Controlling the Degree of Coverage of the Pt Shell in Pd@Pt Core–Shell Nanocubes for Methanol Oxidation Reaction

Xiangyun Xiao 1,†, Euiyoung Jung 2,†, Sehyun Yoo 3, Taeho Lim 3, Jinheung Kim 2,* and Taekyung Yu 1,*

1 Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; xyxiao@khu.ac.kr
2 Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea; jey9207@khu.ac.kr
3 Department of Chemical Engineering, Soongsil University, Seoul 06978, Korea; sehyun7720@daum.net (S.Y.); taeholm@ssu.ac.kr (T.L.)
* Correspondence: jinheung@ewha.ac.kr (J.K.); tkyu@khu.ac.kr (T.Y.)
† These authors contributed equally to this work.

Received: 1 September 2020; Accepted: 27 September 2020; Published: 1 October 2020

Abstract: The synthesis of Pd@Pt core–shell nanocubes was achieved through a direct seed-mediated growth method. This process represents a simple and cost-effective way to produce core–shell nanocubes. The morphology of the Pd@Pt core–shell nanocubes varied from simple cubic to concave cubic, depending on the reducing agent and the Pt content. The selection of the reducing agent is important because the reduction rate is directly related to the shell growth. The catalytic activity and stability of the Pd@Pt core–shell nanocubes in the methanol oxidation reaction were different for the nanocubes with partial and full Pt shells.

Keywords: core–shell; nanoparticles; direct seed-mediated growth; methanol oxidation reaction

1. Introduction

Seed-mediated growth has been widely used to synthesize core–shell nanoparticles because the size, morphology, composition, and structure of the nanoparticles, which affect their properties, can be easily controlled [1–3]. In particular, it has been employed to form noble metal core–shell nanocatalysts with uniform thin shells in aqueous solutions [4–6]. These nanocatalysts have been employed in many applications; however, industrial-scale applications are difficult because of the complex and low-efficiency preparation process and their low yield [7,8].

To obtain core–shell nanoparticles with thin (<2 nm) and uniform shells, the seed-mediated growth method typically involves two steps: (i) first, the core material seed is synthesized, which requires a washing process to remove unreacted species (e.g., metal precursor, reducing agent, capping agent, and surfactant); (ii) second, after re-dispersing the core material in the reacting solution, the shell growth process is carried out. The washing process between the first and second steps is particularly important because the unreacted species may adversely affect the shell formation. Moreover, this process usually increases the cost of manufacturing of nanomaterials. To overcome these issues, we recently developed a direct seed-mediated growth method that allows for a precise shell control in aqueous solutions [9–11]. In this method, the washing process after the synthesis of core material is not necessary, leading to a simple and cost-effective manufacturing procedure. For example, we were able to synthesize Pd@Pt core–shell nanocubes with a finely controlled Pt shell and showed that, compared with commercial Pt/C, the catalytic activity of the nanocubes with extremely low Pt content (0.4 at%) was 2.2 times higher than that in the electrochemical formic acid oxidation [9]. However, the morphology of the
synthesized Pd@Pt core–shell nanocubes was concave cubic, where the Pt shell did not fully cover the surface of the Pd core. Having a full Pt shell may be necessary for the catalysis of certain reactions; therefore, it is necessary to develop a technique to control the degree of Pt coverage on the Pd core.

In the anisotropic growth of nanomaterials, monomer concentration is an important factor that can lead to kinetically controlled growth. Compared with thermodynamically controlled growth, kinetic control can be achieved at low monomer concentrations because the binding energy difference of each crystal facet is maximized under such conditions [12]. For example, in a previous study, anisotropic Pt concave nanocubes were synthesized by slowly adding aqueous NaBH₄ and Pt precursor solutions [13]. The slow addition of these solutions promoted kinetically controlled growth rather than thermodynamically favored growth, thus leading to the formation of concave structures. When the solutions were rapidly added into the reaction mixture, truncated spherical nanoparticles were obtained. This indicates that the morphology of the Pd@Pt core–shell nanocubes could be controlled by adjusting the Pt monomer concentration.

In this study, we report on the control of the coverage degree of the Pt shell in Pd@Pt core–shell nanocubes using a direct seed-mediated growth method. Full and partial Pt shells were obtained by varying the type of reducing agent used to form the shell. A weak reducing agent (citric acid) led to a partial Pt shell, while a strong reducing agent (NaBH₄) resulted in the formation of a full Pt shell on the surface of the Pd nanocubes. The catalytic properties of the core–shell nanocubes may be different depending on whether Pd and Pt coexist on the surface (partial Pt shell) or if only Pt is present (full shell). The electrocatalytic properties of the nanocubes were evaluated in the methanol oxidation reaction (MOR), for which Pd@Pt core–shell nanocubes have a significant effect [14,15]. The MOR is an important reaction at the anode of a direct methanol fuel cell (DMFC), and the activity and stability of the MOR catalyst have a great influence on the performance of a DMFC. We found that in MOR, the activity and stability of the two types of nanocubes were clearly different.

2. Results

The Pd@Pt core–shell nanocubes were synthesized by a direct seed-mediated growth method, which does not require a washing process between the synthesis of the Pd core and the growth of the Pt shell. The powder X-ray diffraction (XRD) patterns of the synthesized core–shell nanocubes indicate the presence of fcc Pd (Joint Committee on Powder Diffraction Standards (JCPDS) file no. 88-2335), possibly due to the low Pt atomic ratio and/or thin Pt shell (Figure S1). The morphology of the Pt shell on the Pd@Pt core–shell nanocubes was modulated by varying the reducing agent used for the formation of the Pt shell. Nanocubes with a partial Pt shell (P-PdPt) were synthesized using citric acid (CA) to reduce the Pt cation, as previously reported [9,10]. Figure 1a–c and Figure S2a–c show transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of P-PdPt nanocubes obtained using different amounts of Pt. It can be seen that the morphology changed from simple cubic to concave cubic as the amount of Pt increased (from 0.6 at% to 13 at%). The atomic ratio of Pd and Pt was measured by an inductively coupled plasma (ICP) spectrometer (Table S1). Energy-dispersive X-ray spectroscopy (EDX) mapping images for these nanocubes indicate that the Pt shell grew mainly on the corners of the Pd cube, leading to the concave cubic morphology with Pd exposed on the plane of the cube (Figure 2a, Figures S1 and S3). When NaBH₄ was used as the reducing agent instead of CA, the nanocubes maintained their cubic shape, and their size increased from 10 to 11 nm as the amount of Pt used in the reaction increased (Figure 1d–f and Figure S2). EDX mapping of the nanocubes with 13 at% Pt clearly shows a full Pt shell covering the Pd surface (Figure 2b and Figure S3). The Pd@Pt core–shell nanocubes with a full Pt shell are referred to as F-PdPt. When the amount of Pt decreased to 0.6 at% in the nanocubes synthesized with NaBH₄, Pt was found in all the planes of the cube, indicating that the shell grew on the [100] facets of the cube (Figure S1). TEM and EDX analyses did not show isolated Pt nanoparticles, confirming that all of the Pt precursor was used to form the Pt shell.
Previous studies on the direct seed-mediated growth of Pd@Pt core–shell nanocubes show that CA induces the growth of Pt enclosed by [110] and [111] facets on the Pd nanocube, thus leading to the formation of a concave structure [9,10]. In addition, the Pd nanocubes used in this work were covered by bromide ions (Br\(^-\)), and it is known that the selective chemisorption of Br\(^-\) on the [100] facets of the Pd nanocubes decreases the growth rate of the Pt shell along the <100> direction. To achieve an even growth of the Pt shell on all facets of the Pd nanocubes, we evaluated reaction conditions that involved a high monomer concentration and NaBH\(_4\), which is a stronger reducing agent than CA. With high monomer concentrations, Pt atoms cannot selectively attach to specific facets of the Pd nanocubes; thus, Pt would evenly deposit on all facets (Figure 3). To further understand the relation between reduction rate and growth behavior, we conducted the reaction using L-ascorbic acid (AA) as the reducing agent in the shell formation step (Figure 4a). Concave nanocubes were obtained, indicating that a

Figure 1. TEM images of (a) Pd@Pt core–shell nanocubes with a partial Pt shell (P-PdPt\(_{0.6}\)), (b) P-PdPt\(_{4.5}\), (c) P-PdPt\(_{13}\), (d) Pd@Pt core–shell nanocubes with a full Pt shell (F-PdPt\(_{0.6}\)), (e) F-PdPt\(_{4.5}\), and (f) F-PdPt\(_{13}\).

Figure 2. EDX mapping images of (a) P-PdPt\(_{13}\) and (b) F-PdPt\(_{13}\). Red and green areas correspond to Pd and Pt, respectively.
weak reducing agent cannot form fully covered Pd@Pt core–shell nanocubes. However, a mixture of isolated Pt nanoparticles and irregularly shaped Pd@Pt core–shell nanocubes with a bumped shell was obtained with high Pt and NaBH₄ concentrations. This demonstrates that a too-high monomer concentration may cause homogeneous nucleation of Pt atoms (Figure 4b). The results indicate that monomer concentration is crucial to control the coverage degree of the Pt shell on the Pd core.

![Reaction pathways for the synthesis of P-PdPt and F-PdPt core–shell nanocubes.](image)

**Figure 3.** Reaction pathways for the synthesis of P-PdPt and F-PdPt core–shell nanocubes.

![TEM images of nanocubes synthesized (a) using L-ascorbic acid (AA) as reducing agent instead of citric acid (CA) and (b) F-PdPt20.](image)

**Figure 4.** TEM images of nanocubes synthesized (a) using L-ascorbic acid (AA) as reducing agent instead of citric acid (CA) and (b) F-PdPt20.

The electrochemical catalytic properties of F-PdPt and P-PdPt were investigated in the MOR. Figure 5 shows the cyclic voltammetry curves of F-PdPt and P-PdPt in an aqueous electrolyte containing 1 M CH₃OH and 1 M KOH. Pd exhibited low MOR activity in alkaline media (Figure S4). The oxidation current density associated with MOR was similar for both F-PdPt and P-PdPt and increased with increasing Pt content. This is because surface Pt serves as the active site of the reaction. It is worth mentioning that F-PdPt₁₃ and P-PdPt₁₃ had high MOR activity close to that of commercial Pt/C (20 wt% Pt), even with small Pt content (3.8 wt% Pt). On the basis of the Pt loading, both F-PdPt and P-PdPt showed significantly higher MOR activity than commercial Pt/C (Figure S3). In binary PdPt MOR catalysts, the electronic effect and bifunctional mechanism enhance the catalytic properties. The former refers to changes in the electronic and/or geometric structure of Pt and Pd that favor MOR due to the interaction of adjacent Pd and Pt [15,16]. This effect mainly occurs in core–shell structures. In addition, during MOR, Pd is more favorable for the dissociative adsorption of H₂O than Pt because Pd–OH is formed. This is known to promote the oxidation of CO species, an intermediate adsorbed on Pt (bifunctional mechanism) [15,17]. The Pd@Pt core–shell structure of F-PdPt likely boosted MOR by...
inducing electronic effects, altering the structure of the Pt shell. In contrast, in P-PdPt, where both Pd and Pt are exposed to the electrolyte, the bifunctional mechanism would have promoted MOR catalysis. Moreover, P-PdPt has a preferential Pt(110) orientation, which favors OH adsorption and may also improve MOR catalysis in alkaline media [18].

![Figure 5. Cyclic voltammetry curves of (a) F-PdPt and (b) P-PdPt core–shell nanocubes with different Pt content in aqueous CH₂OH (1 M) + KOH (1 M). Scan rate was 50 mV s⁻¹.](image)

The chemical stability of F-PdPt and P-PdPt during MOR was tested by a potentiostatic method. Figure 6 shows chronoamperometry curves measured at −0.2 V. A decrease in the current density was observed in all samples; at high Pt content, a high current density was maintained. However, F-PdPt had a higher current density than P-PdPt at the end of the test. This indicates that the former is more stable than the latter. The decrease in the current density occurs mainly due to catalyst poisoning by strongly adsorbed species formed during MOR [19]. Pd@Pt core–shell nanocubes are known to possess high resistance against catalyst poisoning by reducing the binding energy of the adsorbed species [14,15]; this effect was also observed in F-PdPt. However, Pt(110), which is the facet present in P-PdPt, has been reported to be the weakest against catalyst poisoning among all Pt facets [20]. This resulted in the rapid current density decrease seen in Figure 6.

![Figure 6. Chronoamperometry curves of (a) F-PdPt and (b) P-PdPt core–shell nanocubes with different Pt content in aqueous CH₂OH (1 M) + KOH (1 M). Current was recorded at −0.2 V for 3600 s.](image)

3. Materials and Methods

3.1. Materials

Polyvinylpyrrolidone (PVP, MW = 55,000), L-AA (99%), sodium tetrachloropalladate (Na₂PdCl₄, 98%), CA (99.5%), potassium tetrachloroplatinate (K₂PtCl₄, 99.99%), sodium borohydride (NaBH₄, 98%), and potassium bromide (KBr, 99%) were purchased from Sigma Aldrich (St. Louis, MO, USA) and utilized without further purification.
3.2. Synthesis of Pd@Pt Core–Shell Nanocubes

Pd@Pt core–shell nanocubes were synthesized using a direct seed-mediated growth method [9,10]. For the synthesis of the nanocubes with a partial Pt shell (P-PdPt), 36.93 mg of PVP, 50 mg of AA, and 300 mg of KBr were dissolved in 8 mL of deionized water and heated to 80 °C for 20 min under magnetic stirring at 800 rpm. Then, 3 mL of an aqueous solution containing 57 mg of Na₂PdCl₄ was slowly added to the reaction mixture. After 3 h of heating at 80 °C, 0.1 mL of an aqueous CA solution (800 mg/mL) was added. Afterward, 1 mL of aqueous K₂PtCl₄ with different concentrations (0.88, 4.39, and 6.16 mg/mL) was rapidly injected. The solution was then heated to 80 °C for 5 h. The products were collected by centrifugation and washed three times with a deionized (DI) water and acetone mixture. The same experimental procedure was followed to synthesize Pd@Pt core–shell nanocubes with a full Pt shell (F-PdPt) except for the reducing agent; 0.1 mL of an NaBH₄ aqueous solution (1000 mg/mL) was used instead of CA.

3.3. Electrochemical Measurements

The electrochemical experiments were performed using a CHI 760E potentiostat (CH Instruments, Austin, TX, USA) at room temperature. A leak-free Ag/AgCl electrode was used as reference electrode and a Pt mesh (1 × 1 cm⁻²) as counter electrode. The working electrode was a glassy carbon (GC) rotating disk electrode (RDE, 5 mm diameter; Pine Research Instrumentation, Durham, NC, USA). The disk was mechanically polished before each measurement. Ethanol dispersions of F-PdPt/C (Vulcan XC-72) and P-PdPt/C were sonicated for 15 min, and then the catalyst ink was made (1 mg metal catalyst and 45 µL nafion in ethanol solution). In this solution, the concentration of the catalyst was 1.67 mg/mL. The catalyst ink was dispersed by sonication for 15 min and 4.7 µL was dropped onto GC RDE (0.196 cm⁻²) and then dried at room temperature for 15 min prior to the MOR evaluation. The total metal loading was 40 µg cm⁻² for all samples. The voltammetric curves of the MOR were obtained at 50 mV/s in an N₂-saturated aqueous solution containing CH₃OH (1 M) and KOH (1 M) solution. Before the MOR measurements, the electrode surface was cleaned by cycling between −0.9 and 0.3 V in 1 M aqueous KOH (20–40 cycles). To test the durability of the catalysts, the I–t amperometric curve was acquired at −0.2 V for 3600 s.

3.4. Characterization of Pd@Pt Core–Shell Nanocubes

TEM, high-resolution TEM (HRTEM), and energy-dispersive X-ray spectroscopy (EDX) images were captured using a JEM-2100F microscope (JEOL, Akishima, Tokyo, Japan) operated at 200 kV. Powder XRD patterns were obtained with a Rigaku D-MAX/A diffractometer (Rigaku, Akishima, Tokyo, Japan) at 35 kV and 35 mA. The elemental composition of the Pd@Pt core–shell nanocubes was measured using a direct reading echelle inductively coupled plasma (ICP) spectrometer (Leeman, Hudson, NH, USA).

4. Conclusions

Large-scale preparation of nanomaterials requires simple synthetic procedures that involve the least possible number of steps. In this work, we successfully prepared the Pd@Pt core–shell nanocubes with partial and full Pt shells via a direct seed-mediated growth method. The morphology of the nanocubes was controlled using different reducing agents (CA and NaBH₄). This direct seed-mediated growth method could be used for the synthesis of different nanomaterials, including metal@metal core–shell nanoparticles. Moreover, the Pd@Pt core–shell nanocubes showed efficient electrocatalytic activity for MOR, even with a small Pt content. The nanocubes with a full Pt shell (F-PdPt) also exhibited high stability.
Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/10/1133/s1:
Table S1: ICP results of P-PdPt and F-PdPt. Figure S1: XRD patterns of P-PdPt, F-PdPt, and Pd nanocubes. Figure S2: HRTEM images of Pd@Pt core–shell nanocubes. Figure S3: EDX mapping images of PdPt_{0.6} and PdPt_{4.5} core–shell nanocubes. Figure S4: MOR of Pd/C. Figure S5: Cyclic voltammetry curves (based on the Pt loading) F-PdPt and Pd-PtPt.

Author Contributions: Conceptualization, synthesis, characterization, and writing—original draft preparation, X.X. and E.J.; electrocatalysts, S.Y.; supervision, methodology; further data analysis, and writing—review and editing, T.L., J.K., and T.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the NRF grant funded by the Korean government (MSIP) (NRF-2014R1A5A1009799, NRF-2020R1A2C1003885, NRF-2020M3A7B4002030, and NRF-2017R1A5A1015365).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Xia, Y.; Gilroy, K.D.; Peng, H.-C.; Xia, X. Seed-Mediated Growth of Colloidal Metal Nanocrystals. *Angew. Chem. Int. Ed.* 2017, 56, 60–95. [CrossRef] [PubMed]

2. Niu, W.; Zhang, L.; Xu, G. Seed-mediated growth of noble metal nanocrystals: Crystal growth and shape control. *Nanoscale* 2013, 5, 3172–3181. [CrossRef]

3. Losch, P.; Huang, W.; Goodman, E.D.; Wrasman, C.J.; Holm, A.; Riscoe, A.R.; Schwalbe, J.A.; Cargnello, M. Colloidal nanocrystals for heterogeneous catalysis. *Nano Today* 2019, 24, 15–47. [CrossRef]

4. Kim, I.; Seo, M.G.; Choi, C.; Kim, J.S.; Jung, E.; Han, G.H.; Lee, J.C.; Han, S.S.; Ahn, J.P.; Jung, Y.; et al. Studies on catalytic activity of hydrogen peroxide generation according to Au shell thickness of Pd/Au nanocubes. *ACS Appl. Mater. Interfaces* 2018, 10, 38109–38116. [CrossRef]

5. Liu, M.; Gilroy, K.D.; Peng, H.-C.; Chi, M.; Guo, L.; Xia, Y. The effect of surface capping on the diffusion of adatoms in the synthesis of Pd@Au core-shell nanocrystals. *Chem. Commun.* 2016, 52, 13159–13162. [CrossRef]

6. Li, S.; Liu, J.; Zhu, G.; Han, H. Pd@Pt core-shell nanodots arrays for efficient electrocatalytic oxygen reduction. *ACS Appl. Nano Mater.* 2019, 2, 3695–3700. [CrossRef]

7. Liu, R.; Priestley, R.D. Rational design and fabrication of core-shell nanoparticles through a one-step/pot strategy. *J. Mater. Chem. A* 2016, 4, 6680–6692. [CrossRef]

8. Zhou, M.; Wang, H.; El Nahawy, A.O.; Hood, Z.D.; Chi, M.; Xiao, P.; Zhang, Y.; Mavrikakis, M.; Xia, Y. Facile one-pot synthesis of Pd@Pt1L octahedra with enhanced activity and durability toward oxygen reduction. *Chem. Mater.* 2019, 31, 650. [CrossRef]

9. Xiao, X.; Jeong, H.; Song, J.; Ahn, J.-P.; Kim, J.; Yu, T. Facile synthesis of Pd@Pt core-shell nanocubes with low Pt content via direct seed-mediated growth and their enhanced activity for formic acid oxidation. *Chem. Commun.* 2019, 55, 11952–11955. [CrossRef] [PubMed]

10. Han, G.-H.; Xiao, X.; Hong, J.; Lee, K.-J.; Park, S.; Ahn, J.-P.; Lee, K.-Y.; Yu, T. Tailored palladium-platinum nanoconcave cubes as high performance catalysts for the direct synthesis of hydrogen peroxide. *ACS Appl. Mater. Interfaces* 2020, 12, 6328–6335. [CrossRef]

11. Han, G.-H.; Kim, K.Y.; Nam, H.; Kim, H.; Yoon, J.; Lee, J.-H.; Kim, H.-K.; Ahn, J.-P.; Lee, S.Y.; Lee, K.-Y.; et al. Facile direct seed-mediated growth of AuPt bimetallic shell on the surface of Pd nanocubes and application for direct H_{2}O_{2} synthesis. *Catalysts* 2020, 10, 650. [CrossRef]

12. Zhang, H.; Li, W.; Jin, M.; Zeng, J.; Yu, T.; Yang, D.; Xia, Y. Controlling the morphology of rhodium nanocrystals by manipulating the growth kinetics with a syringe pump. *Nano Lett.* 2011, 11, 898–903. [CrossRef] [PubMed]

13. Yu, T.; Kim, D.Y.; Zhang, H.; Xia, Y. Platinum concave nanocubes with high-index facets and their enhanced activity for oxygen reduction reaction. *Angew. Chem. 2011*, 123, 2825–2829. [CrossRef]

14. Xiong, Y.; Ma, Y.; Li, J.; Huang, J.; Yan, Y.; Zhang, H.; Wu, J.; Yang, D. Strain-induced Stranski-Krastanov growth of Pd@Pt core-shell hexapods and octapods as electrocatalysts for methanol oxidation. *Nanoscale* 2017, 9, 11077–11084. [CrossRef] [PubMed]

15. Kim, Y.; Lee, Y.W.; Kim, M.; Han, S.W. One-Pot Synthesis and Electrocatalytic Properties of Pd@Pt Core-Shell Nanocrystals with Tailored Morphologies. *Chem. Eur. J.* 2014, 20, 7901–7905. [CrossRef]
16. Wang, H.; Xu, C.; Cheng, F.; Zhang, M.; Wang, S.; Jiang, S. Pd/Pt core-shell nanowire arrays as highly effective electrocatalysts for methanol electrooxidation in direct methanol fuel cells. *Electrochem. Commun.* 2018, 10, 1575–1578. [CrossRef]

17. Li, H.-H.; Zhao, X.; Gong, M.; Cui, C.-H.; He, D.; Liang, H.-W.; Wu, L.; Yu, S.-H. Ultrathin PtPdTe Nanowires as Superior Catalysts for Methanol Electrooxidation. *Angew. Chem.* 2011, 52, 7472–7476. [CrossRef] [PubMed]

18. Herrero, E.; Franaszczuk, K.; Wieckowski, A. Electrochemistry of methanol at low index crystal planes of platinum: An integrated voltammetric and chronoamperometric study. *J. Phys. Chem.* 1994, 98, 5074–5083. [CrossRef]

19. Jurzinsky, T.; Kammerer, P.; Cremers, C.; Pinkwart, K.; Tubke, J. Investigation of ruthenium promoted palladium catalysts for methanol electrooxidation in alkaline media. *J. Power Sources* 2016, 303, 182–193. [CrossRef]

20. Tripkovic, A.V.; Popovic, K.D.; Momcilovic, J.D.; Drazic, D.M. Kinetic and mechanistic study of methanol oxidation on a Pt (110) surface in alkaline media. *Electrochim. Acta* 1998, 44, 1135–1145. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).