

## Shape Control of Platinum Nanoparticles by Using Different Capping Organic Materials

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Nanometer-sized metal particles are of great interest in modern chemical research, where they find application in such diverse fields as photochemistry,<sup>1</sup> electrochemistry,<sup>1-3</sup> optics,<sup>1-5</sup> and catalysis.<sup>1,6,7</sup> The chemical and physical properties of these particles are distinct from those of the bulk phase and those of isolated atoms and molecules. The specific properties of nano-sized metal particles in catalysis are usually associated with a change in their electronic properties relative to the bulk samples. This change is a result of size effects giving rise to an increase in the surface energy and a characteristic high surface-to-volume ratio. These lead to an enhancement of their catalytic properties<sup>8</sup> as large fractions of the active metal atoms are on the surface and thus are accessible to reactant molecules and available for catalysis.<sup>9</sup>

Catalytic property depends on the size and the shape of the nanoparticles because reactant molecules have different sorption structures on the various surface planes. For example, selectivity of crotonaldehyde hydrogenation to the primary products butyraldehyde and crotyl alcohol depends critically on the Pt particle size and shape (facet).<sup>10</sup> Therefore the synthesis of well-controlled shapes and sizes of nanoparticles could be critical for our understanding of the whole phenomena of catalysis and the design of more ideal catalysts for different chemical transformations.

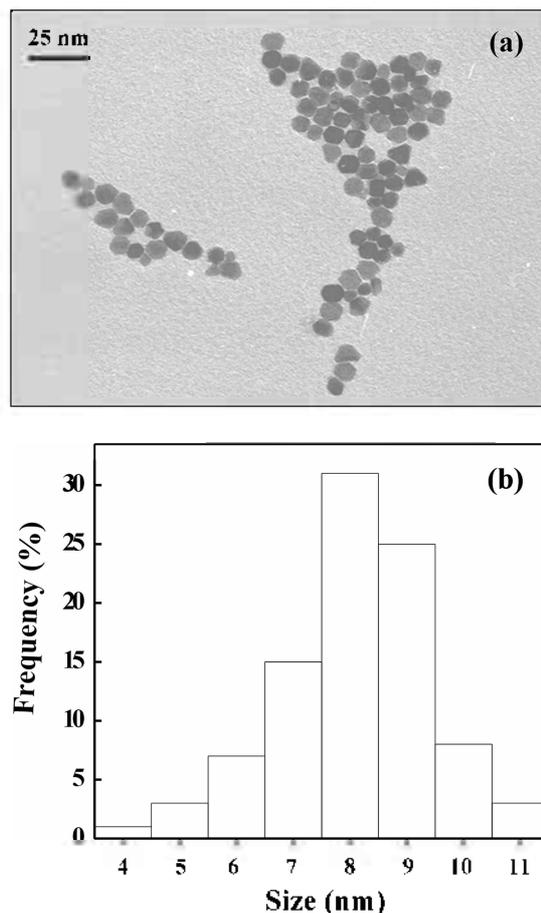
In the present study, truncated octahedral and cubic Pt nanoparticles are respectively synthesized using  $K_2PtCl_4$  solution and the capping material such as polyacrylate and acrylic acid at room temperature. The particle size/shape are characterized by transmission electron microscopy (TEM).

The Pt nanoparticles were prepared by the method of Rampino and Nord<sup>11</sup> and Henglein *et al.*<sup>12</sup> Truncated octahedral nanoparticle was synthesized as follows. 1 mL of 0.1 M sodium polyacrylate as a capping polymer was added to 250 mL containing  $8.0 \times 10^{-5}$  M  $K_2PtCl_4$  solution. The initial concentration ratio of  $K_2PtCl_4$  to polyacrylate was 1 : 5. The pH of the solution was adjusted to 7 with 0.1 M HCl and purged with Ar for 20 min. The platinum complexes were reduced by bubbling  $H_2$  for 5 min. The solution was left for 12 h in the dark. We prepared cubic Pt nanoparticles by adding 8 mL of 0.1 M acrylic acid and following same

procedure. The initial concentration ratio of  $K_2PtCl_4$  to acrylic acid was 1 : 40.

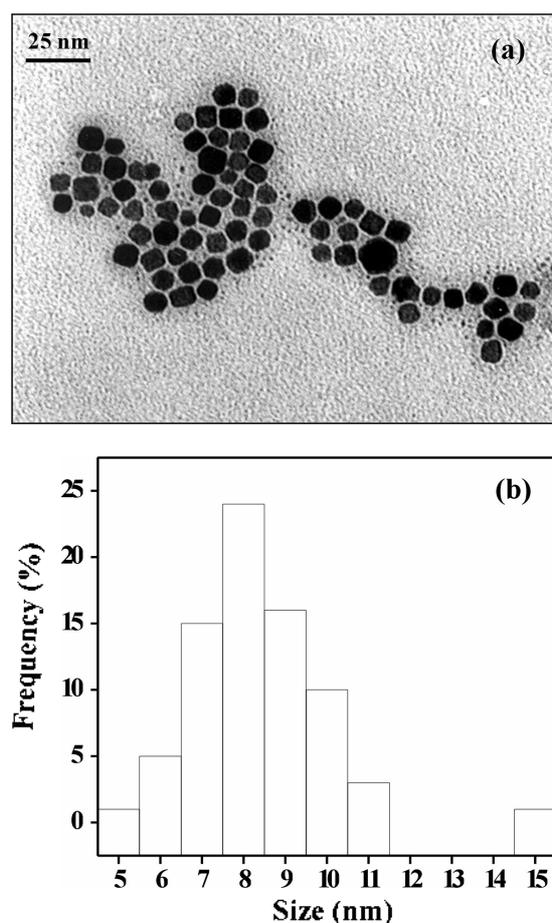
TEM was used to determine the particle size and shape of the Pt nanoparticles studied. TEM images were taken by using a JEM 100C operated at an acceleration voltage of 100 kV at a magnification of 100,000-190,000. The particle size and shape were determined from an enlarged TEM images.

Figure 1a shows a TEM image and Figure 1b exhibits the nanoparticle size distribution prepared with 1 : 5 initial concentration ratio of  $K_2PtCl_4$  to polyacrylate at room temperature. The "squares", the "triangles", and the "hexagons"



**Figure 1.** (a) TEM images of platinum nanoparticles prepared using a 1 : 5 concentration ratio of  $K_2PtCl_4$  to polyacrylate at room temperature and (b) their size distribution.

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**Figure 2.** (a) TEM pictures of platinum nanoparticles synthesized using a 1 : 40 concentration ratio of  $K_2PtCl_4$  to acrylic acid at room temperature and (b) size distribution of cubic nanoparticles.

represent the cubic, tetrahedral, and the truncated octahedral particles, respectively. This image is taken from a randomly chosen part of the substrate, and it is a good representation of the overall sizes and shapes of the particles. The particles are aligned with monolayers, which attached each other through capping material. The distribution measures the size of each nanoparticle presented in the TEM image that consisted of about 80 nanoparticles. Truncated octahedral, tetrahedral, spherical, and shapeless nanoparticles are observed. Among them, truncated octahedral shape shows about 90% population with average size of 8 nm.

Figure 2a indicates clear TEM pictures of Pt nanoparticles in which the particles were synthesized with 1 : 40 concentration ratio of  $K_2PtCl_4$  to acrylic acid. The average size of the particles is about 8 nm with narrow distribution and the shapes are consisted of more than 80% cube and few truncated tetrahedra and octahedra.

Previously, we have synthesized platinum nanoparticles of different shapes such as tetrahedra and cube by changing the ratio of the concentration of the capping material to the

concentration of the platinum cations used at room temperature.<sup>15</sup> The initial ratios of the concentration of the capping material to that of metal cation for cubic and tetrahedral nanoparticles were 1 : 1 and 1 : 5, respectively. In this paper, two different capping materials are used for preparation of high selective truncated octahedral and cubic platinum nanoparticles with narrow distribution. Generally, various shaped nanoparticles of metal and metal oxide have been prepared by different capping materials as a shape controller.<sup>14-16</sup> Shape control of nanoparticles in aqueous systems is performed by capping materials adsorbed onto specific surfaces of the nanoparticles, which reduce the growth rate normal to the adsorbed planes.<sup>16</sup> pH control is also another key factor, since the adsorption of the shape controllers is strongly affected by pH. However, the clear mechanism of shape-dependent synthesis of nanoparticles with evidence is not yet suggested.

In conclusion, we have respectively synthesized truncated octahedral and cubic platinum nanoparticles at room temperature using different capping organic compounds. These materials sizes show 8-10 nm with narrow distribution. Different shape- nanoparticles can be used in shape-dependent reactions to investigate adsorption structure of reactant on surface of the nanoparticles.

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