60 : 4, in which the precursor concentration was the same as the 40 : 4 sample but with the PVP concentration increased by 50%, the proportion of the triangular faced particles increase to >46% with a decrease in the spherical and hexagonal faced particles. Thus, as the concentration of the precursor Pd increases, a larger proportion of triangular faced particles was formed while the proportion of hexagonal faced particles decreases. The proportion of pentagonal particles remains almost unchanged for all the colloids. It was also found that the presence of base also affects the morphology of the Pd nanoparticles, as well as accelerating the reduction rate. Regular triangular face particles are favoured rather than the truncated triangular particles, while the four-sided particles increase markedly in the absence of NaOH.

In summary, the non-supported Pd nanoparticles with well-dispersed and well-defined geometrical faces, including triangular, hexagonal, pentagonal, square and rhombohedral particles, can be synthesized in a novel one-step reaction for the first time. The stabilizer and precursor concentration play important roles in the morphological control. These non-supported Pd nanoparticles have the same FCC structure as the bulk metal.

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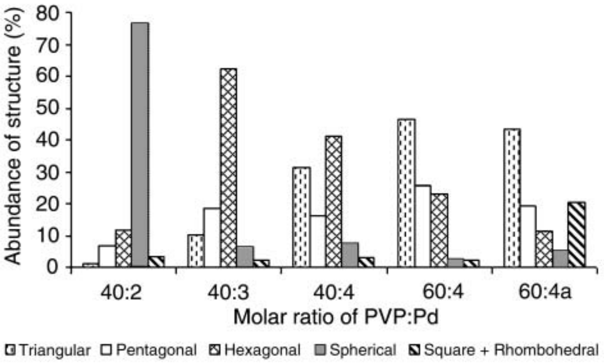

Fig. 3 Morphological distribution of PVP–Pd with molar ratios of 40 : 2, 40 : 3, 40 : 4, 60 : 4 and 60 : 4a, without 0.1 M NaOH, after refluxing for 3 h.

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