Angewandte Chemie

Electrooxidation Catalysts

DOI: 10.1002/anie.200905413

High-Index Faceted Platinum Nanocrystals Supported on Carbon Black as Highly Efficient Catalysts for Ethanol Electrooxidation[**]

Zhi-You Zhou, Zhi-Zhong Huang, De-Jun Chen, Qiang Wang, Na Tian, and Shi-Gang Sun[*]

Platinum nanoparticles supported on carbon black (Pt/C) are the most important electrocatalysts, especially in polymer electrolyte fuel cells.[1] The catalytic activity of Pt nanoparticles is highly dependent on their surface structures. Surface defects, that is, step and kink atoms with low coordination numbers ($CN < 8$), usually exhibit very high chemical reactivity and catalytic activity for most structure-sensitive reactions, for example, oxygen reduction and electrooxidation of small organic fuel molecules.[2] Therefore, the preparation of Pt nanoparticles with a high density of atomic steps on their surface is an effective way to further boost their catalytic activity. However, according to crystal growth habits, the growth of Pt nanocrystals (NCs) tends to form thermodynamic equilibrium shapes such as cubes, tetrahedra, and cuboctahedra, which are bounded by low-index {111} and {100} facets of low surface energy.[3] In theory, atoms with low coordination numbers exist on such nanoparticles only at the edges and vertices, and are thus quite limited. In contrast, high-index planes of Pt single crystals contain a high density of low-coordinate atomic steps and kinks and therefore exhibit very high catalytic activity.[4,5] As a result, the synthesis of Pt nanocrystal catalysts with high-index facets is a desirable and challenging target in the catalysis community.

Recently, we developed an electrochemically shape-controlled method and successfully synthesized tetrahexahedral Pt nanocrystals (THH Pt NCs) enclosed by {730} and vicinal high-index facets.[6] In this method, Pt nanospheres (ca. 750 nm in diameter) were first deposited on glassy carbon (GC) and then subjected to an electrochemical square-wave potential treatment. Through dissolution and recrystallization, THH Pt NCs with a defined size that can be varied from 20 to 200 nm were grown on the GC at the expense of Pt nanospheres. The square-wave potential led to periodic oxygen adsorption and desorption on the Pt NCs' surfaces and played a key role in controlling the surface structure of the Pt NCs and in increasing the quantity of atomic steps. It has been confirmed that the THH Pt NCs exhibit superior catalytic activity to commercial Pt/C catalysts.[6] Other shapes of Pt and Pd NCs bounded by high-index facets, such as trapezohedron with 24 {*hkk*} facets, concave hexoctahedron with 48 {*hkl*} facets, and multiple twinned nanorods with {*hk*0} and {*hkk*} facets have also been synthesized by applying this square-wave potential method.[5,7,8] Note that previously synthesized Pt NCs are all relatively large (greater than 20 nm) and deposited on glassy carbon, which obstructs potential applications such as in fuel cells owing to low utilization efficiency of noble metals. Usually, practical Pt electrocatalysts are supported on carbon black.

Herein, we report our new results in the synthesis of high-index faceted Pt NCs supported on carbon black (HIF-Pt/C) with a size (2–10 nm) comparable to that of commercial catalysts by using a square-wave potential method. The key for decreasing size is the employment of insoluble Cs_2PtCl_6 dispersed on carbon black instead of large Pt nanospheres as the precursor. Aberration-corrected high-resolution transmission electron microscopy (HRTEM) and cyclic voltammetric characterizations revealed that the HIF-Pt/C catalysts contain a much higher density of atomic steps than do commercial Pt/C catalysts. The HIF-Pt/C catalysts exhibit two to three times higher electrocatalytic activity than the commercial Pt/C catalysts for ethanol oxidation thanks to their high density of atomic steps. More importantly, the HIF-Pt/C catalysts can promote the cleavage of the C–C bond of ethanol to generate twice as much CO_2 as commercial Pt/C catalysts under the same conditions, as evidenced by in situ FTIR reflection spectroscopy.

Figure 1 shows TEM images of the HIF-Pt/C catalysts. Platinum nanoparticles are highly dispersed on the carbon black support. The average size of the nanoparticles is (5.1 ± 1.2) nm, as illustrated by the size histogram (Figure 1 c). This size is comparable to that of commercial catalysts (usually 2–10 nm). Energy-dispersive X-ray (EDX) spectroscopy (Figure 1 d) indicates that there are no other impurities besides carbon and oxygen, and the typical weight percent of Pt is about 17 %.

Aberration-corrected HRTEM was employed to characterize the surface structure of the HIF-Pt/C catalysts. This technology provides atomic-resolution images of the outmost layer of nanoparticles, which are important in identifying catalytic active sites.[9] Three aberration-corrected HRTEM images of the HIF-Pt/C nanoparticles are shown in Figure 2, in which the border atoms are clearly resolved. The crystal

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[*] Dr. Z. Y. Zhou, Z. Z. Huang, D. J. Chen, Q. Wang, Dr. N. Tian, Prof. S. G. Sun
State Key Laboratory of Physical Chemistry of Solid Surfaces
Department of Chemistry, College of Chemistry and Chemical Engineering
Xiamen University, Xiamen 361005 (China)
Fax: (+86) 592-2180-181
E-mail: sgsun@xmu.edu.cn

[**] This study was supported by NSFC (20873113, 20833005, and 20933004), the MOST (2007DFA40890), Research Fund for New Teachers of the Doctoral Program of Higher Education of China (200803841035), and Fujian Provincial Department of Science and Technology (2008F3099 and 2008I0025). We thank Zhiying Cheng and Yueliang Li at the Beijing National Centre for Electron Microscopy for the aberration-corrected HRTEM tests.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905413.

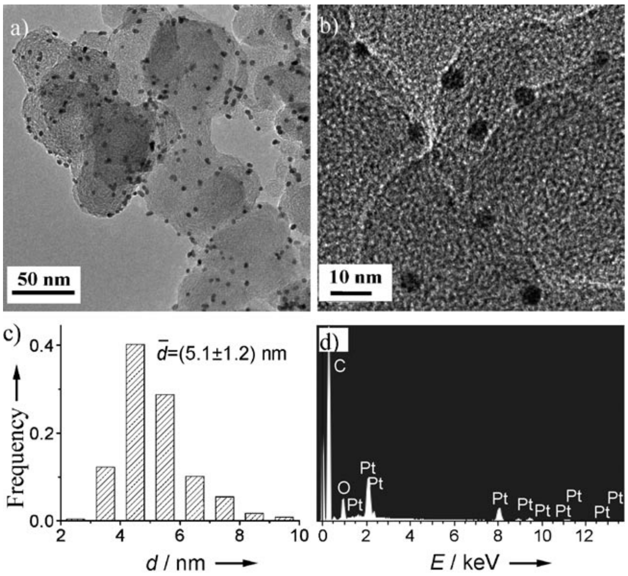

Figure 1. a) Low- and b) high-magnification TEM images, c) size histogram, and d) EDX spectrum of HIF-Pt/C catalysts.

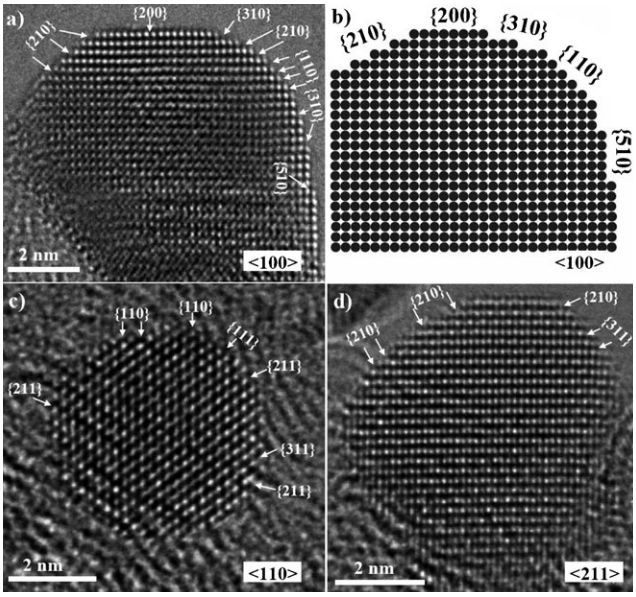

Figure 2. Aberration-corrected HRTEM images of HIF-Pt/C catalysts, showing the high density of atomic steps. Orientation axis and size of the three Pt nanoparticles: a) ⟨100⟩, 7.5 nm; c) ⟨110⟩, 5.0 nm; d) ⟨211⟩, 6.0 nm. b) Models of {110}, {210}, {310}, and {510} atomic steps along a ⟨100⟩ crystal zone axis for comparison with (a).

orientations of three particles (in Figure 2 a, c, d) are along the ⟨100⟩, ⟨110⟩, and ⟨211⟩ axes. The shape of these NCs is not spherical, as some small facets can be clearly observed. More importantly, these NCs possess a high density of low-coordinate atomic steps, such as {110}, {210}, {310}, {510}, {211}, and {311} steps that can be identified on the border atoms (a model is shown in Figure 2 b, and detailed assignments of step sites are given in Figures S1–S4 in the Supporting Information). These structural features are significantly different from those reported. For example, Gontard et al.[9] have shown aberration-corrected HRTEM images of commercial Pt nanoparticles (ca. 6 nm) also supported on carbon black, on which most of surface sites were {100} or {111} microfacets.

Although HRTEM can be used to identify the surface structure, it can only detect a limited number of nanoparticles. In contrast, electrochemical voltammetric methods can provide overall structural information on catalysts. Previous studies have shown that low-coordinate step atoms on Pt high-index planes can promote oxygen adsorption.[10] As a result, a larger current (generated by oxygen adsorption on Pt surfaces) can be observed at low potential in cyclic voltammograms recorded in aqueous H_2SO_4 solution. In this way, the electric charges of oxygen adsorption can be correlated to the quantity of Pt atomic steps. Figure 3 compares the cyclic voltammograms of the HIF-Pt/C and commercial Pt/C (20 wt %, Johnson Matthey) recorded in 0.1 M H_2SO_4. As expected, a larger current of oxygen adsorption and desorption can be observed on the HIF-Pt/C in the potential range of 0.40 to 0.75 V. It was determined that the electric charge density of oxygen adsorption on the HIF-Pt/C catalyst is 166 $\mu C\,cm^{-2}$, while it is only 136 $\mu C\,cm^{-2}$ on the commercial Pt/C sample. Such cyclic voltammetry data also confirm effectively that the HIF-Pt/C catalysts present a higher density of Pt atomic steps on their surface than the commercial Pt/C does.

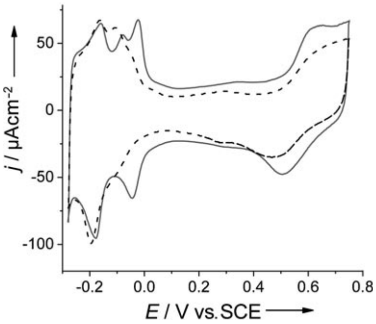

Figure 3. Cyclic voltammograms of HIF-Pt/C (——) and commercial Pt/C (-----) in 0.1 M H_2SO_4. Scan rate: 50 $mV\,s^{-1}$. SCE = saturated calomel electrode.

Currently, the commercialization of direct ethanol fuel cells (DEFC) is severely hampered by the sluggish kinetics and incomplete oxidation of ethanol on platinum-based catalysts. The HIF-Pt/C catalysts exhibit very high activity towards ethanol electrooxidation. Figure 4 a depicts the steady-state cyclic voltammograms of the HIF-Pt/C and commercial Pt/C catalysts in a mixture of 0.1 M ethanol and 0.1 M $HClO_4$ at 60 °C, that is, at the normal operating temperature of a DEFC. The oxidation current has been normalized to the electroactive Pt surface area calculated from the electric charges of hydrogen adsorption and desorption. In the potential scan in the positive direction, HIF-Pt/C showed an onset potential (measured at $j = 0.05\ mA\,cm^{-2}$) of 0.14 V, which is shifted negatively by

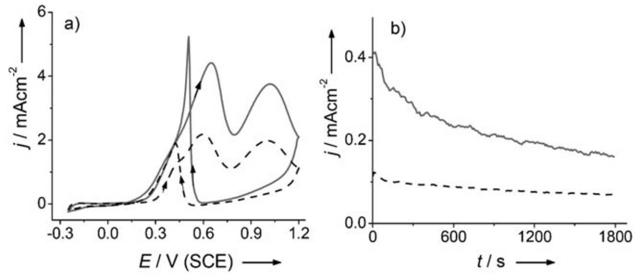

Figure 4. Electrocatalytic properties of HIF-Pt/C (——) and commercial Pt/C (-----) for ethanol oxidation. a) Steady-state cyclic voltammograms (100 mV s^{-1}). b) Current–time curves measured at 0.25 V in a mixture of 0.1 M ethanol and 0.1 M $HClO_4$ at 60 °C.

100 mV from the value of 0.24 V measured for the commercial Pt/C sample. Moreover, in the potential scans in both positive and negative directions, the current density measured on the HIF-Pt/C catalysts is about twice that of the commercial Pt/C catalysts.

To evaluate the electrocatalytic activity and stability of the catalysts under continuous operating conditions, long-term chronoamperometric experiments were carried out.[11] Figure 4 b shows the current versus time curves recorded at 0.25 V for 1800 seconds. The HIF-Pt/C catalysts maintain a current density that is 2.3–3.5 times higher than that of the commercial Pt/C, thus demonstrating a significantly enhanced electrocatalytic activity.

It has been reported that Pt high-index planes can promote the cleavage of the C–C bond and produce more CO_2 for ethanol electrooxidation than low-index planes,[12] as atomic steps have a large number of dangling bonds and can strongly interact with ethanol to weaken the C–C bond. The HIF-Pt/C catalysts contain a high density of atomic steps. As a consequence, they should boost the complete oxidation of ethanol. To confirm this property, in situ FTIR spectroscopic studies were carried out.

Figure 5 illustrates in situ FTIR spectra of ethanol oxidation on the HIF-Pt/C and commercial Pt/C catalysts at 0.60 V. The upward band at 1044 cm^{-1} is the signature peak for the C–O stretching vibration of CH_3CH_2OH, representing the consumption of ethanol by oxidation. The downward band at 2343 cm^{-1} is attributed to CO_2. This band reflects the cleavage of the C–C bond for ethanol oxidation. The band near 1720 cm^{-1} is the stretching vibration of the C=O bond in acetic acid and acetaldehyde. A well-defined band at 1280 cm^{-1} is the characteristic absorption of C–O stretching in acetic acid, which is usually employed for quantitative analysis of acetic acid.[13] The detailed assignment of IR bands is listed in Table S1 in the Supporting Information. Obviously, more CO_2 and less acetic acid are formed on the HIF-Pt/C catalysts for ethanol oxidation than on commercial Pt/C catalysts. The integrated band intensities of CO_2 at 2343 cm^{-1} and acetic acid at 1280 cm^{-1} are 0.216 and 0.203, respectively, on the HIF-Pt/C catalysts; corresponding values are 0.131 and 0.276 on the commercial Pt/C sample. Thus, the ratio of band intensities of CO_2 to acetic acid on HIF-Pt/C is double that on commercial Pt/C (1.06 vs. 0.475). The time-resolved FTIR spectra clearly illustrate a fast increase in CO_2 band intensity on HIF-Pt/C compared to that on commercial Pt/C (Figure S5 in the Supporting Information). The in situ FTIR results reveal clearly that, compared with commercial Pt/C, HIF-Pt/C catalysts do have enhanced reactivity for breaking the C–C bond in ethanol; as a consequence, they show a higher selectivity for the complete oxidation of ethanol to CO_2.

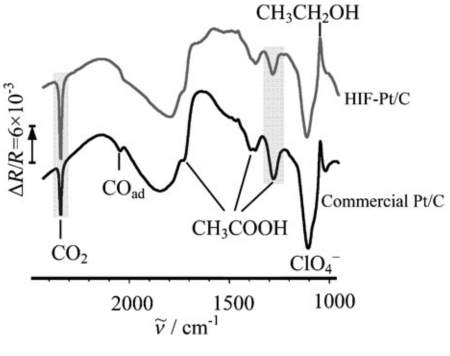

Figure 5. In situ FTIR spectra of ethanol oxidation on HIF-Pt/C and commercial Pt/C at 0.60 V in a mixture of 0.1 M ethanol and 0.1 M $HClO_4$. Reference potential was −0.25 V.

In conclusion, high-index faceted Pt nanocrystals with a size of approximately 2 to 10 nm supported on carbon black (HIF-Pt/C) were synthesized by an electrochemical square-wave potential method. Electrocatalytic tests of ethanol oxidation demonstrated that the HIF-Pt/C catalysts, thanks to their high density of atomic steps, exhibited catalytic activity and selectivity for CO_2 at least two times higher than those of commercial Pt/C catalysts. This study is of great significance in the synthesis of highly active Pt/C catalysts and also in the improvement of the efficiency of direct ethanol fuel cells.

Experimental Section

The HIF-Pt/C catalysts were synthesized by the following procedures: 1) Insoluble Cs_2PtCl_6 dispersed on carbon black as precursor was first prepared by ultrasonic treatment of a mixture of Cs_2SO_4 (25.0 mg), Vulcan XC-72 (20.0 mg), and $H_2PtCl_6\cdot 6H_2O$ (20.0 mg) in isopropyl alcohol (ca. 7 mL). 2) The resulting inky mixture (10 μL) was transferred onto a glassy carbon (GC, $\phi = 5$ mm) electrode and then immediately dried in a vacuum drying oven. 3) The GC electrode with Cs_2PtCl_6 precursors was transferred into 0.1 M H_2SO_4 and was subjected to a square-wave potential ($f = 10$ Hz, $E_L = -0.30$ V, $E_U = 1.20$ V vs. SCE) for 20 min.

The morphology and surface structures of HIF-Pt/C catalysts were characterized by aberration-corrected HRTEM (FEI Titan 80–300), which was conducted at the Beijing National Centre for Electron Microscopy.

Electrochemical preparation and characterization were carried out in a standard three-electrode cell working with a 263 A potentiostat/galvanostat (EG&G). A saturated calomel electrode (SCE) was used as reference electrode, and all potentials are quoted versus the SCE scale. Electrocatalytic oxidation of ethanol was measured in a mixture of 0.1 M ethanol and 0.1 M $HClO_4$ at 60 °C, and a commercial 20 wt % Pt/C sample (Johnson Matthey) was used as comparison material. The experimental details of in situ FTIR reflection spectroscopy were described previously.[14]

Received: September 27, 2009

Keywords: electrochemistry · heterogeneous catalysis · infrared spectroscopy · nanoparticles · platinum

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