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Rapid and Efficient Synthesis of Platinum Nanodendrites with High Surface Area by Chemical Reduction with Formic Acid

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Platinum nanoarchitectures consisting of a large number of edges and corner atoms are highly favorable for enhancing the catalytic performance and efficient utilization of platinum materials. In a recent study, we have shown that Pluronic F127 triblock copolymer can assist the formation of dendritic platinum nanoparticles (Wang, L.; Yamauchi, Y. *J. Am. Chem. Soc.* **2009**, *131*, 9152−9153). Herein, we expand this concept to produce platinum nanodendrites (PNDs) with interconnected arms by using various types of nonionic organic molecules. The PDNs with complex nanoarchitectures are produced simply by sonicating treatment of an aqueous solution containing K_2PtCl_4 precursor and formic acid in the presence of nonionic organic molecules without the need for any template, seed-mediated growth, and additive. As-produced PDNs were shown to be active as nanoelectrocatalysts for electro-oxidation formic acid. The investigated nonionic organic molecules include nonionic surfactants, e.g., Pluronic F127, Brij 700, Tetronic 1107, and polymer, e.g., poly(vinyl pyrrolidone) (PVP) and poly(1-vinylpyrrolidone-*co*-vinyl acetate) (PVP-*co*-VA). The typical PNDs produced with Pluronic F127 possess platinum atomic crystalline state with large domains and show high surface area (32 $m^2\,g^{-1}$). The proposed approach is highly favorable for facilitating the producing of PNDs in a wide range of platinum precursor concentrations. Because of its high flexibility and simple implement, the proposed approach can be considered as a very general and powerful strategy for producing PNDs with high surface area and open dendritic nanostructures for commercial devices. Furthermore, the dual roles of formic acid in synthesis of PNDs, i.e., reducing agent and structure-directing agent, are tentatively proposed based on the investigation results.

1. Introduction

Nanoarchitectured materials, especially noble metal nanomaterials, have attracted considerable interest because of the fact that their fascinating properties can be effectively tuned by rationally tailoring their morphologies.[1] Various noble metal nanomaterials with specific features and desired functions, such as gold nanocorolla,[2] silver nanorices,[3] porous platinum nanoparticles,[4] concave polyhedral Pd nanocrystals,[5] etc., have been produced, which are inspired by their promising applications as new optical devices, electrochemical devices, catalysts, etc. Among various noble metal nanomaterials, nanostructured platinum is of particular interest, primarily because of its unique catalytic properties.[6] Much effort has been devoted to the manipulation of the features of platinum materials at nanoscale to achieve high surface area and desired utilization efficiency,[7] resulting in multifarious platinum materials, such as nanowire,[8] nanofibers,[9] nanotubes,[10] nanocages,[11] nanodendrites,[12] multiarmed nanostar,[13] etc., have been successfully produced.

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Rational design and synthesis of platinum nanostructures offer a promising chance to enhance catalytic performance and utilization efficiency of platinum nanomaterials. To date, there have been two general synthetic routes, i.e., template and templateless routes, to produce platinum materials with specific features. Among various template routes, sacrificial templates, e.g., Co,[14] Ag[15] nanostructures, and micelle templates, e.g., surfactant,[16] are highly valuable for producing platinum nanomaterials with hollow structures, and lyotropic liquid crystals (LLCs) made of nonionic surfactants are universal template for producing platinum with mesoporous structures.[9,10,17] Template synthetic routes provide predetermined approaches for effectively producing unique platinum nanostructures, whereas additional procedures are required for preparation and removal of the templates, which limit large-scale producing platinum nanomaterials.[18] Templateless routes represent another kind of effective strategies to produce desired platinum morphologies, e.g., anisotropic features, in which thermal decomposition of platinum precursors in organic solvents, e.g., amines or alcohols,[18,19] seed-mediated growths,[13] and triggered growths by trace amount additives, e.g., iron species (Fe^{3+} or Fe^{2+})[20] and NO_3^-,[21] are three popular strategies. Although templateless synthetic routes have been demonstrated as effective approaches for morphology-controlled synthesis of platinum nanostructures, the involved high temperature, long duration, and multisteps complicate the synthetic procedure and retard producing platinum nanomaterials in large quantities. Developing a facile and efficient strategy to produce platinum nanomaterials with high surface area, in high yield and large quantities, is an urgent topic to be solved.

Among various tactics, design and synthesis of platinum nanodendrites (PNDs) with interconnected arms provid a promising strategy to improve the specific surface area of platinum nanomaterials. Furthermore, the presence of open dendritic nanostructures in the PNDs structures can contribute to the high accessibility of guest species, and the rich edges and corner atoms derived from the dendritic structures of the PNDs are highly desired for enhancing the catalytic performance.[13,20c]

Herein, a rapid, one-step, and efficient route was proposed to directly produce PNDs with high surface area in high yield, which was carried out simply by sonicating treatment of an aqueous solution containing K_2PtCl_4 and Pluronic F127 block copolymer [PEO_{100}-$PPO_{65}PEO_{100}$, in which PEO was poly(ethylene oxide) and PPO was poly(propylene oxide)] in the presence of formic acid at room temperature without the need for any template, seed-mediated growth, and additive. Furthermore, similar PNDs could be produced by replacing Pluronic F127 with various types of nonionic organic molecules, such as nonionic surfactants (e.g., Brij 700 and Tetronic 1107) and nonionic polymer (e.g., poly(vinyl pyrrolidone) (PVP) and poly(1-vinylpyrrolidone-*co*-vinyl acetate) (PVP-*co*-VA)). The proposed approach could be considered as a very general and powerful strategy for producing PNDs.

2. Experimental Section

2.1. Materials. K_2PtCl_4, 88% formic acid (HCOOH, 23.34 M), $NaBH_4$, hydrazine monohydrate, PVP (K-30, M_w 40 000), sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Pluronic F127 (M_w 12 600), Brij 700 (M_w. 4670), Tetronic 1107 (M_w 15 000), PVP-*co*-VA (M_w 50 000), were obtained from Sigma. Commercial Pt catalyst (Platinum black, HiSPEC 1000) was purchased from Johnson Matthey company.

2.2. Typical Synthesis of PNDs. In a typical synthesis, 1 mL of 15 mM K_2PtCl_4 aqueous solution containing 10 mg of Pluronic F127 was placed in a small beaker, and then 1 mL of 88% formic acid was quickly added, making the final K_2PtCl_4 and Pluronic F127 concentrations 7.5 mM and 5 mg/mL, respectively. The mixture solution was then put into an ordinary ultrasonic cleaner using a 56 kHz operating frequency (J&L Co., China, JL-60DT) for 12 min. The color of the reaction solution changed within 12 min from transparent light brownish-yellow to brown, and then to opaque black. The product was isolated and residual Pluronic F127 was removed after 12 min of reaction by centrifugation at 8000 rpm for 20 min, followed by consecutive washing/centrifugation cycles three times with water. The collected product was dried and/or redispersed in water with sonicating to produce a colloidal suspension for further characterization.

2.3. Characterizations. Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were carried out using a JEOL JEM-2100F operated at 200 kV equipped with energy-dispersive spectrometer (EDS) analyses. The sample for TEM and HRTEM characterization was prepared by depositing a drop of dilute sample solution on a carbon-coated copper grid and dried at room temperature. Wide-angle powder X-ray diffraction (XRD) pattern were obtained with a Rigaku Rint 2500X diffractometer with monochromated Cu Kα radiation (40 kV, 100 mA) operated by using a step scan program (step width 0.05°). Nitrogen adsorption−desorption data was obtained by using a Belsorp 28 apparatus (Bel Japan, Inc.) at 77 K. UV−visible absorption spectra were recorded using a JASCO V-570 UV−vis−NIR spectrometer. Fourier transform infrared (FT-IR) spectroscopy was conducted with a Nicolet 4700 infrared spectrometer.

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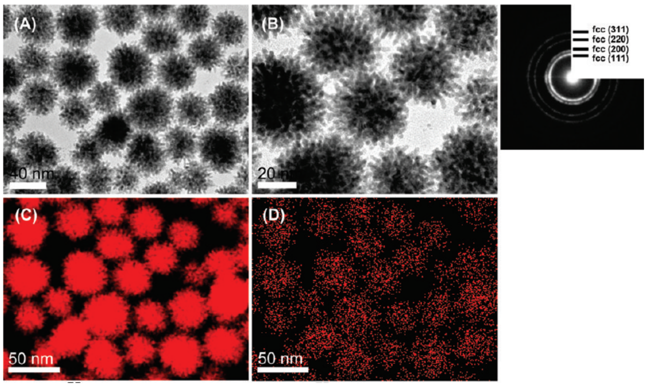

Figure 1. (A, B) TEM images, (C) HAADF STEM image, and (D) the corresponding platinum elemental mapping image of the PNDs produced by the typical synthesis. The inset image in (B) is the selected-area electron diffraction pattern.

2.4. Electrocatalytic Investigations. Cyclic voltammograms (CVs) experiments were performed by using a CHI 842B electrochemical analyzer (CHI Instrument, USA). A conventional three-electrode cell was used, including a Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire as counter electrode, and a working electrode. The working electrode included a bare Pt bulk electrode (3 mm in diameter, purity 99.99%) or a modified glassy carbon electrode (GCE) (3 mm in diameter) for different cases. The modified GCE was coated with either as-produced PDNs or commercial Pt catalyst with the same Pt loadings of 4 μg and dried at room temperature. Formic acid electro-oxidation measurements were carried out in a solution of 0.5 M H_2SO_4 containing 0.25 M HCOOH at a scan rate of 50 mV s^{-1}.

3. Results and Discussion

The essence of the proposed synthesis was the reduction of K_2PtCl_4 by formic acid in the presence of Pluronic F127 triblock copolymer in aqueous solution according to the reduction process: $K_2PtCl_4 + HCOOH \rightarrow Pt + 2HCl + 2KCl + CO_2$. The hydrophobic PPO groups in the Pluronic 127 polymer were favorably adsorbed onto the deposited platinum surface in this reaction system and then facilitated the formation of the well-dispersed PNDs.[7d] UV−visible spectra (see Figure S1 in the Supporting Information) testified the complete reduction of platinum complex.[16,22] TEM images of the typically produced product were shown in Figure 1A,B. The image obtained at lower magnification (Figure 1A) indicated the as-prepared platinum nanostructures were well-dispersed complex nanodendrites and strikingly uniform in morphology. The particle sizes were roughly distributed from 20 to 50 nm. Higher magnification image (Figure 1B) displayed the well-defined PNDs were assembled with plentiful interconnected arms. These interconnected arms, with around 2.5 nm in width, resulting in the interspaces inside the individual entity. The dendritic nature of the PNDs was more evident in the images obtained by scanning TEM (STEM) using a high-angle annular dark-field (HAADF) (Figure 1C and see Figure S2 in the Supporting Information). The HRTEM images of the individual PND shown in Figure 2A further indicated the PND was a dendritic entity with interconnected arms branching in various directions and the lattice fringes were coherently extended across over several arms, revealing that the individual PND has a multiple-crystalline nature. The observed lattice fringes in Figure 2B correspond to the (111) planes of platinum both because the *d*-spacing was 0.23 nm and the dihedral angle was around 70°.

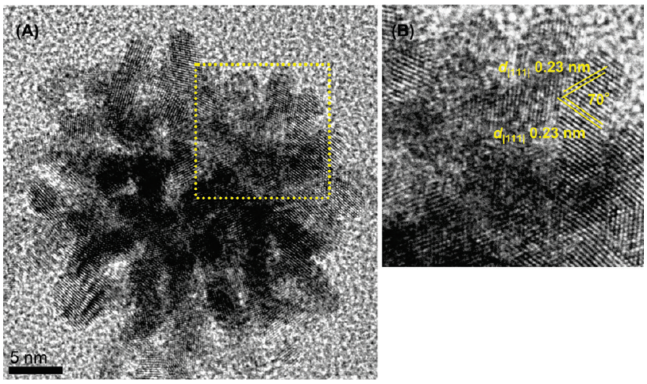

Figure 2. (A) Highly magnified TEM image of one PND and (B) filtered image of the square area in A.

The chemical composition of the obtained PNDs was detected by energy dispersive X-ray (EDX) analysis of the samples coated on the TEM grids. The EDX spectrum testified the existing of the platinum element in which the peaks of the corresponding element platinum were distinct and other signals were originated from the TEM grid (see Figure S3 in the Supporting Information). The corresponding platinum elemental map (Figure 1D) further revealed that the platinum element was distributed in conformity to the PNDs' form (Figure 1C). The EDX spectrum and element map results clearly testified that the as-prepared PNDs were composed exclusively of metallic platinum. The XRD pattern of the PNDs was for randomly oriented face-centered-cubic (fcc) platinum crystals (see Figure S4 in the Supporting Information) in which five peaks were assigned to (111), (200), (220), (311), and (222) facets of platinum crystal diffractions.[8] The observed XRD pattern was consistent with the selected area electron diffraction (SAED) pattern of the sample (inset image in Figure 1B). Both the XRD and SAED patterns demonstrated that the PNDs were well-crystallized.

The demonstrated synthetic route could be readily scaled up to provide enough quantity for the N_2 adsorption analysis. Branching out was a promising strategy to improve the specific surface area of platinum nanomaterials. The as-produced PNDs showed high specific surface area, 32 m^2 g^{-1} (see Figure S5 in the Supporting Information). Barrett−Joyner−Halenda (BJH) pore-size distribution analysis displayed the dominating pore sizes were approximate to 2.3, 3.8, and 5.8 nm (inset in Figure S5 in the Supporting Information), most likely originating from the interspaces among the interconnected arms of the individual entity. High surface area was critical for platinum nanomaterials in catalytic applications. For

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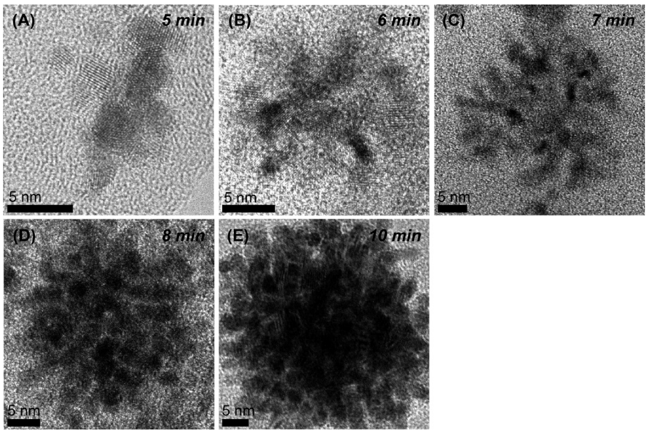

Figure 3. TEM images of the platinum nanostructures sampled at different reaction times: (A) 5, (B) 6, (C) 7, (D) 8, and (E) 10 min, respectively.

comparison, the surface area of the commercial platinum catalyst, e.g., JM HiSPEC 1000 (platinum black), was around 27 m^2 g^{-1}; porous platinum nanoparticles and platinum nanospherical nanofoams prepared by using complicated organic phase and by liposomal aggregation, respectively, had surface areas of 14[4b] and ~27 m^2 g^{-1},[23] respectively. It is worth noting that the product had a nearly "clean" surface after consecutive washing/centrifugation cycles with water (see Figure S6 in the Supporting Information).[7d,24] It meant that the PDNs were freed from strongly capping molecules that might block the platinum active sites in catalytic application.[24]

To elucidate the shape evolution of the PDNs, different stages of the formation of these dendritic nanostructures have been followed and the results were presented in Figure 3. As shown in Figure 3, primary irregular nanoparticle with tubers in random directions has been formed in the investigated first stage, most likely by aggregation of the discrete platinum nanoparticles. With the continuous platinum reduction by formic acid, platinum atomic addition continuously occurred, resulting in the continuous growth of the intermediate particles, and then more and more secondary branches began to grow from the bodies and the main branches, simultaneously, until the complete consumption of platinum precursor in the reaction solution (Figure 3). Around 12 min, the color of the reaction solution kept stable opaque black, suggesting that the reaction was complete and the mature structures of the nanoparticles were obtained (Figure 1A, B). The continuous formation of primary particles combined with the various particle growth periods of different particles over the entire reaction resulted in a broad size distribution.[7c,12a] This type of nanocrystal growth, formation of initial multifaceted particles with tubers followed by anisotropic autocatalytic growth, was previously observed for the formation of hyperbranched Ag nanostructures[25] and platinum nanoparticles.[7d]

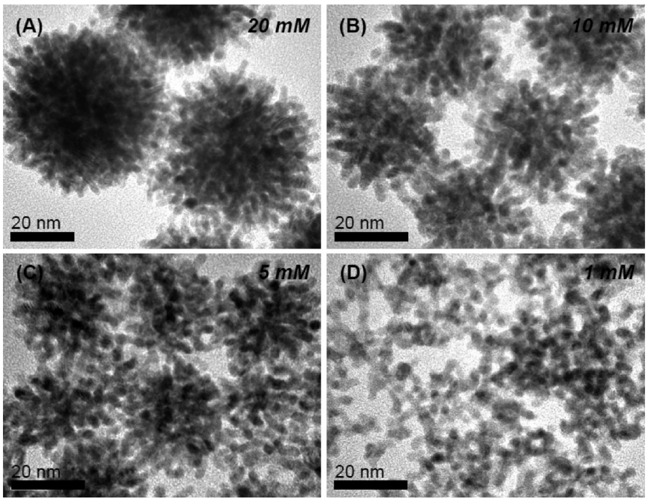

Figure 4. Typical TEM images of the platinum nanostructures prepared by different platinum precursor concentrations: (A) 20, (B) 10, (C) 5, and (D) 1 mM, respectively.

Usually, the formation of anisotropic metal nanostructures is highly dependent on the concentrations and ratios of the reagents.[4a,25,26] To demonstrate the adjustability of the proposed synthetic route, we performed investigations in which the concentrations of formic acid and Pluronic F127 were kept constant concentration while the concentration of K_2PtCl_4 was varied under the identical conditions used for preparing the typical PDNs. TEM images of the resulting products were shown in Figure 4. As shown in Figure 4, well-dispersed PDNs with similar dendritic morphology could be obtained when the platinum precursor concentrations ranged from 5 mM to 20 mM (Figure 4A−C). The platinum precursor concentration affected the formation rate of the monomer Pt^0 (seeds) and the corresponding rates for nucleation and crystal growth. High monomer concentration was favorable for the formation of highly branched metal nanoparticles.[18] When the platinum precursor concentration further decreased to 1 mM, the amount of free platinum atoms in the solution was too low to construct PDNs, resulting in nanoclusters in ill-defined form (Figure 4D). These investigations demonstrated the proposed synthetic approach was highly favorable for facilitating the producing of PNDs in a wide range of the K_2PtCl_4 precursor concentrations. This advantage made the proposed approach remarkably different from previous demonstrations of synthesis of PNDs, which highly relied on the selected platinum precursor concentration.[4a] It was also noted that although the proposed synthesis was applicable for a wide range of platinum precursor concentrations, varying the concentrations of formic acid and Pluronic F127 in the typical synthesis would result in the product form change. For instance, decreasing the concentration of formic acid led to dendritic platinum nanoclusters with irregular form only (see Figure S7 in the

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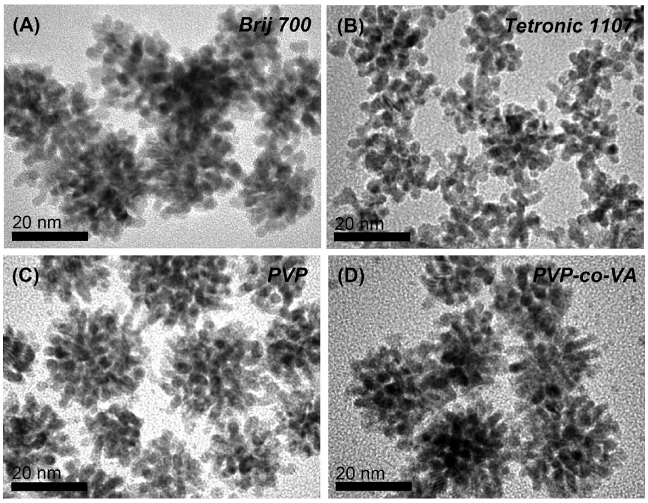

Figure 5. TEM images of the platinum nanostructures prepared by replacing Pluronic F127 with different nonionic organic molecules: (A) Brij 700, (B) Tetronic 1107, (C) PVP, and (D) PVP-*co*-VA, respectively, under the identical conditions used for preparing typical PNDs.

Supporting Information); higher Pluronic F127 concentration resulted in irregular platinum nanoparticles (see Figure S8A,B in the Supporting Information) and lower Pluronic F127 concentration resulted in regular PNDs together with irregular platinum nanoclusters (see Figure S8C in the Supporting Information). The optimum concentrations of formic acid and Pluronic F127 used in the typical synthesis were favorable for producing PNDs with high quality.

To further illustrate the flexibility of the proposed approach, investigations were performed by replacing Pluronic F127 triblock copolymer with four sampled nonionic organic molecules with different molecular structures (Chart S1). Figure 5A−D showed the PNDs prepared with Brij 700, Tetronic 1107, PVP, and PVP-*co*-VA, respectively. As shown in Figure 5, similar well-defined PNDs could also be obtained after the replacing of Pluronic F127 with different nonionic organic molecules. It should be noted that ionic surfactant was not available in the investigated system. When cationic surfactant, e.g., CTAB, was introduced in this system, floccule immediately appeared in the yellow reaction solution due to the existed anionic platinum species, $[PtCl_4]_2^{2-}$, which immediately interacted with cationic species CTA^+, resulting in the formation of the CTA^+-$[PtCl_4]_2^{2-}$ complexes.[27] Anionic surfactant, e.g., SDS, used in this system, bulk precipitation was quickly observed, possibly attributing to the rather weak capping ability of SDS onto the deposited platinum surface. Nonionic surfactants (i.e., Brij 700 and Tetronic 1107) anchored onto the deposited platinum surface with their hydrophobic groups, while nonionic polymers (i.e., PVP and PVP-*co*-VA) adsorbed onto the deposited platinum surface by their pyrrolidone groups. The fact that nonionic organic molecules with different molecular structures were equally capable of producing similar PNDs demonstrated that the exact molecular structures or groups of the nonionic organic molecules were not vital for achieving the dendritic platinum growth. It suggested that although the intentionally introduced nonionic organic molecules assisted the dendritic platinum growth and were favorable for producing well-dispersed PNDs, they were not an exclusive prerequisite to direct the dendritic platinum growth. Otherwise, the final morphologies of these products would be greatly varied when different nonionic organic molecules with different molecular structures were used, which were not observed. These investigations implied the possibility of a structure-directing role of formic acid.

To explore the more roles of formic acid in the investigated system, investigation was performed under the identical conditions used for producing typical PNDs in the absence of any nonionic organic molecules. As a result, only bulk precipitation was obtained. It was recognized that nanoparticles tended to agglomerate and settle down in the solution without capping agent. After being strong sonicating, the collected bulk precipitation was dispersed in water for TEM characterization and the result was shown in Figure S9 in the Supporting Information. As shown in Figure S9, other than spherical or near-spherical nanostructures that were usually observed in bulk precipitations, the collected bulk precipitation was composed with dendritic nanostructures, demonstrating that even in the absence of any purposely added structure-directing agent, formic acid was favorable for dendritic platinum growth.

Because platinum itself has an inherently symmetric nature of fcc structure,[4a,6b] the formation of anisotropic branch nanostructures from metals with highly symmetrical crystals in an isotropic aqueous medium requires breaking the nature of the crystal symmetry.[1e] Usually, the introduced seed[13] or structure-directing agent[1a] can facilitate driving fcc metals to form anisotropic nanostructures. It was noted that no seed was added and there was excessive formic acid with carboxyl group existing in the reaction system of the proposed synthesis (Figures 1 and 5). It has been demonstrated that organic molecules with carboxyl groups possessed the binding ability onto deposited metal surface and could serve as effective structure-directing agent to produce anisotropic metal nanostructures. For instance, citrate was very active for the formation of highly anisotropic Ag nanostructures with its carboxyl groups.[28] Such examples helped understanding the result that formic acid was possibly responsible for directing the platinum anisotropic growth in the investigated system with its carboxyl group (see Figure S9 in the Supporting Information). In the absence of purposely added structure-directing agent and capping agent (see Figure S9 in the Supporting Information), most likely, besides acting as a reducing agent, formic acid molecules played another important role, i.e., structure-directing agent, resting with its carboxyl group. The

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carboxyl group of formic acid could adsorb onto the specific crystal facets of deposited platinum surface and lead to various growth rates in different facets, resulting in the appearance of anisotropic morphologies. Because of the min molecular size of formic acid, the spatial stability of the product was very low, resulting in precipitation of these structures (see Figure S9 in the Supporting Information). As comparisons, after purposely adding stabilizing agent into the reaction systems (Figures 1 and 5), well-dispersed nanostructures with more branches and bigger sizes could be obtained, implying that the purposely added nonionic organic molecules assisted the dendritic platinum growth and improved the stability of the produced nanostructures.

Further investigations were performed by replacing formic acid with other commonly used reducing agent, i.e., hydrazine or $NaBH_4$, in current system and the results were shown in Figure S10 in the Supporting Information. As shown in Figure S10, only nearly spherical nanostructures along with discrete platinum nanoparticles were obtained when hydrazine or $NaBH_4$ replaced formic acid. These investigations demonstrated that formic acid was critical to produce highly anisotropic PDNs in current system. The absence of functional group possessing the binding ability onto the deposited platinum surface in hydrazine and $NaBH_4$ systems (Scheme S1) combing with the unsuitable reducing abilities of $NaBH_4$ and hydrazine could help understand that the carboxyl group in formic acid molecule combing with the suitable reducing ability of formic acid were favorable for dendritic platinum growth. These investigations further helped understanding that the formic acid served as both reducing agent and structure-directing agent in current system. Recently, formic acid has been testified to be an effective reducing agent used for producing anisotropic platinum nanostructures, e.g., platinum nanowires.[29] It should be pointed out that the role of formic acid in the existing demonstrations of producing anisotropic platinum nanostructures was no more than a reducing agent to reduce the platinum precursor and the structure-directing role of the formic acid in such a synthesis has been largely ignored, to the best of our knowledge.

The combination of the dual roles of formic acid (i.e., reducing agent and structure-directing agent) with the assistances of nonionic organic molecules to anchor and stabilize platinum nanostructures was the key to produce well-dispersed PNDs. Given the availability of the extraordinary roles of formic acid in producing PNDs, together with the diversity of nonionic organic molecules, there were clearly tremendous scopes for producing PNDs by the proposed simple means.

To date, only limited successes to produce PNDs have been achieved. Moreover, to achieve these successes, organic solvents,[4a,18] templates,[12b] and seeded growths[13] were common prerequisites. Therefore, the proposed synthetic strategy could be considered as a more simple, rapid, and efficient route to produce PNDs with high surface areas in high yield. Recently, we developed a facile route assisted by triblock copolymer Pluronic F127 to produce dendritic platinum nanoparticles in which the unique conformation of Pluronic F127 molecules was critical for the formation of the dendritic platinum nanoparticles.[7d] Remarkably different from our previous demonstration, the current demonstration did not relied on the selected shape-directing agent to direct the dendritic platinum growth. The extraordinary roles of formic acid acted as both effective reducing agent and structure-directing agent, which were revealed for the first time based on the investigation results, were helpful for understanding the appearance of the different morphologies in our current and previous demonstrations. With triggering by the extraordinary roles of formic acid, hyperdendritic platinum nanostructures could be easily and efficiently produced by such a simple, rapid and universal means. Traditionally, nonionic surfactants were widely utilized as LLCs-templates for preparation of mesoporous nanomaterials, e.g., silica[30] and metal-based mesoporous materials.[17d] The proposed novel approach was distinctly different from the LLCs-template approaches and provided a more rapid, efficient and general route to directly produce platinum nanostructures with open dendritic structures, which might promisingly create new opportunities for making high performance catalyst used in commercial devices.

As an initial demonstration, the electrocatalytic activity of the typical PNDs produced by Pluronic F127 (as displayed in Figure 1) toward the electro-oxidation of formic acid was tested. As shown in Figure S11 in the Supporting Information, when PNDs modified GCE used in 0.5 M H_2SO_4 solution containing 0.25 M formic acid, remarkable catalytic current was observed (see Figure S11a in the Supporting Information) and no catalytic current was detected in the absence of formic acid (see Figure S11b in the Supporting Information), indicating that the catalytic current was arising from the electro-oxidation of formic acid by the PNDs. The observed catalytically voltammetric feature for formic acid electrocatalytic oxidation on the PNDs was consistent with those obtained on the bulk platinum (see Figure S11c in the Supporting Information) and commercial Pt catalyst (Figure S11d in the Supporting Information) surfaces. For comparison, the catalytic currents of the PNDs, commercial Pt catalyst, and bulk platinum at 0.72 V were 1.2, 0.81, and 0.32 mA cm^{-2}, respectively, indicating that the PNDs showed higher electrocatalytic activity than those of the commercial Pt catalyst and bulk platinum. The mass current densities per unit mass of Pt were further compared by using the peak current at 0.72 V. The mass current density for the PNDs was

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evaluated to be 66.3 mA mg^{-1}, which was about three times higher than the current density of 21.1 mA mg^{-1} for the commercial Pt catalyst. Considering the nanoarchitectures of the PNDs with interconnected arms, the enhanced electrocatalytic activity of the PNDs over the commercial Pt catalyst and bulk platinum might be ascribed to higher surface-to-volume ratios, enough absorption sites, and surface permeability. The electrocatalytic activities of the PNDs produced by the other four different nonionic organic molecules (as shown in Figure 5) toward the electro-oxidation of formic acid were further tested (see Figure S12 in the Supporting Information). The catalytic currents at 0.72 V were 1.1 mA cm^{-2} for the PNDs produced by Brij 700, 1.3 mA cm^{-2} for the PNDs produced by Tetronic 1107, 1.0 mA cm^{-2} for the PNDs produced by PVP, and 0.9 mA cm^{-2} for the PNDs produced by PVP-*co*-VA, respectively. For further comparison, the mass current densities per unit mass of Pt at 0.72 V were 65.5, 67.2, 64.7, and 62.3 mA mg^{-1} for the PNDs produced by Brij 700, Tetronic 1107, PVP, and PVP-*co*-VA, respectively. These PNDs shown in Figure 5 displayed similar electrocatalytic activities with that of the PNDs produced by Pluronic F127 (as shown in Figure 1). The structural features of the PNDs described in this study offered favorable abilities for diverse catalytic applications.

4. Conclusion

A water-based, rapid and efficient chemical route to directly produce PNDs, in high yield, was demonstrated simply by sonicating treatment of an aqueous solution containing K_2PtCl_4 and formic acid in the presence of nonionic organic molecules. As-produced PDNs were shown to be active as nanoelectrocatalysts for electro-oxidation formic acid. The proposed approach was strikingly unlike the accumulated demonstrations that highly relied on the selected shape-directing agent to direct the dendritic platinum growth, and was highly favorable for facilitating the producing of PNDs in a wide nature of platinum precursor concentrations. Because of its high flexibility and simple implement, the proposed route could be considered as a very general and powerful strategy for producing PNDs. Furthermore, the demonstrated route could be readily scaled up. The proposed facile route was highly valuable for routinely producing PNDs with high surface area and open dendritic nanostructures for commercial devices.

Besides, the dual roles of formic acid in synthesis of metal nanostructures, i.e., reducing agent and structure-directing agent, were tentatively proposed based on the investigation results. We expect the new insight could help deepen understanding of the roles of formic acid in synthesis of anisotropic nanostructures from other metals with highly symmetrical crystals and thus facilitate the creation of novel anisotropic metal nanostructures designed for various applications with desired functions.

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Supporting Information Available: Additional TEM images, EDX spectrum, UV−visible spectra, FT-IR spectra, N_2 adsorption/desorption isotherm data, and reaction equations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.