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Kenya Kani

Qingdao University of Science and Technology, National Institute for Materials Science, University of Queensland,
kk895@uowmail.edu.au

Mohamed B. Zakaria

Qingdao University of Science and Technology, National Institute for Materials Science, Tanta University

Jianjian Lin

Qingdao University of Science and Technology, jl824@uowmail.edu.au

Abdulmohsen Alshehri

University of Wollongong

Jeonghun Kim

University of Queensland, jhkim@uow.edu.au

See next page for additional authors

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Abstract

Platinum (Pt) is known as one of the most promising electrocatalysts, and nanostructured Pt materials have enhanced its activity due to their abundant catalytically active sites derived from their high surface area. Herein, we synthesize fascinating dendritic Pt nanoparticles (DPNs) by a softtemplating method using hexadecyltrimethylammonium chloride (CTAC) as a pore-forming agent. The dissolved negatively charged Pt precursor (PtCl_4^{2-}) effectively interact with the surfactant. The particle size of the obtained DPNs is around 20 nm, and the pore walls are composed of Pt nanocrystals. The obtained DPNs show good electrocatalytic activity towards methanol oxidation reaction (MOR) compared to commercial Pt black (PtB), and its stability is also higher than that of PtB

Disciplines

Engineering | Physical Sciences and Mathematics

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Synthesis and Characterization of Dendritic Pt Nanoparticles by Using Cationic Surfactant

Kenya Kani,^{1,2,3} Mohamed B. Zakaria,^{*1,2,4} Jianjian Lin,¹ Abdulmohsen Ali Alshehri,⁵ Jeonghun Kim,³ Yoshio Bando,^{2,6} Jungmok You,⁷ Md Shahriar A. Hossain,³ Jiang Bo,^{*2} and Yusuke Yamauchi^{*1,3,7}

¹College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China

²International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

³School of Chemical Engineering, School of Mechanical and Mining Engineering, and Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, QLD 4072, Australia

⁴Department of Chemistry, Faculty of Science, Tanta University, Tanta (31527), Egypt

⁵Department of Chemistry, King Abdulaziz University, P.O. Box. 80203, Jeddah 21589, Saudi Arabia

⁶Australian Institute of Innovative Materials (AIIM), University of Wollongong, North Wollongong, NSW 2500, Australia

⁷Department of Plant & Environmental New Resources, Kyung Hee University, 1732 Deogyong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, South Korea

E-mail: mohamed.hegazy3@science.tanta.edu.eg (M. B. Zakaria), JIANG.Bo@nims.go.jp (J. Bo), y.yamauchi@uq.edu.au (Y. Yamauchi)

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Yusuke Yamauchi

After receiving his Ph.D. in 2007 from Waseda University (Japan), Professor Yamauchi joined NIMS to establish his own research group. In 2016, he joined University of Wollongong (Australia) as a professor. Recently, he moved to The University of Queensland (UQ) to be a full professor at School of Chemical Engineering and AIBN. He concurrently serves as an honorary group leader in NIMS, a visiting/guest professor in several universities (Waseda University, Kyung Hee University, Tianjin University, King Saud University, Nanjing Tech Univ. etc), an associate editor of *Journal of Materials Chemistry A*, The Royal Society of Chemistry (RSC). In the last 10 years, Professor Yamauchi has made tremendous contributions in the field of functional nanoporous materials and their applications in energy storage, catalysis, sensing, and separation. He has published more than 600 papers in internationally-refereed journals with around 25,000 citations with *h*-index > 80 and was selected as one of the world's most highly cited researchers in Chemistry by Thompson Reuters in 2016 and 2017.



Abstract

Platinum (Pt) is known as one of the most promising electrocatalysts, and nanostructured Pt materials have enhanced its activity due to their abundant catalytically active sites derived from their high surface area. Herein, we synthesize fascinating dendritic Pt nanoparticles (DPNs) by a soft-templating method using hexadecyltrimethylammonium chloride (CTAC) as a pore-forming agent. The dissolved negatively charged Pt precursor (PtCl_4^{2-}) effectively interact with the surfactant. The particle size of the obtained DPNs is around 20 nm, and the pore walls are composed of Pt nanocrystals. The obtained DPNs show good electrocatalytic activity towards

methanol oxidation reaction (MOR) compared to commercial Pt black (PtB), and its stability is also higher than that of PtB.

Keywords: Mesoporous metals | Platinum | Surfactants

1. Introduction

Noble metals (*e.g.*, Au, Pt, Pd) have been considered as good catalysts due to their remarkable chemical stability and high catalytic activity, and they have been applied to various reactions such as hydrogenation, oxygen reduction reaction (ORR), methane oxidation reaction (MOR), and organic synthesis.¹⁻⁴

Among them, Pt has been especially widely used as a catalyst, however, such noble metals are quite expensive, because the demand for them has been increasing due to their advantages for utilization despite there is insufficient global supply. In order to solve this problem, new Pt nanostructures must be prepared with enhanced activity, and considerable research has been conducted, for instance, on Pt-alloys and core-shell structures.^{5–8} Another way to overcome this issue is using Pt nanoparticles supported on mesoporous materials (e.g., silica, carbon).^{9,10}

Dendritic/nanoporous Pt materials can be synthesized to gain more active sites on their surfaces as well as high accessibilities for guest species from outside.¹¹ To date, a number of syntheses of dendritic/nanoporous Pt materials with various morphologies have been reported, including films,^{12–14} nanoparticles,^{15–17} and nanorods.¹⁸ There have been several strategies to create such porous materials, for example, dealloying techniques,^{19,20} the electrochemical micelle assembly method,¹² and traditional soft- and hard-templating methods.^{13,14,21} Among them, aqueous solutions with low-concentrations of surfactant have been recently applied to synthesize dendritic/nanoporous materials due to the simplicity and flexibility of this method. Recently, a variant of this method using polymeric micelles has attracted especially great interest because it is easy to remove the template, and the pore size can be simply controlled by changing the molecular weights of block polymers or the solvent.^{22,23} In terms of pore-forming agents, cationic surfactants, especially hexadecyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium chloride (CTAC), are also available and have been utilized to synthesize mesoporous Pd.²⁴

Herein, we describe a simple synthesis of dendritic Pt nanoparticles (DPNs) by a soft-templating method using CTAC as a template for the first time, and they show remarkable advantages in electrocatalytic activity. Our DPNs were prepared by reducing Pt precursor (K_2PtCl_4) with ascorbic acid (AA) in the presence of CTAC solution, in which the CTAC acted as a pore-forming agent.

2. Experimental Section

Chemicals. K_2PtCl_4 , AA, methanol (99.8%), and acetone (99.5%) were purchased from Nacalai Tesque, Inc. CTAC and 0.5 M H_2SO_4 solution were purchased from Wako Pure Chemical Industries, Ltd. Pt counter electrode and Ag/AgCl reference electrode were purchased from ALS Co., Ltd. Pt black (PtB) and 0.05 wt% Nafion were purchased from Sigma-Aldrich Co. LLC. All the chemicals were used without further purification steps.

Preparation of Dendritic Pt Nanoparticles. CTAC (20 mg) was first dissolved in pure water (4.5 mL). Next, 0.5 mL of K_2PtCl_4 solution (40 mM) was added into this solution. The solution was kept in an 85 °C water bath for 1 min until the color turned clear. Then, 2 mL of AA solution (0.1 M) was added into this solution, and the color changed to black in just a few seconds. After the reduction reaction proceeded for 2 hours in the water bath, the product was collected by centrifugation at 14,000 rpm for 20 min, and the residual CTAC was removed by six consecutive washing/centrifugation cycles with acetone and water.

Characterization. A scanning electron microscope (SEM, HITACHI S-4800) was used to observe the morphologies of the DPNs at 10 kV accelerating voltage. A JEOL JEM-2100F was applied to obtain information regarding the interior structures of DPNs by collecting transmission electron microscope (TEM) and high resolution TEM (HRTEM) images at 200 kV accelerating voltage. Wide-angle X-ray diffraction (XRD) measurements on the obtained powders were conducted on a RIGAKU Smartlab diffractometer at 2 deg. min⁻¹ scanning rate with Cu K α radiation (40 kV, 30 mA). Small angle X-ray scattering (SAXS) profiles were recorded on a RIGAKU NANO-Viewer. The instrument used Cu K α radiation (40 kV, 30 mA). The Pt precursor solution and Pt precursor-CTAC mixed solution were studied with a JASCO V-570 UV-vis-NIR spectrometer.

Methanol Oxidation Reaction (MOR). Cyclic voltammetry (CV) and chronoamperometry (CA) were conducted in order to investigate the electrochemical active surface area (ECSA) and electrochemical catalytic activity towards the MOR. In these electrochemical measurements, we employed a typical three-electrode system composed of an Ag/AgCl reference electrode (3 M KCl), a Pt wire counter electrode, and a modified glassy carbon electrode (GCE, 3 mm diameter) as working electrode. The modified GCE was coated with 10 μ g of DPNs and dried at room temperature. Its surface was covered with 5 μ L Nafion solution (0.05 wt %) and dried for subsequent electrochemical measurements. Before starting the experiments, the modified GCE was electrochemically activated by potential cycling between -0.2 V and +1.5 V (vs. Ag/AgCl) in 0.5 M H_2SO_4 until the obtained CV curves showed the same characteristics as normal Pt electrode. After that, MOR measurements were carried out at 0.05 V s⁻¹ scan rate in 0.5 M H_2SO_4 solution including 0.5 M methanol, and CA measurements were performed at 0.6 V constant potential for 3600 s.

3. Results and Discussion

The morphologies of DPNs were observed with SEM and TEM. According to the SEM images (Figure 1a, b), the nanoparticles are highly uniform in shape and possess numerous well-dispersed pores. The interior structure of nanoparticles can be seen from the TEM image (Figure 1c), and from the differences in the contrast, it is proved that the nanoparticles have well-dispersed pores. The average particle size is 20 ± 2 nm, according to a calculation from 200 particles on the TEM and SEM images (Figure 1d). The small angle X-ray scattering (SAXS) pattern for the obtained DPNs shows a broad peak at 1.3 nm^{-1} ($d = 4.8 \text{ nm}$), indicating the presence of periodicity of nanoporous structure (Figure 2a). The wide-angle XRD pattern shows five remarkable peaks of pure face-centered cubic (*fcc*) Pt structure, and they can be attributed to the (111), (200), (220), (311), and (222) reflections, respectively (JCPDS 04-0802) (Figure 2b).

For further investigation of the atomic structures, selected-area electron diffraction (SAED) patterns and HRTEM images were collected (Figure 3). Figure 1c is a typical TEM image of DPNs, and it is clear that there are interconnected crystals throughout the nanoparticles. The SAED pattern can be regarded as reflecting the *fcc* Pt structure as the X-ray diffraction

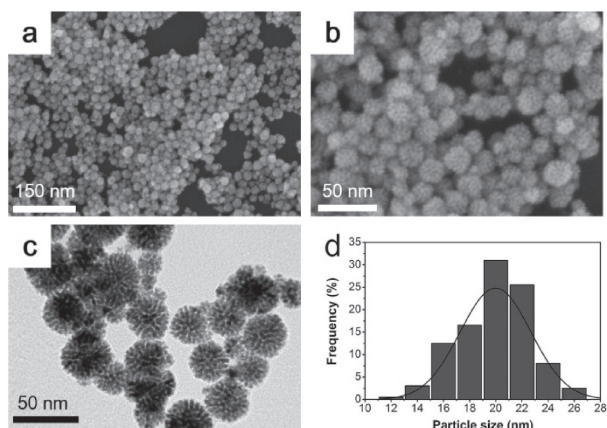


Figure 1. (a) Low-magnification SEM and (b) high-magnification SEM images, (c) TEM image, and (d) histogram of the particle size of DPNs.

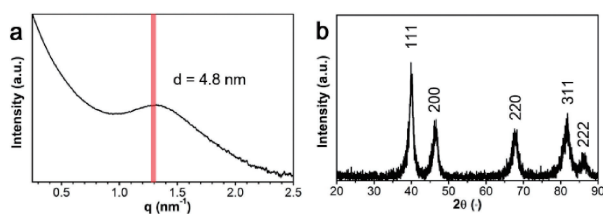


Figure 2. (a) SAXS profile and (b) wide-angle XRD pattern of DPNs.

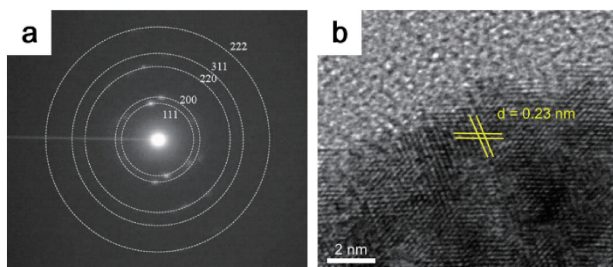


Figure 3. (a) SAED pattern of a single DPN. (b) High resolution TEM image of DPN on the edge.

(XRD) indicates, which is strong evidence that the pore walls are highly crystallized (Figure 3a). Also, the lattice spacing assessed from HRTEM shows good agreement with the *fcc* Pt {111} crystal planes (Figure 3b).

To understand the formation mechanism of DPNs, ultraviolet-visible (UV-vis) absorption measurement was carried out for K_2PtCl_4 (black) and $\text{K}_2\text{PtCl}_4 + \text{CTAC}$ solution (red), respectively (Figure 4). In the spectra of the $\text{K}_2\text{PtCl}_4 + \text{CTAC}$ solution, two remarkable peaks were exhibited at 220 and 240 nm that cannot be seen in the individual K_2PtCl_4 spectrum.²⁵ This means that anionic $[\text{PtCl}_4]^{-2}$ species can be connected with cationic $[\text{CTA}]^+$ surfactant, and $[\text{PtCl}_4]^{-2}\text{-}[\text{CTA}]^+$ complex micelles are formed subsequently. Similar situation was observed in our previous study.²⁴ To the best of our knowledge, utilizing this connection for the synthesis of DPNs is novel and might lead to further syntheses of various dendritic/nanoporous metal materials.

As a control experiment, when the Pt source was reduced in the absence of CTAC, no specific porous structures can be observed (Figure 5a). From this fact, it is obvious that CTAC

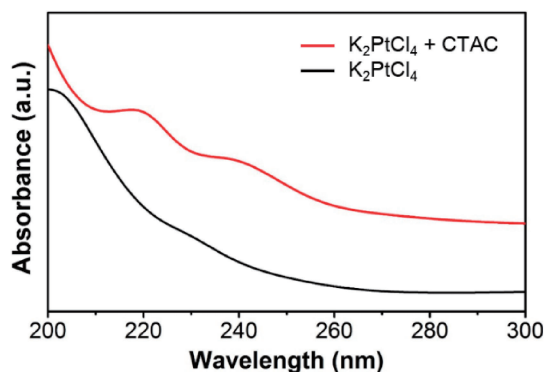


Figure 4. UV-vis spectra of K_2PtCl_4 and $\text{K}_2\text{PtCl}_4 + \text{CTAC}$ solutions.

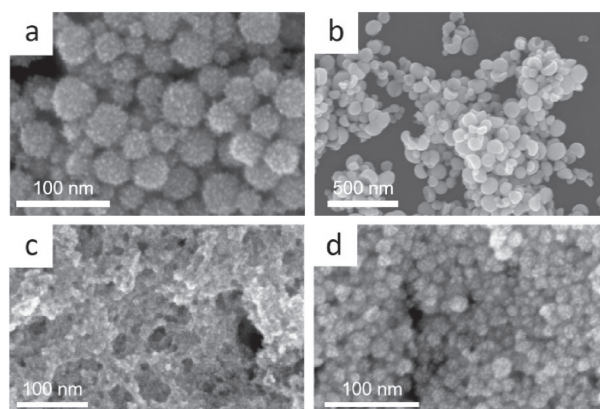


Figure 5. (a, b) SEM images of Pt nanostructures obtained from (a) surfactant-free solution and (b) 5 mg CTAC-containing solution. (c, d) SEM images of Pt nanostructures reduced by (c) NaBH_4 and (d) N_2H_4 .

micelles act as a pore-forming agent. Even in the presence of surfactant, the final products do not possess pores inside them when the amount is insufficient to induce micellization (below the critical micelle concentration (CMC)) (Figure 5b). AA is widely used as a common reduction agent due to its mild reductive capability and nontoxicity. There is no doubt that AA plays one of the most significant roles in obtaining well-ordered structures, since the structures are far from that of as-prepared DPNs when NaBH_4 and N_2H_4 are employed as reduction agents (Figure 5c, d). This evident collapse in structure for both of them is caused by their strong reactivity.

We examined the electrocatalytic activity of the as-prepared DPNs for the MOR in comparison to PtB catalyst. CV measurement was conducted in 0.5 M H_2SO_4 solution for both DPNs and PtB (not shown). Clear features of hydrogen and oxygen adsorption/desorption on the DPN catalyst were proof of the cleanliness of the catalyst surface. The ECSA of each catalyst was calculated from the hydrogen desorption peak, using the charge density for the desorption of an adsorbed hydrogen monolayer ($210 \mu\text{C cm}^{-2}$). The calculated ECSA values of the DPNs and PtB were $30.6 \text{ m}^2 \text{ g}^{-1}$ and $22.7 \text{ m}^2 \text{ g}^{-1}$, respectively, which indicates that DPNs have a higher surface area due to its dendritic porous structure.

Typical CV curves were obtained to investigate their electrocatalytic activity towards MOR in 0.5 M H_2SO_4 solution

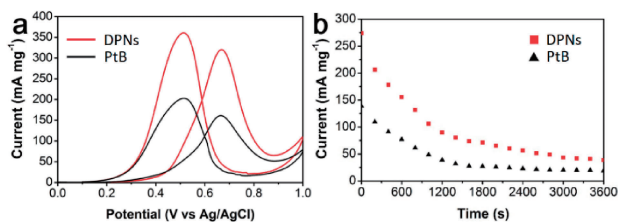


Figure 6. Mass-normalized CV curves (a) for the MOR and CA curves (b) obtained at 0.6 V for 3600 s. The CV curves were recorded in 0.5 M H₂SO₄ solution including 0.5 M methanol at 0.05 V s⁻¹ scan rate.

including 0.5 M methanol (Figure 6a). Two specific methanol oxidation peaks are observed in the anodic and cathodic sweeps at 0.67 V and 0.51 V, respectively. The peak currents of DPNs (320 mA mg⁻¹) in the anodic sweep are higher than that of PtB (161 mA mg⁻¹). Even after normalizing the currents by the ECSAs, the DPNs still show higher current density (DPNs: 1.05 mA cm⁻², PtB: 0.71 mA cm⁻²). This might be because there are abundant low-coordinated atoms such as steps and kink sites on the DPN surface. The stability of such a promising electrocatalyst is another crucial point for industrial applications. In this work, the CA measurements were conducted at 0.6 V for 3600 s to evaluate the performance of both catalysts (Figure 6b), and the DPNs show higher stability in comparison to that of PtB. It is revealed that the fascinating dendritic porous structures can be retained, even after long continuous MOR measurements.

4. Conclusions

We have succeeded in the synthesis of well-organized DPNs by using a cationic surfactant as a novel pore-forming agent. Because the highly crystallized frameworks have a number of active sites, the electrocatalytic activity and stability of our DPNs can be improved in comparison to commercial PtB catalyst. We believe that this simple method can be applied for various syntheses of dendritic/nanoporous metal materials in the future.

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