Block Copolymer-Assisted Solvothermal Synthesis of Bimetallic Pt-Pd Nanoparticles

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1   **Abstract**

2   We report the synthesis of bimetallic Pt-Pd nanoparticles by simultaneous reduction of platinum
3   acetylacetonate and sodium tetrachloropalladate using N,N-dimethylformide as both solvent and reductant
4   through a solvothermal method. A triblock copolymer, poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide),
5   works as a structure directing agent to control the morphology of the nanoparticles by preventing the self-
6   aggregation of small nanocrystals. The homogeneous Pt-Pd nanoparticles exhibit an enhanced
7   electrocatalytic activity and stability compared with commercial Pt black.

8

9   **Keywords:** block copolymer, solvothermal method, platinum, palladium, methanol oxidation reaction

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1. Introduction

Platinum (Pt) based nanomaterials with unique properties have attracted tremendous interest in applications such as electrochemical catalysis, fuel cells, sensors, and automotive industries due to their high catalytic activity and stability. Even if their high activity enables a high power output in fuel cells, the scarcity and cost of Pt materials remain their main drawback [1]. Great efforts have been focusing on lowering the Pt loading by using Pt-based alloys with different morphology and composition. An effective technique aiming to reduce the cost while improving the electrolytic performance of Pt catalysts is to partially substitute the Pt with other secondary metal [2].

Pt-containing alloy nanoparticles, such as PtCu, PtNi, PtPd, and PtRu, have attracted increasing interest as electrocatalysts. The synergetic co-existence of two metals leads a superior performance compared with monometallic Pt nanoparticles [3-6]. Recently, scientists have prompted to synthesize metal nanoparticles with rough surface, instead of the commonly reported nanoparticles with smooth surface. Specific morphologies can dramatically improve the accessible surface area and allow an effective use of the inner regions.

Surfactants and block copolymers (*e.g.*, F127, Brij 58) have been commonly used as structure- and/or shape-directing agents for the preparation of metallic nanomaterials [7-10]. Bimetallic or trimetallic metal nanoparticles have been synthesized by reducing the metal sources in the hydrophilic domains of ethylene oxide of the block copolymers [7,8]. A new core-shell-corona type triblock copolymer poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) (PS-*b*-P2VP-*b*-PEO) have attracted a lot of attention recently due to the distinct character of each block and the various potential applications. A variety of inorganic hollow nanoparticles and mesoporous thin films have been already reported [11-13]. It is reasonable to extend the application of triblock copolymer to the preparation of noble metal (*e.g.*, Pt, Pd) nanomaterials.

It has been generally known that N,N-dimethylformide (DMF) can be used not only as an organic solvent, but also as a reductant for several metal species [14]. The generation of silver (Ag) and gold (Au) nanostructures in the presence of DMF without the addition of seeds reveals the reducing ability of DMF [15,16]. The boiling point of DMF is high and its ability to dissolve a wide range of chemicals (*e.g.* block

copolymers, several metal precursors) was a legitimate motivation to use this solvent in the synthesis of Pt-Pd nanoparticles with high surface area.

In this study, we describe a block copolymer-assisted solvothermal method to easily synthesize Pt-Pd nanoparticles by using DMF as solvent and reductant. Metal sources (platinum acetylacetonate and sodium tetrachloropalladate) and triblock copolymer (PS-*b*-P2VP-*b*-PEO) as structure directing agent are first dissolved in DMF. During the formation of the Pt-Pd nanoparticles, PS-*b*-P2VP-*b*-PEO plays a significant role to orient the assembly of small nanocrystals and control the shape and size of the final product. The obtained Pt-Pd nanoparticles exhibit improved electrocatalytic activity compared with commercial Pt black.

2. Experimental

2.1. Materials

Poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) (PS-*b*-P2VP-*b*-PEO) triblock copolymer was purchased from Polymer Source. Platinum acetylacetonate (Pt(acac)₂, Alfa Aesar), sodium tetrachloropalladate (II) (Na₂PdCl₄, Wako), ruthenium acetylacetonate (Ru(acac)₂, Alfa Aesar), and solvent N,N-dimethylformamide (DMF, Wako) were used without further purification.

2.2. Preparation of Pt-Pd nanoparticles

20 mg of Pt(acac)₂ and 20 mg of Na₂PdCl₄ were added to 10 mL of PS-*b*-P2VP-*b*-PEO solution in DMF (2 g·L⁻¹). After complete dissolution, the reaction mixture was sealed in the PTFE-lined vessel and heated in a furnace at 200 °C for 20 h. The solution color was changed to black, indicating the deposition of metal nanoparticles (**Scheme 1**). The vessel was allowed to cool to ambient temperature before opening. The black precipitate was separated from the mixture by centrifugation. It was washed and centrifuged in DMF 5 times. The Pt-Pd nanoparticles were dried in a vacuum oven and collected for further characterization.

2.3. Characterization

The morphology of the metal nanoparticles was observed under field emission scanning electron microscope (SEM, HITACHI SU-8000). High angle annular dark field scanning transmission electron

microscopy (HAADF-STEM) image was taken by transmission electron microscope (TEM, JEOL JEM-1210). The crystal structure was collected from a wide-angle X-ray diffractometer (XRD, Rigaku RINT 2500X) at a scanning rate of $2^{\circ} \cdot \text{min}^{-1}$. X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM (ULVAC-PHI) source with Al K α X-ray was performed to determine the elemental composition of the catalyst at room temperature. A CHI 842B electrochemical analyzer (CHI Instrument, USA) was utilized for electrochemical measurements of the Pt-Pd nanoparticles and the commercial Pt black by using a three-electrode cell composed of a reference electrode (Ag/AgCl electrode), a counter electrode (Pt wire) and a working electrode (glassy carbon electrode coated with 10 μg of samples) in 0.5 M H₂SO₄ and 0.5 M methanol.

3. Results and discussion

The Pt-Pd nanoparticles were synthesized by co-reduction of Pt(acac)₂ and Na₂PdCl₄ with the assistance of a PS-*b*-P2VP-*b*-PEO triblock copolymer. On the SEM images (**Figure 1a-b**), it can be observed that all the nanoparticles have rough surfaces. The particle size of the obtained Pt-Pd nanoparticles ranges from 20 nm to 30 nm. In the absence of triblock copolymer, heavily aggregated nanoparticles with different sizes and morphologies were obtained. Thus, the triblock copolymer used in this study plays an important role to control the growth of nanoparticle and achieve a good dispersion. The atomic structure was investigated in more details by TEM (**Figure 1c-d**). The flower-shaped nanoparticles possess a rough surface distinguishable from different contrasts. The high resolution TEM (HR-TEM) image of a single nanoparticle clearly indicates a highly crystallized framework. Both lattice inter-fringe distance (0.23 nm) and dihedral angle ($\sim 70^{\circ}$) are assignable to the (111) plane of a *fcc* crystal (inset of **Figure 1d**). A wide-angle XRD profile reveals the (111), (200), (220), (311) and (222) peaks in agreement with the *fcc* crystal structure (**Figure 2a**). Because the crystal lattices of Pt and Pd are similar (99.23%), their diffraction peaks cannot be distinguished from one another. Nanoscale elemental mapping is further required to observe the elemental distribution on the nanoparticles. It is revealed that Pd is mainly concentrated in the center region while most of Pt is located on the exterior of the nanoparticle (**Figure 3**). Thus, the core and the shell of the obtained Pt-Pd nanoparticles cannot be completely distinguished regarding their composition [17,18].

1 In the present system, the $[\text{PdCl}_4]^{2-}$ species were preferentially deposited even though the standard
2 reduction potential (E^0) of Pt^{2+} species (Pt^{2+}/Pt : +1.118 V vs. SHE) is higher than $[\text{PdCl}_4]^{2-}$ species ($[\text{PdCl}_4]^{2-}$
3 /Pd: +0.591 V vs. SHE) [19]. A similar tendency was observed in our previous work, when K_2PtCl_4
4 ($[\text{PtCl}_4]^{2-}/\text{Pt}$: +0.76 V vs. SHE) and Na_2PdCl_4 were used as metal sources. In the presence of organic
5 additives (*e.g.* surfactants), the standard reduction potential is not always the decisive factor to control the
6 kinetics as the reduction rate of Pd and Pt species becomes rather complicated [20]. Various complex
7 morphologies, which cannot simply be explained by the standard reduction potentials, have been reported
8 [21-23].

9 XPS analysis was used to detect the metallic state of Pt and Pd, as presented in **Figure 2b**. Both doublets
10 of Pt $4f$ and Pd $3d$ can be deconvoluted in two contributions attributed to zerovalent and divalent metals [24].
11 The specific asymmetric double peaks 71.2 eV (Pt $4f_{7/2}$) and 74.6 eV (Pt $4f_{5/2}$) can be attributed to Pt^0 . The
12 other doublet at 72.1 eV (Pt $4f_{7/2}$) and 76.0 eV (Pt $4f_{5/2}$) indicates the existence of a relatively smaller amount
13 of Pt^{II} . The spectrum of Pd presents similar results. Two large asymmetric peaks 335.4 eV for Pd $3d_{5/2}$,
14 340.7 eV for Pd $3d_{3/2}$ and two smaller peaks 336.1 eV for Pd $3d_{5/2}$ and 342.2 eV for Pd $3d_{3/2}$ correspond to
15 Pt^0 and Pt^{II} , respectively. Similar attributions were previously reported in literatures (**Table S1**). The metallic
16 states Pt^0 and Pd^0 have a relatively larger contribution and the samples are predominantly composed of non-
17 oxidized state. Thus, the above XPS results strongly support that DMF is an efficient reductant for metal
18 precursors. The content of Pt and Pd was measured to be 35.3% and 64.7%, respectively, which does not
19 match with the stoichiometric ratio from the precursor sources (50 % for each). This indicates that the Pd
20 salt was completely reduced, while, the reduction of Pt salt was insufficient, as mentioned previously.

21 In order to generalize this solvothermal method, dendritic Pt-Ru nanoparticles were also synthesized by
22 replacing sodium tetrachloropalladate (II) to ruthenium acetylacetonate. The uniformly sized porous Pt-Ru
23 nanodendrites are shown in **Figure S1**. The average particle size is around 30 nm, which is similar to the
24 aforementioned Pt-Pd nanoparticles. According to the elemental mapping images, both Pt and Ru are more
25 homogeneously distributed compared to the Pt-Pd nanoparticles prepared under the same conditions (**Figure**
26 **S2**).

Pt-based bimetallic nanoparticles have demonstrated excellent electrocatalytic activity towards methanol oxidation reaction, due to synergistic effect and specific electronic arrangement [25]. **Figure 4a** shows the typical CVs of the Pt-Pd nanoparticles in 0.5 M H₂SO₄ at a scan rate of 50 mV·s⁻¹. For comparison, commercially available Pt black (PtB) was also tested (**Figure S3**). The electrochemically active surface area (ECSA) can be theoretically obtained by calculating the region of hydrogen desorption from -0.2 V to 0.2 V [26]. The calculated ECSA of the Pt-Pd nanoparticles is 24.99 m²·g⁻¹ (normalized by the sample mass) which is three times higher than for commercial Pt black (8.60 m²·g⁻¹) and higher than for the Pt-Pd nanoparticles prepared without triblock copolymer (18.56 m²·g⁻¹). This can be expected as the Pt-Pd nanoparticles have a rough surface containing a multitude of kinks and steps which can efficiently improve the electrocatalytic ability.

Furthermore, the representative linear-sweep voltammograms (LSVs) toward methanol electrooxidation in 0.5 M H₂SO₄ containing 0.5 M CH₃OH solution are shown in **Figure 4b**. The representative methanol oxidation peaks can be observed between 0.6 and 0.8 V [27,28]. The Pt-Pd nanoparticles exhibited superior catalytic activity with higher current density (230 mA·mg_{Pt}⁻¹). This value is about twice more than the dendritic Pt spheres (112 mA·mg_{Pt}⁻¹) [29] and around four times higher than the commercial Pt black (56 mA·mg_{Pt}⁻¹). It is easier to perform the methanol oxidation reaction on the Pt-Pd nanoparticles. Even after 100 cycles between 0.0 V and 1.0 V, the CVs still show high catalytic activity, although the current density is slightly lower (**Figure 4c**). Typical chronoamperometric measurements were also performed to investigate the stability. A higher initial current and slower decay rate is observed for the Pt-Pd nanoparticles in **Figure 4d**. Even after 2000 s, the Pt-Pd nanoparticles exhibit a higher current density compared to the commercial Pt black. The Pt-Pd nanoparticles show an excellent candidate as a potential new electrocatalyst. Unlike the commercial Pt black, they show a superior tolerance to undesirable agglomeration of the active sites (**Figure S3**). As shown in **Figure 2a**, pseudo Pt-Pd alloy hetero-interface should be formed due to perfect matching of Pd and Pt crystal lattices (inset of **Figure 1d**). Such Pt-Pd alloy surface can reduce the electronic binding energy in Pt, thereby facilitating the C-H cleavage reaction in methanol decomposition [30,31]. Thus, Pt-Pd nanoparticles with designed alloy compositions (*e.g.* Pt and Pd ratios) can realize superior catalytic activity.

1   **4. Conclusions**

2   Solvothermal method is a facile one-pot synthesis to prepare Pt-based bimetallic nanoparticles. PS-*b*-
3   P2VP-*b*-PEO triblock copolymer works as a structure directing agent and inhibits aggregation, while DMF
4   is a good reductant in top of being a commonly used organic solvent. From the detailed characterization,
5   high resolution TEM and wide-angle XRD proved that the framework can be assigned to a *fcc* crystalline
6   structure. The Pt-Pd nanoparticles exhibit superior electrochemical activity, especially for methanol
7   oxidation reaction. The high active surface area, rough surface and heterogeneous interface between Pt and
8   Pd significantly participate to increase methanol electrooxidation activity.

9

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1 **Scheme 1**

PS-*b*-P2VP-*b*-PEO in DMF
with Pt(acac)₂ and Na₂PdCl₄

2

3 **Scheme 1** Photographs of reaction solutions.

4

5

1 **Figure 1**

2
3 **Figure 1** (a-b) SEM images and (c-d) TEM images of Pt-Pd nanoparticles.
4
5

1 **Figure 2**

2 **Figure 2** (a) Wide-angle XRD profile and (b) XPS spectra of Pt 4f and Pd 3d of Pt-Pd nanoparticles.

Figure 3 (a) HAADF-STEM image and nanoscale elemental mapping of (b) Pd, (c) Pt, and (d) overlapping image of Pd and Pt in Pt-Pd nanoparticles.

Figure 4

Figure 4 (a) CVs for Pt-Pd nanoparticles and Pt black in 0.5 M H_2SO_4 solution, (b) LSVs in 0.5 M H_2SO_4 containing 0.5 M CH_3OH solution, (c) CVs in 0.5 M H_2SO_4 containing 0.5 M CH_3OH solution (up to 100 cycles), and (d) chronoamperometric curves.