Carbon-Monoxide-Assisted Synthesis of Ultrathin PtCu Alloy Nanosheets and Their Enhanced Catalysis

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Abstract: Ultrathin PtCu alloy nanosheets are synthesized by a facile, one-pot, templateless hydrothermal method with the use of carbon monoxide (CO) as the capping agent. Due to their unique structure and possible synergistic effect, the ultrathin nanosheets show higher catalytic activity in hydrogen evolution and hydrogenation reactions. The developed method is also expected to generate exciting opportunities in creating ultrathin nanostructures with a wide range of alloy compositions for various catalytic applications.

Owing to the distinctive structures and abundant active sites, ultrathin noble metal nanosheets have been recently emerging as a class of promising catalysts for applications in renewable energy conversion and fine chemical industry. Noble metal nanomaterials with ultrathin nanostructures have been mainly synthesized by methods such as surfactant mediated synthesis, microwave-polyl reduction, template-assisted synthesis, solvothermal methods, and self-assembly of nanoparticles. Up to now, however, there is still lack of an effective but general method to prepare freestanding ultrathin noble metal nanosheets. As for the synthesis of noble metal nanosheets, introducing CO or formaldehyde as a reducing agent has been recently developed as one of the most successful synthetic strategies. In the early synthetic work involving the use of CO as a reducing agent, the influence of CO on the reducing kinetics was considered as the main factor for the formation of high-quality metal nanocrystals. The importance of CO in the controlled synthesis of ultrathin noble metal nanosheets was later demonstrated. For instance, with the use of CO, our group has successfully obtained freestanding ultrathin Pd and Rh nanosheets. The presence of CO in the synthesis of ultrathin Pd nanosheets was also confirmed by Yang’s group. The effect of CO on the controlled synthesis of ultrathin metal nanosheets was attributed to the strong preferential adsorption of CO on (111) facets of Pd or Rh. With the strong adsorption of CO, metal deposition on (111) facets was inhibited, leading to the formation of anisotropic nanosheets. It should also be noted that, besides the use of CO, introducing formaldehyde has developed as an effective approach to prepare metal nanosheets as well. By using formaldehyde as a reducing agent, the successful synthesis of metal nanosheets, such as Ru nanosheets, Rh nanosheets, and PtCu alloy nanosheets, has been well-demonstrated in the literature. In fact, the decomposition of formaldehyde may produce CO. Therefore, it is reasonable to propose that the formation of many noble metal nanosheets could be related to the involvement of CO molecules in the synthesis. In this work, we report the use of CO as an effective synthetic approach to prepare ultrathin PtCu nanosheets. With lower amounts of Pt and abundant active sites, various ultrathin Pt-based alloy nanomaterials have been demonstrated to show enhanced catalytic activities. In this work, the presence of CO is confirmed as a critical factor for the formation of PtCu alloy ultrathin nanosheets. In previous studies, the preferential CO adsorption of pure Pt (100) typically led to the formation of Pt nanocubes when CO was introduced in the synthesis. Obviously, introducing Cu alters the adsorption preference of CO from Pt (100) to Pt (111), making the anisotropic formation of PtCu nanosheets possible. With the unique ultrathin nanostructure, the as-prepared ultrathin PtCu alloy nanosheets exhibit excellent catalysis in the hydrogen evolution reaction and nitrobenzene hydrogenation.

In a typical synthesis of PtCu alloy nanosheets, CO was used as the morphology controller. A mixed solution of Pt(acac)2, Cu(acac)2, poly(vinylpyrrolidone) (PVP) and KI in formamide (see Supporting Information for more details) was transferred to a glass pressure vessel. After being charged with CO to 1 bar, the vessel was heated from room temperature to 130 °C in 30 min and kept at this temperature for 3.0 h. The black products were collected by centrifugation, and washed several times with water-acetone mixture.

The low resolution TEM images (Figure 1a and Figure S1 in the Supporting Information) revealed that well-dispersed nanosheets were the dominant products with a yield of ≈80%, and the nanosheets had an average lateral length of 13 nm. The EDX data showed that the nanosheets were composed of Pt and Cu elements with an atomic ratio of 58% and 42% (Figure S2), which was close to the Pt:Cu atomic ratio of 5.5:4.5 as
measured by inductively coupled plasma mass spectrometry (ICP-MS). Therefore, the obtained products consisted of mainly ultrathin PtCu nanosheets. The high-resolution TEM and corresponding fast Fourier transform (FFT) pattern images (Figure 1b–d) clearly showed well-resolved and continuous crystal lattice, reveals good crystallinity for the obtained nanosheets. The observed lattice fringes corresponded to a d-spacing of 0.220 nm, smaller than the (111) lattice spacing (0.226 nm) of face-centered cubic (fcc) Pt, suggesting the formation of PtCu alloy. The 1/3(422) reflections appeared in the FFT pattern image (Figure 1d) could result from the occurrence of stacking faults that was parallel to the basal (111) planes or the ultrathin nature of the PtCu nanosheets. The average thickness of the as-prepared nanosheets was measured to be ≈1.6 nm less than 7 atomic layers thick (Figure S3 a–b). The ultrathin feature of the nanosheets was also clearly revealed by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Figure S3 c). The EDS mapping analysis (Figure S3 d) showed that the element distributions of Pt and Cu nicely overlapped, demonstrating the compositional homogeneity within the alloy nanosheets. As shown in Figure S4, the powder X-ray diffraction (XRD) pattern of the PtCu nanosheets was identified to be an fcc structure. The diffraction peaks were located between those of pure fcc Pt (PDF # 04-0802) and Cu (PDF # 65-9026) crystal phases, and no characteristic peaks of copper oxides were detected, confirming the formation of PtCu alloy.

Forming alloy nanocrystals from different metal components often modulate the electronic structures of each metal component. We therefore investigated the electronic structure of the prepared PtCu nanosheets by using X-ray photoelectron spectroscopy (XPS) (Figure S5). Compared to the standard value for Pt⁰, the Pt 4f binding energy in PtCu alloy nanosheets was negatively shifted by ca. 0.34 eV, suggesting the evident change in the Pt electronic structure and further confirming the formation of PtCu alloy. The Pt/Cu ratio estimated from the XPS data was about ≈59:41, agreeing with the results calculated by EDX and ICP-MS. The XPS spectrum of PtCu nanosheets displayed Cu 2p peaks at 932.6 eV and 952.4 eV, indicating the presence of Cu⁰. All of the results consistently indicated that PtCu alloy nanosheets with ultrathin thickness have been successfully synthesized.

In order to better understand the formation process of these alloyed PtCu nanosheets, the nanocrystals yielded at different reaction time were investigated by TEM and ICP-MS (Figure 2). At the early stage of the reaction (1 h), nanosheets with an average size of about 5 nm were produced (Figure 2a). As shown in Figure 2b, when the reaction time was extended to 3 h, nanosheets with a bigger size of 13 nm were generated. However, when the reaction time was further increased to 6 h, no significant change in the structure, size or the thickness was observed (Figure 2c). All of the samples collected at different reaction times were also characterized by ICP-MS. As shown in Figure 2d, the molar ratio of Cu and Pt atoms corresponding to the products under the different reaction time, respectively, obtained by ICP-MS.

The presence of I⁻ ions in the synthesis was critical to the formation of ultrathin PtCu nanosheets. The syntheses in the absence of KI (Figure 3a) or replacing KI with KBr (Figure 3b) led to the formation of nanoparticles instead of nanosheets. As shown in Figure 3c, the nanosheets formed under the optimal conditions were characterized by XRD. The XRD pattern of the nanosheets was consistent with the fcc structure of PtCu alloy. The peaks were indexed to (111), (200), and (220) planes, confirming the formation of a single-phase PtCu alloy.
but also reduce Cu. The Cu was used as the Cu precursor, the PtCu nanosheets were obtained as well. In this study, we now demonstrate a) HER polarization curves obtained with PtCu nanosheets (NS), PtCu nanoparticles (NP), and Pt black catalysts as indicated without IR correction; b) corresponding Tafel plots.

As expected, no formation of nanosheets was observed when Cu was not introduced in the synthesis (Figure S7). In the absence of Cu precursor, Pt nanochains were obtained via an oriented attachment from Pt nanoparticles with (100) as their major exposure facets. And it should be noted that in the absence of Pt precursor, the Cu precursor could not be reduced to Cu even with a long reaction time (130 °C, 6 h) in the presence of CO, indicating that the reduction of Cu precursor was facilitated by the preformed Pt crystal nuclei through the autocatalytic growth mechanism. During the reaction, the growth process of metal precursors, the preferential CO adsorption of PtCu (111) controlled the formation of ultrathin nanosheets. The major role of PVP in the synthesis was to prevent the aggregation of nanosheets. In the absence of PVP, PtCu alloy nanosheets were also produced, but the obtained nanosheets were heavily aggregated (Figure S8).

The electrochemical properties of PtCu alloy nanosheets, PtCu nanoparticles (Figure S9) and Pt black were first investigated by cyclic voltammetry (CV) in a 0.05 M H$_2$SO$_4$ solution. Using hydrogen adsorption-desorption method in conjunction with CV (Figure S10), the electrochemically surface areas (ECSA) of PtCu alloy nanosheets was determined to be 49.3 m$^2$/g$_{Pt}$, respectively. Which was larger than that for PtCu nanoparticles (27.5 m$^2$/g$_{Pt}$) and commercial Pt (19.8 m$^2$/g$_{Pt}$). The catalytic performances of the PtCu alloy nanosheets, PtCu alloy nanoparticles and commercial Pt black then were investigated in hydrogen evolution reaction (HER), an important half-reaction in the electrochemical water splitting for hydrogen generation using the same Pt loading (4 µg$_{Pt}$). HER activities of the PtCu alloy nanosheets and Pt black were also measured in the N$_2$-saturated 0.05 M H$_2$SO$_4$ without IR compensation. The currents were normalized to the electrode area (0.196 cm$^2$). As shown in Figure 4a the ultrathin PtCu alloy nanosheets achieved current densities of 50 and 100 mA cm$^{-2}$ at overpotentials of 39 and 55 mV, respectively. In comparison, PtCu nanoparticles or Pt black needed an overpotential of 72 or 111 mV to reach the current density of 100 mA cm$^{-2}$. The corresponding Tafel plots (Figure 4b) indicated the ultrathin PtCu nanosheets possessed a smaller Tafel slope (23 mVdec$^{-1}$) than PtCu nanoparticles (34 mVdec$^{-1}$) and Pt black (53 mVdec$^{-1}$). The
catalytic stability of the nanosheets was further evaluated. Compared to PtCu nanoparticles and Pt black, the nanosheets showed a remarkable durability in HER, with only a slight performance loss after 5000 cycles (Figure S11). The enhanced electrochemically performance of the nanosheets was due to their high ECSA and the alloy effect. These results demonstrated that the PtCu alloy nanosheets were an excellent catalyst for HER in acidic medium, compared to another Pt-based catalysts.56–49

Beyond electrocatalysis, Pt-based nanomaterials are currently widely used as efficient heterogeneous catalysts for hydrogenation reactions. Well-defined alloy nanomaterials often exhibit better catalytic properties than their monometallic counterparts.50–52 In this study, hydrogenation of nitrobenzene was chosen as a model reaction to demonstrate the catalytic advantage of the PtCu nanosheets over PtCu nanoparticles and conventional Pt catalysts. PtCu nanosheets and PtCu nanoparticles were loaded on active carbon (XC-72) with a mass ratio of 10% for the catalysis evaluation. The molar ratio of Pt to nitrobenzene was 0.1%. As shown by in Figure 5a, the hydrogenation process proceeded very fast over PtCu nanosheets. Nitrobenzene was completely hydrogenated into aniline within one hour. In comparison, the conversion efficiency of the PtCu nanoparticles and Pt/C (10 wt%) was little lower. Less than 73% and 44% nitrobenzene was hydrogenated within the same reaction time. Under the same conditions, XC-72 did not show any activity (Figure S12). The turnover frequency (TOF) of PtCu nanosheets with respect to nitrobenzene conversion reached 78,970 h⁻¹, better than PtCu nanoparticles (43,370 h⁻¹) and Pt/C (23,530 h⁻¹). More importantly, the PtCu nanosheets exhibited an excellent catalytic stability (Figure 5b). There was no obvious decay in the first four cycles using the same catalyst. The yield of aniline was slightly decreased by 7% in the following three cycles. Moreover, the catalytic efficiencies of the PtCu nanosheets were much higher than that reported in previous studies on Pt based alloy nanocrystals.53 The enhanced catalytic performances of PtCu nanosheets might be due to their abundant surface catalytic sites and also the synergistic effect of the two metallic components. The enhanced hydrogenation activity demonstrated that controlling the synthesis of alloy nanocrystals with two-dimensional (2D) ultrathin structures is indeed an efficient strategy to improve the catalytic performance.

In summary, a CO-assisted synthetic method has been successfully developed for the preparation of freestanding ultrathin PtCu alloy nanosheets. The use of CO was demonstrated to play a crucial role in the anisotropic formation of PtCu alloy nanosheets. Thanks to the ultrathin nanostructures and alloy effect, the obtained PtCu alloy nanosheets exhibited enhanced catalytic activities towards hydrogen evolution reaction and hydrogenation reaction, making them a promising catalyst for both energy conversion and chemical industry applications. Moreover, the developed method is expected to provide new opportunities in creating ultrathin nanostructures with a wide range of alloy compositions for various catalytic applications.

Experimental Section

Preparation of PtCu alloy nanosheets

In a typical synthesis of PtCu alloy nanosheets, 20 mg Pt(acac)₂, 13 mg Cu(acac)₂, 100 mg PVP, and 50 mg KI were dissolved in 10 mL formamide. The resulting homogeneous yellow solution was transferred to a glass pressure vessel. The vessel was then charged with CO to 1 bar and heated at 130 °C for 3.0 h before it was cooled to room temperature. The dark products were precipitated by acetone, separated via centrifugation and further purified by a water-acetone mixture.

Hydrogenation of nitrobenzene

A 10 mL ethanol dispersion of PtCu nanosheets (containing 1 μmol Pt) supported on 1.8 mg active carbon (XC-72) was added in a glass pressure vessel. After sonication, 100 μL nitrobenzene (1 mmol) was added to the catalyst suspension. The pressure vessel was then purged with H₂ gas and heated at 130 °C for 3.0 h. The reaction mixture was stirred at room temperature to have the catalytic hydrogenation proceed. During catalysis, samples were withdrawn at regular intervals, filtered, and analyzed by gas chromatography (GC).

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