

Research Article

Efficient Rapid Microwave-Assisted Route to Synthesize Monodispersive Pt Nanoparticles and Their Electrocatalytic Activity for Methanol Oxidation

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Received 15 November 2013; Accepted 13 April 2014; Published 4 May 2014

Academic Editor: Alireza Talebitaher

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High monodispersive Pt nanoparticles (NPs) have been prepared via two facile and environmentally-friendly procedures, either through a traditional solvothermal route (T-Pt NPs) or via a microwave-assisted route (M-Pt NPs). The transmission electron microscopy (TEM) shows the high Monodispersity for T-Pt NPs with the average diameter being ca.2.79 nm and the pod-like nanostructure for M-Pt NPs, which indicate the efficiency of both methods. An optimal choice of protocol allows reducing the reaction time from 2 hours (T-Pt NPs) to 20 minutes (M-Pt NPs). The electrocatalytic activities of as-prepared Pt NPs were investigated by cyclic voltammetry, showing very high catalytic activity for a methanol oxidation reaction.

1. Introduction

Recently, synthesis of platinum NPs with controlled sizes and shapes has stimulated extensive research owing to its unusual physical and chemical properties in developing highly active Pt NPs for fuel cell reactions [1, 2], bioimaging [3], chemical sensors [4], drug carrier for drug delivery systems (DDS) [5], and so forth. Because of the high surface area, a large number of edges and corner atoms for Pt NPs, it is generally accepted that both catalytic efficiency and selectivity are highly dependent on the size and shape of the platinum material [6–8]. For instance, due to the high surface area and enough absorption sites, the three-dimensional (3D) dendritic platinum display high active as nanoelectrocatalyst for the reduction of dioxygen and oxidation of methanol [9]. Both Pt cubic nanoboxes and hollow spheres exist higher activity than their solid particles in oxygen reduction reaction or methanol oxidation reaction, indicating a strong shape-dependent catalytic property [2, 10]. Therefore, it is imperative to develop synthetic routes to prepare nonagglomerated, uniform Pt NPs with a well-controlled size and a narrow size distribution. Up to date, serials methods have been developed to synthesize Pt NPs with desired

morphologies in cube [2, 5], multioctahedral [11], dendritic [12], flower [13], and one-dimensional nanostructure [14]. Recently, the mesoporous structure of Pt NPs becomes one of the hot research topics and obtains considerable progresses by Yamauchi group [15–17]. And also, serials of alloy or core-shell Pt NPs have also been synthesized [18, 19]. Despite this, developing a reliable, facile, and environmentally-friendly strategy for the production of high monodispersive Pt NPs still remains a challenge.

Herein, two facile and environmentally-friendly procedures were proposed to synthesize high monodispersive Pt NPs, either through a traditional solvothermal route (T-Pt NPs) or via a microwave-assisted route (M-Pt NPs). Microwave-assisted synthesis is a relatively new chemical method to accelerate chemical reactions, which have been widely applied in the nanomaterials preparation [20–23]. The use of the microwave-assisted route has several advantages over other existing methods in terms of energy efficiency and shorter reaction time from hours to minutes. Compared to the previous polyol synthesis route, the water-based system can provide a more environmentally benign route to the synthesis of Pt NPs, because it does not involve toxic organic solvents.

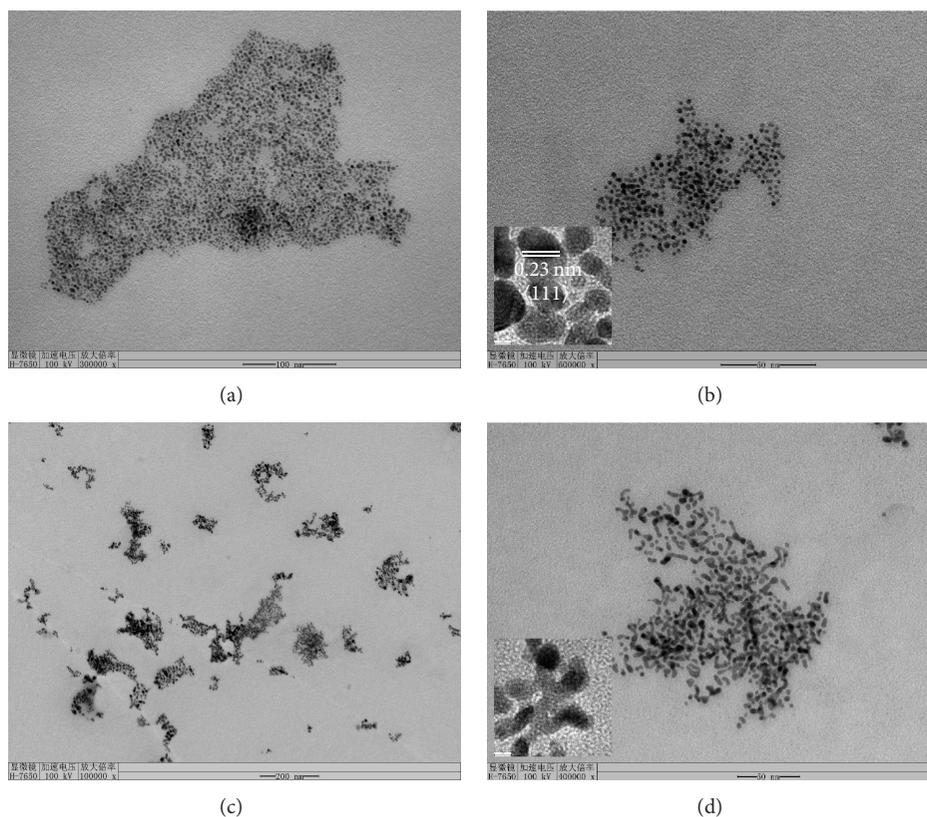


FIGURE 1: TEM images of as-prepared Pt NPs with different magnification for (a-b) T-Pt NPs and (c-d) M-Pt NPs.

2. Experimental Section

In a typical synthesis, PVP (~0.0025 mmol) was completely dispersed into 15 mL distilled water with the assistance of ultrasound irradiation. After that, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dispersed in ethylene glycol (EG) solution (7 mL, 9.65×10^{-6} mol/mL) was added into the aforementioned aqueous solution under the sonication. For solvothermal route, the mixed solution was loaded into the 50 mL Teflon lined autoclave, which was maintained at 200°C for 2 h. For microwave-assisted route, the microwave-assisted reactions were carried out in a focused single-mode microwave synthesis system (Discover, CEM, 2.45 GHz, 300 W). Reactions at elevated pressure and temperature were performed in 10 mL vial, and the temperature was accurately controlled by automatic adjusting of microwave power at 200°C for 20 min. After reactions, the products were cooled down to room temperature. The final products were collected by centrifugation, washed several times with water and ethanol, and dried at 50°C under vacuum condition. The samples are designated as T-Pt NPs for solvothermal procedures and M-Pt NPs for microwave-assisted reaction.

The morphology and composition of the products were analyzed by transmission electron microscopy (TEM) and X-ray powder diffraction patterns (XRD), which were conducted on an H-7650 and Bruker D8 ADVANCE X-ray powder diffractometer with GADDS HTS and $\text{Cu K}\alpha$ radiation ($\lambda = 0.154184$ nm). Electrochemical measurements are per-

formed on an Epsilon/100BWBAS electrochemical working system. A glassy carbon electrode modified with Pt NPs is employed as working electrode. A platinum foil is served as the counter electrode and a saturated calomel electrode (SCE) is used as the reference electrode.

3. Results and Discussion

Figures 1(a) and 1(b) are the typical TEM images for T-Pt NPs with different magnification, indicating the high monodispersity for as-prepared products. Inserted is the high resolution TEM (HRTEM) image of a single Pt NPs, displaying a single crystal nature for T-Pt NPs. The fringes with lattice spacing of 0.23 nm can be indexed as {111} of face-centered cubic (fcc) Pt. Figures 1(c) and 1(d) are the TEM images for M-Pt NPs, showing the pod-like nanostructure. A few NPs display the multiarm nanostructure. HRTEM studies (Figure 1(d), inserted) show that these nanopods have lattice fringes of 0.23 nm, corresponding to the interplane distance of {111} planes in fcc-Pt. The crystalline nature of the Pt nanopods suggests that these nanocrystals were formed through an overgrowth mechanism rather than the random aggregation of small nanocrystals [10], which is due to the rapid heating and shorter reaction time function of microwave irradiation. The mean diameter for T-Pt NPs is 2.79 nm (Figure 2(a)), which is consistent with the HRTEM results (Figure 1(b), inserted). Based on Figure 1,

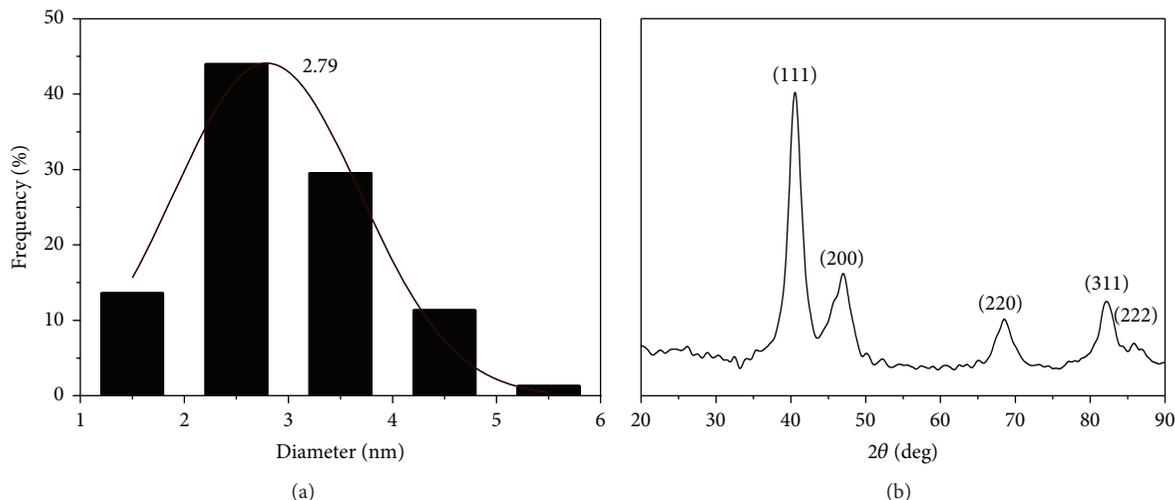


FIGURE 2: (a) The statistical result of size distribution for T-Pt NPs, (b) XRD pattern for as-prepared T-Pt NPs.

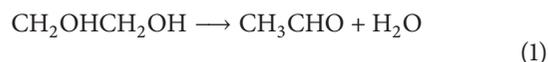
one could find that both the traditional solvothermal route and microwave-assisted route are effective routes for the synthesis of high monodisperse Pt nanoparticles via the given experimental conditions. However, for microwave-assisted route, the reaction time was reduced from 2 hours (T-Pt NPs) to 20 minutes (M-Pt NPs), indicating the reduced energy consumption. The XRD pattern of as-prepared Pt NPs is shown in Figure 2(b). The diffraction peaks at 39.8, 46.2, 67.5, 81.3, and 85.88 can be assigned to reflections from the (111), (200), (220), (311), and (222) planes of the face-centered cubic (fcc) Pt. The average size of the Pt NPs is 3.1 nm, calculated by the Debye-Scherrer formula on the basis of the Pt (111) plane, which coincides with the result from the Pt NPs size distribution histogram in the error (Figure 2(a)).

In the water-based system, contrast experiments were carried out in detail to obtain universal protocols for high monodisperse Pt NPs. Keeping the other experimental conditions constant, it is not easy to obtain the ideal result using sodium oleate instead of PVP. However, high monodisperse Pt NPs could be obtained using ascorbic acid as reducing agent at appropriate sodium oleate concentration. For this system, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was firstly dispersed in distilled water rather than EG solution (9.65×10^{-6} mol/mL). At optimal conditions (2.7×10^{-5} mol/mL for sodium oleate, 6.7×10^{-7} mol/mL for ascorbic acid), both samples show high monodisperse nature with average ca. 3 nm for T-Pt (Figures 3(a) and 3(b)) NPs and ca. 2.4 nm for M-Pt NPs (Figures 3(c) and 3(d)), respectively. Based on Figure 3, one could see that there is no obvious difference for the as-prepared Pt NPs via the solvothermal (T-Pt NPs) and microwave-assisted routes. In order to further understand the influence of concentration of surfactants on Pt NPs growth, the process was carried out with different sodium oleate concentrations. It is found that the aggregative Pt NPs (not shown here) could be obtained if the surfactant concentration was decreased down to 2.7×10^{-6} mol/mL.

Electrocatalytic activity of the Pt NPs toward methanol oxidation reaction (MOR) was studied by cyclic voltammetry in a nitrogen-saturated 0.5 M CH_3OH -0.5 M H_2SO_4 solution

at a scan rate of 50 mV s^{-1} , and the CV curves are shown in Figure 4. Line a is the curve on behalf of the bare glassy carbon electrode in 0.5 M H_2SO_4 solution. Line b is representative of bare glassy carbon electrode in 0.5 M H_2SO_4 and 0.5 M CH_3OH mixed solution. Line c stands for Pt NPs modified glassy carbon electrode in 0.5 M H_2SO_4 and 0.5 M CH_3OH mixed solution. Compared with lines a and b, it can be seen from line c that there is a strong peak at 0.68 V, which is the oxidation peak of CH_3OH oxidized to HCHO . The peak at 0.39 V should be primarily attributed to the removal of the residual carbon species, such as CO_{ads} , formed in the forward scan. The peak ratios between positive and negative scans are ca. 1.8, indicating relatively complete oxidation of methanol to carbon dioxide [24]. All these results confirmed the high catalytic activity of as-prepared Pt NPs for MOR.

Here, the efficiencies of two methods of synthesizing monodisperse Pt NPs are compared using the ethylene glycol as reducing agent, either through a traditional solvothermal procedure or via microwave-assisted method. It is well known that microwave irradiation provides rapid and uniform heating of reagents, solvents, and intermediates. This rapid MW heating also provides uniform nucleation and growth conditions, leading to homogeneous nanomaterials with smaller sizes [20–23]. In the polyol reactions, EG was as a sacrificial reductant of Pt ions according to the following mechanism [25]:



Firstly, EG was rapidly changed into CH_3CHO up to given temperature; simultaneously the Pt metallic ions are reduced to metallic Pt NPs by CH_3CHO .

4. Conclusion

A universal water-based protocol was developed to synthesize high monodisperse Pt NPs with spherical or pod-like shape, using a traditional solvothermal route or via a

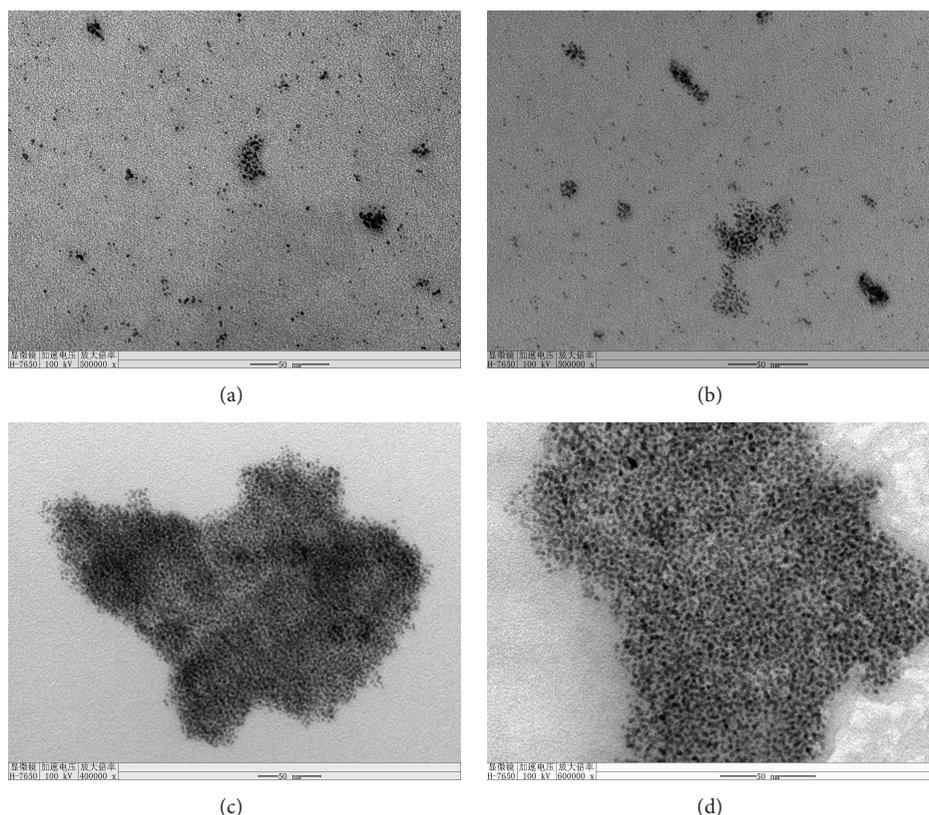


FIGURE 3: TEM images of as-prepared Pt NPs with different magnification for (a-b) M-Pt NPs and (c-d) T-Pt NPs using sodium oleate as surfactant and ascorbic acid as reducing agent.

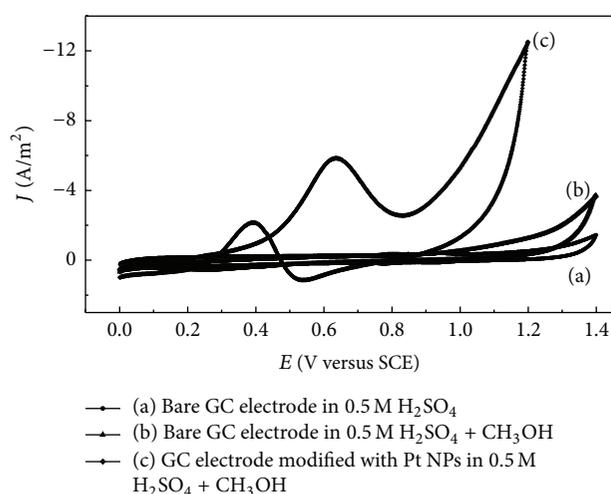


FIGURE 4: CVs of the Pt NPs (the potential was applied with a scanning rate of 50 mVs^{-1}).

microwave-assisted route. Due to the rapid heating from microwave irradiation, the overgrowth of Pt nanocrystals results in the pod-like morphology for M-Pt NPs. However, the microwave-assisted route is the more efficient method to overcome tedious and time-consuming process and reduces the reaction time from several hours to several minutes. CVs confirmed the high catalytic activity of as-prepared Pt NPs for MOR.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (nos. 21101087, 21375057, and 21205057) and Shandong Province Natural Science Foundation (no. ZR2010BQ030).

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