Advanced Powder Technology 27 (2016) 1862–1867

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Rapid Communication

Facile synthesis of platinum octahedra and cubes through the manipulation of reduction kinetics

Sang-Il Choi *

Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu 702-701, Republic of Korea

ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form 23 April 2016
Accepted 25 April 2016
Available online 2 May 2016

Keywords:
Platinum
Reduction kinetics
Shape-control
Octahedron
Cube

ABSTRACT

Control over the shape of platinum nanocrystals has received great interests owing to their correlations with structure sensitive catalytic reactions such as CO/HC oxidation, NO_x reduction, H_2 oxidation, O_2 reduction, and petroleum reforming. Pt octahedra and cubes are the well-known model catalysts for the low-index {1 1 1} and {1 0 0} faceted nanocrystals, respectively. In this work, a facile synthesis of Pt octahedra and cubes was conducted by manipulating the reduction kinetics. The reduction kinetics for the Pt precursor was altered by adjusting the volume ratio of oleylamine (OAm) and oleic acid (OAc) as the co-stabilizers and the coordination ligands in the reaction mixture. The morphologies of well-controlled Pt octahedra and cubes were observed by typical transmission electron microscopy.

1. Introduction

Platinum is a key catalyst to facilitate various chemical reactions including CO/HC oxidation and NO_x reduction in catalytic converters, H_2 oxidation and O_2 reduction in fuel cells, and petroleum reforming [1–9]. However, due to the scarcity in the Earth's crust and thus the high price of Pt, it is essential to reduce the amount of Pt required in a reaction or to maximize the catalytic activity of a Pt-based catalyst [10,11]. All of the applications as mentioned above have been recognized as the structure-sensitive reactions, because the binding strength between Pt active sites and the adsorbed chemical species can be adjusted on different arrangements of Pt atoms at surface and thus the shape of nanocrystals [12,13]. Therefore, controlling the shape of the Pt nanocrystals has been intensively studied in order to achieve the development of Pt-based catalyst [14–17]. Since the El-Sayed group reported shape-controlled Pt nanocrystals in 1996 [14], various shapes of Pt nanocrystals such as cube, tetrahedron, octahedron, icosahedron, cuboctahedron, sphere, dendrite, wire, rod, and plate have been prepared and explored for applications in catalysis [11,13–19]. In the case of O_2 reduction reaction, the specific activity for low index facets of Pt single crystals shows the trend in the order of $Pt\{100\} \ll Pt\{111\} \approx Pt\{110\}$ [20]. Therefore, Pt octahedra and rhombic dodecahedra can be more active toward the O_2 reduction than the Pt cubes. Similarly, catalytic selectivity of benzene hydrogenation reaction was investigated on different shapes of Pt nanocrystals [21]. The result indicates that both cyclohexane and cyclohexene were produced on Pt cuboctahedra, whereas cyclohexane was produced on Pt cubes.

The shape of Pt nanocrystals can be controlled by both thermodynamic and kinetic factors [22]. The thermodynamic control is based on the use of capping agents to minimize the surface free energies of nanocrystals. Recently, aromatic molecules were used as the facet-selective capping agents for the synthesis of Pt nanocrystals [23]. Because the phenyl ring preferentially binds to {1 1 1} surfaces, Pt tetrahedra were obtained as the major product. The kinetic control, the other approach for the shape-control of nanocrystals, is based on the manipulation of reduction rate of Pt precursor and thus the generation amount of Pt atoms and the growth of nanocrystals. It was reported in a recent review that the reduction kinetics can be modulated under the different reaction conditions including Pt precursors, reducing agents, surfactants, additives, and reaction temperature and time [16]. In a previous study, Yang and co-workers demonstrated that the decrease of pH value could enhance the reduction rate of Pt precursors, resulting the shape evolution of Pt nanoparticles from porous particle to cube and to cuboctahedron [24].

Since Pt{1 1 1} facets show more active catalytic behaviors than Pt{1 0 0} in O_2 reduction and hydrogenation of unsaturated compounds, many researchers have been intensively explored to synthesize Pt octahedra [5,11,16,17,25]. Despite the efforts placed on the synthesis, thermodynamically favored truncated octahedral shape was commonly observed to minimize the surface energy

* Tel.: +82 53 950 7369; fax: +82 53 950 6330.
E-mail address: sichoi@knu.ac.kr

http://dx.doi.org/10.1016/j.apt.2016.04.020
0921-8831/

[21,24]. Recently, several groups demonstrated the synthesis of well-controlled Pt octahedra by adding transition-metal additives, which could be alloyed with Pt [5,16,17,25]. However, because the catalytic behavior is highly dependent on the alloying elements of Pt-based catalysts, those products cannot be the model of Pt{111} faceted nanocrystals. Therefore, the shape control of Pt octahedra with the clean surface is highly desirable for investigating their catalytic properties compared to the two dimensional Pt{1 1 1} substrates. Here this study demonstrates, for the first time, that a facile synthesis of Pt octahedra and cubes was achieved by manipulating the reduction kinetics without adding any metal additives, preserving clean Pt surfaces. The shape of Pt nanocrystals can be altered by adjusting the volume ratio of oleylamine (OAm) and oleic acid (OAc) as the co-stabilizers and the coordination ligands.

2. Experimental procedures

2.1. Chemicals and materials

Platinum(II) acetylacetonate ($Pt(acac)_2$, 97%), palladium acetylacetonate ($Pd(acac)_2$, 99%), sodium tetrachloro palladate (Na_2PdCl_4, 99.99%), iridium acetylacetonate ($Ir(acac)_3$, 97%), citric acid (99.5%), OAm (70%), OAc (90%), poly(vinyl pyrrolidone) (PVP, Mw = 55,000), and benzyl alcohol (99.8%) were purchased from Sigma–Aldrich. Ethanol (200 proof) was obtained from VWR. All the chemicals were used as received. Deionized (DI) water with a resistivity of 18.2 MΩ cm was used for all experiments.

2.2. Synthesis of Pt octahedra

For the synthesis of Pt octahedra with an average edge length of 25 nm, 10 mL of benzyl alcohol containing 20 mg of $Pt(acac)_2$, 2 mL of OAm and 2 mL of OAc was heated to 200 °C for 10 min at a heating rate of 18 °C min^{-1} and kept at 200 °C for 1 h. The reaction mixture was allowed to cool down to room temperature. The resulting Pt octahedra were precipitated out by adding toluene (5 mL) and ethanol (10 mL). After centrifugation at 3000 rpm for 10 min, the Pt octahedra were dispersed in organic solvents such as toluene and hexane.

2.3. Synthesis of Pd or Ir nanocrystals

For the synthesis of Pd or Ir nanocrystals, 15.5 mg of $Pd(acac)_2$ or 24.9 mg of $Ir(acac)_3$ was added into 10 mL of benzyl alcohol containing 2 mL of OAm and 2 mL of OAc, then the mixture was heated to 200 °C for 10 min at a heating rate of 18 °C min^{-1} and kept at 200 °C for 1 h. The resulting products were washed and collected by following the same work-up procedure of Pt octahedra.

2.4. Synthesis of Pd–Pt core–shell nanostructures

In a typical synthesis of Pd octahedra, Na_2PdCl_4 (57 mg), citric acid (180 mg), and PVP (105 mg) were added in a mixture of 3 mL of ethanol and 8 mL of DI water. The resulting solution was then heated at 80 °C in air under magnetic stirring for 3 h and cooled down to room temperature. The final product was dispersed in 11 mL of benzyl alcohol after washing with DI water three times. For the synthesis of Pd–Pt core–shell nanostructures, 3 mL of benzyl alcohol containing Pd octahedra was added into 7 mL of benzyl alcohol containing 20 mg of $Pt(acac)_2$ and 10 mg of PVP. Then the mixture was heated to 200 °C for 10 min and kept at 200 °C for 1 h. The product was washed and collected by following the same work-up procedure of Pt octahedra.

2.5. Morphological, structural, and elemental characterizations

TEM images were taken using a Hitachi-HT7700 microscope operated at 120 kV by drop casting the nanoparticle dispersions on carbon-coated copper grids and drying under ambient conditions.

3. Results and discussion

3.1. Synthesis of Pt octahedra

Facile synthesis of Pt octahedra with an average edge length of 25 nm was conducted in 10 mL of benzyl alcohol containing 20 mg of $Pt(acac)_2$, 2 mL of OAm, and 2 mL of OAc by heating the reaction mixture to 200 °C for 10 min and kept at 200 °C for 1 h. Benzyl alcohol and $Pt(acac)_2$ are used as a solvent and a Pt precursor, respectively. OAm and OAc serve as co-stabilizers and the coordination ligands in a manner similar to the previous works reporting OAm/OAc based synthesis of Pt and bimetallic Pt–M alloy nanocrystals [26,27]. No metal additives were added to control the shape of Pt nanocrystals in this protocol. During the reaction, the color of the solution changed from light yellow to black, indicating the reduction of Pt ions to Pt atoms then formation of Pt nanocrystals. As shown in a typical transmission electron microscopy (TEM) image (Fig. 1), the sample contained 80% octahedra and 20% particles with other shapes such as cuboctahedra and truncated octahedra. The schematic illustrations in the TEM image exhibit two different projected shapes of an octahedron, including rhombus and hexagon, due to the different orientations of an octahedron to the electron beam.

3.2. Manipulation of reduction kinetics

3.2.1. Effect of OAm

We then investigated the formation of the Pt nanocrystal by manipulating the reduction rates. It is well-known that the OAm and OAc serve as surface stabilizers to disperse nanocrystals in organic solvents. In addition to the role of OAm, it plays as a

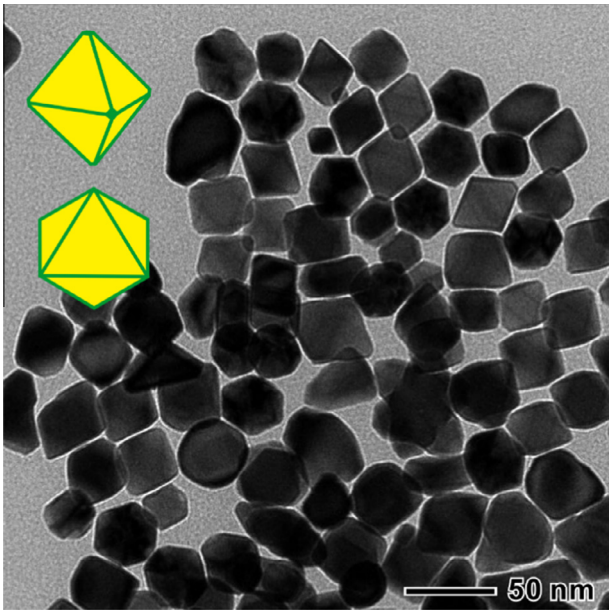

Fig. 1. TEM image of Pt octahedra synthesized by heating the mixture of $Pt(acac)_2$, oleylamine, oleic acid, and benzyl alcohol to 200 °C at a heating rate of 10 °C min^{-1} and kept at 200 °C for 1 h. The illustrations show two different projected shapes of an octahedron.