CHEMISTRY of MATERIALS

VOLUME 8, NUMBER 6 JUNE 1996

Communications

"Cubic" Colloidal Platinum Nanoparticles

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Received February 9, 1996
Revised Manuscript Received April 16, 1996

Transition metals have long been used as catalysts in the form of dispersions stabilized on inorganic substrates such as silica gel, alumina, and activated charcoal.[1] More recently, colloidal platinum nanoparticles have been used as catalysts and photocatalysts in solutions.[2] Aqueous colloidal platinum particles are mostly prepared by the reduction of a platinum salt by hydrogen, photochemical, pulse-radiolytical, or thermal methods.[2]

Catalytic reactivity of metal particles is undoubtedly linked to the nature of surfaces involved in the catalysis. Determining the particle shape and consequently the atomic arrangements in the crystal planes forming the surfaces is essential to our understanding of the whole phenomena of catalysis and the design of more "ideal" catalysts for different chemical transformations. In this letter, we are reporting on the synthesis of platinum nanoparticles of cubic shapes in an aqueous medium, without a substrate and at 25 °C, for the first time. These cubic-shaped nanoparticles were not observed previously in the gas phase or in the colloidal phase without a substrate. The synthesis of the cubic-shaped nanoparticles adds a new structure to the list of already known shapes, i.e., tetrahedra, icosahedra, and cubooctahedra, of platinum particles. The cubic particles have large surface-to-volume ratios and may prove to have significantly different reactivity and selectivity in catalysis.

The cubic nanoparticles were prepared by the method of Rampino and Nord[3] and Henglein et al.[4] for the synthesis of colloidal platinum. A solution of 1×10^{-4} M K_2PtCl_4 was prepared in 250 mL of water, to which we added 0.2 mL of 0.1 M of sodium polyacrylate (average MW 2100). Ar gas was bubbled in the solution for 20 min. Afterward, the reduction of platinum ions was carried out by bubbling hydrogen gas vigorously into the solution for 5 min. The reaction vessel was tightly sealed and left overnight. After 12 h, the solution turned lightly golden and the absorption spectrum showed the formation of platinum colloids.

Geometrical and crystal structures of Pt particles were determined using high-resolution transmission electron microscopy (HRTEM). A Hitachi HF-2000 transmission electron microscope (TEM), equipped with a field emission gun (FEG, 200 kV) which is a highly coherent and bright source, allows high-resolution imaging with a point-to-point image resolution better than 0.23 nm and lattice resolution of 0.1 nm. The experimental images are recorded digitally using a charge couple device (CCD) camera, which allows subsequent processing and quantitative modeling. The TEM specimen was prepared by placing the Pt particles on an amorphous carbon film which is thinner than 20 nm.

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S0897-4756(96)00119-6 CCC: $12.00

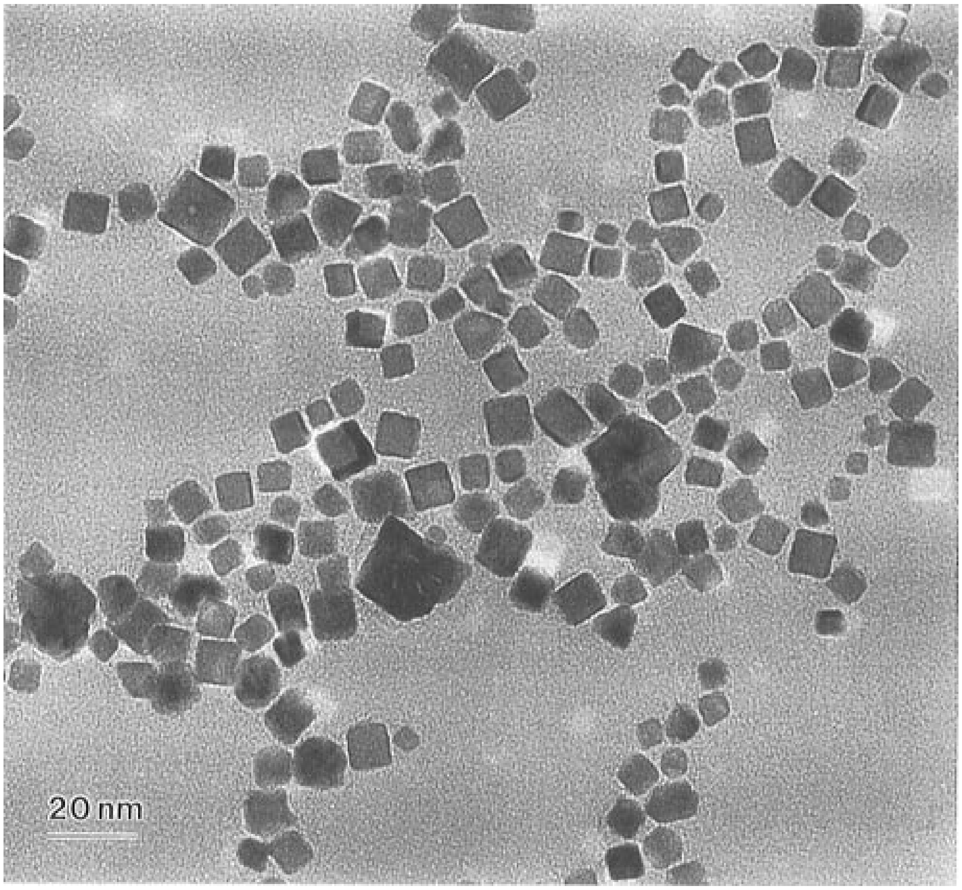

Figure 1. Low-magnification TEM image of the platinum particles showing the abundance of the cubic-shaped particles.

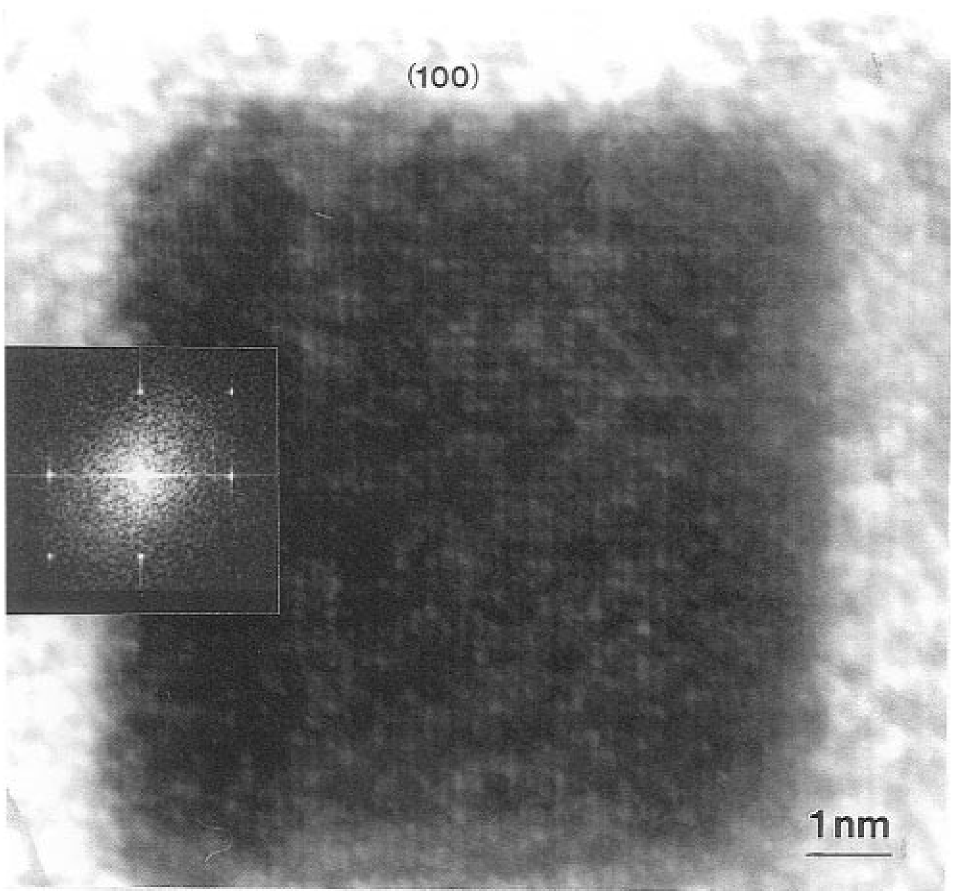

Figure 2. High-magnification TEM image of a cubic-shaped platinum nanoparticle showing the {100} plane. Also, the optical diffractogram of the image is shown (inset).

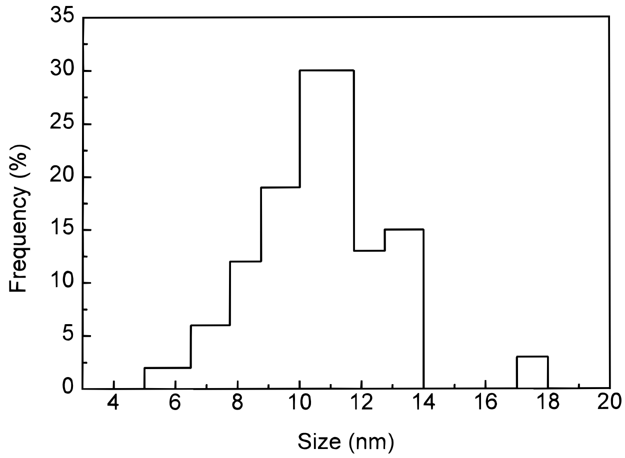

Figure 3. Histogram showing the size distribution of cubic Pt nanoparticles.

Figure 1 shows a low magnification image of the cubic nanoparticles. The "squares", the "triangles", and the "hexagons" represent the cubic, tetrahedral, and the icosahedral and cubooctahedral (depending on their orientation with respect to the electron beam) 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. These particles range in size from 4 to 18 nm with an average size of 11 nm, as shown in Figure 3.

HRTEM is also used to determine the facets of the synthesized cubic Pt nanoparticles. Figure 2 shows a high-resolution lattice image of a typical Pt nanoparticle which is oriented with the [100] direction parallel to the incident beam. The distances between the adjacent lattice fringes is the interplanar distance of Pt {200}. The nanoparticles show flat surfaces with {100} facets. The Fourier transform of the lattice image gives the optical diffractogram of the particle, which explicitly indicates the [100] orientation of the particle. The nonsymmetric distribution of the spots in the diffractogram is due to a slight misorientation of the crystal and the astigmatism of the objective lens. The Pt particles have fcc structure without lattice relaxation.

Previously, Jefferson et. al.[5] have shown that heating platinum/ alumina to 500 °C in a flowing mixture of H_2S and H_2 induces [100] faceting of platinum particles. These cubic-shaped platinum particles are coated with sulfur and stabilized on alumina.[5] Hayek reported on epiataxially grown platinum nanoparticles with {100} facets stabilized on amorphous Al_2O_3.[6] However, these shapes were determined to be half-octahedral, or truncated octahedral.[6] Platinum particles on graphite surfaces also showed {100}and {111} surfaces, indicating the cubo-octahedral structures.[8,9] Others have found the shapes of platinum nanoparticles on supported materials to be tetrahedral,[10] icosahedral,[10] and rhombohedral.[11] Also, Wang et al.[7] showed that Pt nanoparticles on SiO_2 and Al_2O_3 supports exhibit cubiclike shapes. However, these particles showed rounded shapes with {111} faceted corners, and the {100} surfaces were not flat, which probably was due to the high-temperature sintering technique. Our Pt nanoparticles show clearly flat facets and there are no {111} faceted corners. In addition, our particles are synthesized at room temperature, and in the absence of any support material or surface deposits.

The mechanism for growth of monodispersed colloidal particles, i.e., the kinetics of "growth by diffusion", is discussed by Riess.[12] A thermodynamic model, which accounts for the size distribution of the gold colloids as the ratio of the capping material to that of the metal salt is varied, also is given.[13] However, the mechanism for the nucleation and growth of shape-controlled nanoparticles has not been reported. All previously synthesized Pt nanoparticles were found to be cubooctahedron, icosahedron, or tetrahedron. It is argued[14] that these structures are thermodynamically most stable. These arguments use minimization of the surface energy of the nanoparticles as the determining factor in the formation of specifically shaped particles. Perhaps in the formation of the cubic nanoparticles by use of a capping material, the kinetics of growth and/or the thermodynamics of the system as a whole (including the capping material) play an important role, e.g., the free energy.

The cubic-shaped nanoparticles of platinum are formed in the presence of the polymer (sodium polyacrylate), which acts as a capping material. The presence of the polymer in the solution of colloids is now believed to have mainly two functions. First, it stops the growth of the particles at a small size distribution. Second, it prevents individual colloidal particles from coalescing with each other, thus giving the colloids a higher degree of monodispersity. The role of the capping material in controlling shape is yet another factor that should be considered and which we are now investigating. Its importance in controlling the size of gold nanoparticles has already been demonstrated and discussed in term of a thermodynamic model.[13]

The "protected" colloids have been shown to be as efficient in catalysis as the "unprotected" colloids.[1] The cubic-shaped nanoparticles have six {100} surfaces. These surfaces might increase the selectivity and reactivity of the particles in certain catalytic reactions. This work is presently in progress.

In conclusion, we have synthesized platinum cubic nanoparticles at room temperature without any material support or surface deposits which have not been done before. These particles have fcc structure with six {100} surfaces. They range in size from 4 to 18 nm. Since platinum is a versatile catalyst, the catalytic behavior of the cubic platinum may prove useful in certain reactions.

Acknowledgment. We wish to thank the Office of Naval Research (Grant N00014-95-1-0306) for its financial support of this project.

CM9601190

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