Electrochemical Decontamination of Platinum Nanocrystals and its Applications for Methanol Electrooxidation

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Abstract: Polyvinylpyrrolidone (PVP) is an effective surface-capping agent for engineering metal surface structure but is hardly to be thoroughly removed. In this study, the electrochemical treatment was applied for the decontamination of polyvinylpyrrolidone (PVP) on platinum (Pt) nanocrystals. Spherical, cubic, octahedral and cuboctahedral Pt nanocrystals were prepared by the colloidal method with PVP K30 as the capping agent. Electrochemical decontamination of Pt nanocrystals was performed by using square-wave potential steps and methanol electrooxidation was used as a probe reaction. High-frequency potential steps were set up between a high voltage and a low voltage to avoid surface distortion. Cyclic voltammetry (CV) and chronoamperometry measurements were used to evaluate the catalytic activity of the cleaned Pt nanocrystals for methanol. The results showed that electrochemical decontamination was an effective way to clean Pt nanocrystals and the cuboctahedral Pt nanocrystals displayed the best electrocatalytic activity for methanol electrooxidation.

1. Introduction

Shape-controlled synthesis of platinum-group metals is of fundamental and practical importance in energy catalysis field. Both anode oxidation reaction and cathode reduction reaction are very sensitive to the surface structure and the exposed surface sites [1-3]. PVP is one of the most effective surface-active capping agents for the morphology control of Pt-based nanocrystal. The main reason is that the addition of PVP can simply obtain uniform nanocrystals loaded on various carbons with good reproducibility [4-5].

Because PVP can combine strongly with the surface of platinum through chemical adsorption, it can prevent the direct interaction between the surface active sites and the reagent molecules, thus reducing the activity or selectivity of catalytic reaction [6]. Even if Pt nanocrystals were carefully cleaned by extensive washing with organic solvents, the distinctive hydrogen adsorption/desorption peaks of Pt CVs in blank sulfuric acid were still inconspicuous. This is mainly ascribed to the high-molecular-weight PVP which can strongly block the Pt active sites [7-8]. Therefore, it is necessary to apply a thorough cleaning process for Pt nanocrystals before electrochemical measurements.

Various methods have been reported in the literature for the removal of surface-capping PVP from the nanoparticle surface. The most effective method should be the heat-treatment of PVP-capped nanoparticles at different temperatures. However, the particle shapes experienced a dramatic transformation into spherical-like shapes when the temperature is raised above \( \sim 500 \) °C At higher temperatures, surface melting becomes obvious leading to coalescence of the surfaces of neighboring nanocrystals and a decrease in the volume occupied by the assembled nanocrystals and hence, careful control of temperatures is necessary for the heat-treatment method [9]. Another technique for removal of stabilizer from nanoparticles is by using UV–ozone exposure in order to eliminate the traces of PVP.
still presenting on the surface [10-11]. However, it is difficult to generalize this technique and the results depend on the chemical nature of the specimen and the capping agents. The removal of PVP has also been reported by applying CV up to 1.5 V [12-13], CO-adsorption-induced removal [14]. However, it has been generally accepted that too many cycles up to high potentials may degrade the surface structure [15-16]. Especially, Pt(100) surface could only maintain its structure under 0.9 V. While, CV cycles below 0.9 V couldn’t clean PVP adsorbed on Pt nanocrystals. Applying a high voltage to the Pt surface will introduce defects to the primary surface. That is mainly because oxygen could adsorb on the Pt(100) surface in the potential region higher than 0.9 V and oxygen atom could crowd out some Pt atoms from its equilibrium position [17]. This process is irreversible. Therefore, it is of great significance to develop a simple and efficient cleaning method for Pt nanocrystals to avoid using too many organic solvents. In this work, a facile electrochemical decontamination method was applied to the PVP-capped Pt nanocrystals by square-wave potential steps. High-frequency potential steps were set up between a high voltage and a low voltage to remove the chemically adsorbed PVP molecules without disturbing the surface structure and its performances. Methanol electrooxidation was then adopted as a probe reaction to evaluate the electrocatalytic activity and stability of treated Pt nanocrystals.

2. Experimental Section

2.1 Synthesis of Pt nanocrystals
Pt nanocrystals were synthesized by the colloidal method described previously [15]. The precursor Pt salt is H₂PtCl₆·6H₂O, and the stabilizer is PVP K30. Briefly, 3 mL 0.375 M PVP and 1.5 mL 0.0625 M H₂PtCl₆·6H₂O solutions in ethylene glycol (EG) were added gradually to the boiling EG over a 16-min period. The resulting mixture was refluxed for an additional 5 min. The product was then centrifuged and washed by a large amount of acetone, ethanol, and hexane before the electrochemical test. Different amounts of AgNO₃ solution in EG were added to the reaction mixture prior to the addition of PVP and Pt precursors to adjust the morphology of Pt nanocrystals. For Pt cube, cuboctahedron and octahedron synthesis, Ag salt/Pt salt molar ratio were adjusted to 1.1 mol %, 11 mol %, and 32 mol %, respectively.

2.2 Characterization and electrochemical measurements
Transmission electron microscopy (TEM) and high-resolution transmission microscopy (HRTEM) experiments were made on a JEM-3010 microscope operated at 300 kV. Before the electrochemical measurements, Pt nanocrystals with different shape were dispersed in ultra-pure water by sonicating for at least 20 min and then 6 μL suspension was transferred to the surface of a glassy carbon (GC) electrode with a diameter of 4 mm with a micropipette. The GC electrode was then dried in air at room temperature. A saturated Hg/Hg₂SO₄ electrode and Pt foil were used as the reference and counter electrode, respectively. Conventional three-compartment electrochemical cells were used for all the electrochemical tests. The electrolyte solution was deaerated with high-purity Ar (99.99%) for at least 20 min before each measurement. Cyclic voltammograms (CVs) were taken in the potential region of 0.05 ~ 1.2 V. Chronoamperometric curves were performed at 0.80 V for 600 s after a potential step from 0.05 V in 0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH. All electrochemical measurements were performed with a CHI electrochemical workstation (CH Instruments, model CHI750d) at room temperature (ca. 20 °C). All the potentials in this paper are calibrated to a reversible hydrogen electrode (RHE).

3. Results and Discussion

3.1 Morphology characterization of platinum nanocrystals
Figure 1 shows TEM and HRTEM images of cubic (a, d), octahedral (b, e) and cuboctahedral (c, f) Pt nanocrystals synthesized in this reaction. These Pt nanocrystals are uniform in shape with a narrow
size distribution (cubic Pt: 7.0 nm, octahedral Pt: 10.0 nm, cuboctahedral Pt: 9.5 nm). The HRTEM image (Figure 1d) of a Pt cube demonstrates the exposed (100) facets with an interplanar spacing of 0.20 nm. While HRTEM image of Pt octahedra demonstrates an interplanar spacing of 0.23 nm, in which all side faces are covered with (111) facets. The cuboctahedral Pt was covered by both (100) and (111) facets.

According to the reaction mechanism proposed by Yang’s group, the Ag⁺ ion plays a crucial role in controlling the shape and surface structure of the Pt nanocrystals. As the concentration of Ag ion increases in the reaction mixture, the majority of the Pt particles changes from the cubes to the cuboctahedra, and eventually to the octahedra [15].

3.2 Electrochemical testing
In our previous tests, the as-prepared and carefully washed platinum nanocrystals were used for the electrocatalytic oxidation of methanol. However, no electrooxidation current was detected. Therefore, a repeated potential step sequence between 0.05 V and 1.4 V with a pulse width of 0.5 s was applied to the PVP-capped Pt nanocrystals. The short pulse width was selected to avoid long-time oxygen adsorption and its influence on surface structure. Figure 2a shows the CV curves of spherical platinum nanocrystals before and after electrochemical treatment in 0.5 molꞏL⁻¹ H₂SO₄ solution with a scanning rate of 0.05 Vꞏs⁻¹. As can be seen in Figure 2a, the adsorption and desorption peaks of hydrogen and oxygen are very small before electrochemical cleaning since the active sites were blocked by chemically adsorbed PVP. After electrochemical treatment for 100 steps, the featured hydrogen and oxygen peaks become clear and tend to stabilize. This indicates that the potential step treatment can effectively remove PVP species strongly adsorbed on platinum surfaces which were hard to be removed by solvent washing method. At the same time, this method could protect the surface structure from reconfiguration so that the catalytic activity of platinum nanocrystals with different morphologies could be distinguished in the subsequent methanol electrooxidation experiments.

It has been widely accepted that the hydrogen adsorption/desorption peaks of CVs for Pt in H₂SO₄ solution is highly sensitive to the surface morphology of Pt, which could be used to characterize the predominant surface of Pt particles [18-20]. Figure 2b shows stable CV curves platinum nanocrystals with different morphologies after electrochemical treatment in 0.5 molꞏL⁻¹ H₂SO₄ solution. As shown

![Figure 1. TEM and HRTEM images of cubic (a, d), octahedral (b, e) and cuboctahedral (c, f) Pt nanocrystals.](image-url)
in this figure, the CVs display the typical shape for the blank voltammograms of Pt. The curves show the presence of adsorption states associated with (110) and (100) sites at 0.12 and 0.27 V, respectively [21]. The relative peak height for the (110) and (100) Pt sites is an important information for the shape and dominant facet yield of the Pt nanoparticles [16]. Spherical Pt nanocrystals show clear representative polycrystalline Pt features, which has a higher (110) peak height than (100) peak [22]. For the octahedral and cubic shape Pt nanoparticles, the current in the potential range between 0.11 ~ 0.23 V is a bit higher than that of spherical Pt in the CV curve, which is an indication of the Pt nanoparticles containing mainly (111) facets and (100) step sites. These electrochemical results are in good agreement with the TEM images. It has been known that (100) surface with long-range ordered domains will be destroyed under the potential higher than 0.9 V while (111) facets could maintain the stable surface structure until 1.2 V [23]. Therefore, the shoulder around 0.35 V which indicates the existence of long-range ordered (100) terrace sites was not well identified.

Figure 2. (a) CVs of spherical platinum nanocrystals before and after potential step treatment; (b) CV curves of Pt nanocrystals of different morphologies in 0.5 mol·L⁻¹ H₂SO₄ solution.

Figure 3. (a) CVs and (b) Chronoamperometric curves of methanol electrooxidation on Pt nanocrystals of different morphologies in 0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH. Figure 3 shows (a) the CVs and (b) chronoamperometric (CA) curves of methanol electrooxidation on Pt nanocrystals of different morphologies in 0.5 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ CH₃OH. It should be
clearly seen in Figure 3a that hydrogen adsorption was depressed significantly in the solution containing methanol. This was due to the dissociative adsorption of methanol. It was known that methanol started to decompose on Pt from 0.05 V and the resulting intermediates (COad, etc) adsorb on the Pt surfaces, which will poison the surface sites for methanol oxidation. This was regarded as the indirect oxidation of methanol. In the higher potential region, these intermediates were oxidized and the direct oxidation of methanol will occur. For the cubic Pt nanocrystals as an example, during positive scanning process, the onset potential of methanol electrooxidation was 0.45 V. The peak potential located at 0.85 V with a peak current density of 1.06 mA·cm⁻², which included both the oxidation of methanol dissociative adsorption species (i.e. indirect oxidation of methanol) and the direct oxidation of methanol from aqueous solution. In the higher potential region, the electrode surface will be covered by adsorbed oxygen species. In the negative scanning process, along with the desorption of oxygen species, methanol oxidation appeared again and resulted in another oxidation peak with a maximum current density of 0.88 mA·cm⁻² at 0.72V. As the potential sweep negatively, the dissociative adsorption of methanol occurred and poisonous intermediates formed and occupied Pt surface sites again, which would retard the direct oxidation of methanol and cause the oxidation current decrease. As can be seen from Figure 3a, the platinum nanocrystals after electrochemical cleaning show quite different catalytic activity for methanol electrooxidation. The positive oxidation peak currents decrease in the order of cuboctahedral Pt > cubic Pt > spherical Pt > octahedral Pt. The peak current for cuboctahedral Pt was 5 times higher as that of octahedral Pt. On the other hand, the residual current in the hydrogen region of octahedral Pt was much higher than others, indicating the octahedral Pt has better resistance to methanol dissociative adsorption. It has been proved that methanol proceeds via both direct and indirect pathways which are governed by the initial C–H and O–H bond activation, respectively [24]. The primary path requires an ensemble size of between 3~4 Pt atoms and is much more structure sensitive than the secondary path. That’s the intrinsic reason for the morphology-dependent electrooxidation activity of methanol. Furthermore, Oezaslan and co-workers found that PVP-based impurities have more pronounced effects on the Pt hydr(oxide) region than on the hydrogen ad/desorption region [25], thus the electrochemical cleaning of PVP will show more important impact on the direct-oxidation of methanol in higher potential region.

It has been previously reported by Wieckowski that methanol electrooxidation activity at Pt low index crystal planes increased in the order of Pt(111) < Pt(100) < Pt(110) [22]. Furthermore, the stepped surfaces, which were considered as models for surface defects, could also give some practical instructions for shape-dependent electrocatalysis. For example, Housmans and co-workers found that methanol oxidation activity on Pt(n(111)×(110)) high index planes increased with the step density, suggesting that the presence of steps with a (110) orientation catalyzes methanol decomposition, CO oxidation and also the direct methanol oxidation [26; 27]. In addition, the catalytic activity of nanoparticles of well-defined edges and large surface boundaries are said to be greatly dependent on the bounding planes where catalytic activity follows the (111) < (100) < (110) order, as in the case of hydrogen-related reactions [28-30]. In a previous paper reported by Feliu and co-workers [31], different surface sites on platinum samples have been quantitatively analyzed by specific site-probe reactions. It has been shown clearly that for the surfaces of cubic and octahedral Pt nanoparticles, the ordered domains were mainly (100) and (111) sites. While the ordered domains for spherical Pt represented a much smaller fraction of the total surfaces. In their cover picture, they suggested that the current for (110) sites was mainly attributed to the edge and corner atoms of a cuboctahedral Pt particle. Therefore, it is reasonable to suppose that the much higher activity of cuboctahedral Pt originated from its higher fraction of edge and corner Pt atoms.

The stability of the catalysts with different morphologies has also been investigated by CA curves recorded at 0.80 V, which was shown in Figure 3b. A large anodic current is observed on cuboctahedral Pt with only a small drop. A large current is also found on cubic Pt and spherical Pt, whereas a much lower current is observed on octahedral Pt. The final methanol electrooxidation current density on cuboctahedral Pt after 600 s is nearly 13 times higher than that on octahedral Pt. The electrooxidation activity and stability for methanol increase in the order cuboctahedral Pt > cubic
Pt > spherical Pt > octahedral Pt, which is in accordance with the results of CV curves. These results provide a reasonable guidance for the structure and shape design of Pt nanocrystals, especially for the electrocatalysts with high index facets, which have been considered as promising candidate for practical catalysis applications [32].

4. Conclusions
In this study, we developed a facile electrochemical decontamination method of PVP on Pt nanocrystals by electrochemical treatment and investigated its influences on the electrooxidation of methanol. Pt nanocrystals with different morphologies was synthesized by the colloidal method. The as-prepared Pt nanocrystals were electrochemically cleaned by square-wave potential steps before electrocatalytic performance measurements. It was found that the high-frequency potential step method was an effective method for the thorough decontamination of PVP on platinum nanocrystals and protection of preferential-oriented surfaces. More and more surface sites were exposed as the potential steps proceeding, which was clearly indicated from the increasing hydrogen and oxygen adsorption/desorption peaks of the CV curves. The electrochemically cleaned Pt nanocrystals were then applied to methanol electrooxidation. The results showed that the cuboctahedral Pt nanocrystals displayed the best catalytic activity and stability for methanol electrooxidation in acidic solution. The electrocatalytic activity of Pt nanocrystals for methanol increases in the order of cuboctahedral Pt > cubic Pt > spherical Pt > octahedral Pt. This work puts forward a simple and effective method for the thorough decontamination of PVP-capped Pt surfaces and is helpful in understanding the relationship between the electrochemical performances and the surface structure of the catalysts.

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References
[1] Xia Y., Xiong Y., Lim B. and Skrabalak S. E. (2009) Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? Angewandte Chemie-International Edition, 48: 60-103.
[2] Tian N., Zhou Z.-Y., Sun S.-G., Ding Y. and Wang Z. L. (2007) Synthesis of Tetrahexahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. Science, 316: 732-5.
[3] Tao A. R., Habas S. and Yang P. (2008) Shape control of colloidal metal nanocrystals. Small, 4: 310-25.
[4] Fernandez P. S., Ferreira D. S., Martins C. A., Troiani H. E., Camara G. A. and Martins M. E. (2013) Platinum nanoparticles produced by EG/PVP method: The effect of cleaning on the electro-oxidation of glycerol. Electrochimica Acta, 98: 25-31.
[5] Hei H., Wang R., Liu X., He L. and Zhang G. (2012) Controlled synthesis and characterization of nobel metal nanoparticles. Soft Nanoscience Letter, 2: 34-40.
[6] Xie S. F., Choi S. I., Xia X. H. and Xia Y. N. (2013) Catalysis on faceted noble-metal nanocrystals: both shape and size matter. Current Opinion in Chemical Engineering, 2: 142-50.
[7] Lopez-Sanchez J. A., Dimitratos N., Hammond C., Brett G. L., Kesavan L., White S., Miedziak P., Tiruvalam R., Jenkins R. L., Carley A. F., Knight D., Kiely C. J. and Hutchings G. J. (2011) Facile removal of stabilizer-ligands from supported gold nanoparticles. Nature Chemistry, 3: 551-6.
[8] Niu Z. and Li Y. (2014) Removal and Utilization of Capping Agents in Nanocatalysis. Chemistry of Materials, 26: 72-83.
[9] Wang Z. L., Petroski J. M., Green T. C. and El-Sayed M. A. (1998) Shape Transformation and
Surface Melting of Cubic and Tetrahedral Platinum Nanocrystals. The Journal of Physical Chemistry B, 102: 6145-51.

[10] Crespo-Quesada M., Andanson J. M., Yarulin A., Lim B., Xia Y. N. and Kiwi-Minsker L. (2011) UV-Ozone Cleaning of Supported Poly(vinylpyrrolidone)-Stabilized Palladium Nanocubes: Effect of Stabilizer Removal on Morphology and Catalytic Behavior. Langmuir, 27: 7909-16.

[11] Baker L. R., Kennedy G., Krier J. M., Van Sproonsen M., Onorato R. M. and Somorjai G. A. (2012) The Role of an Organic Cap in Nanoparticle Catalysis: Reversible Restructuring of Carbonaceous Material Controls Catalytic Activity of Platinum Nanoparticles for Ethylene Hydrogenation and Methanol Oxidation. Catalysis Letters, 142: 1286-94.

[12] Solla-Gullón J., Montiel V., Aldaz A. and Clavilier J. (2000) Electrochemical characterisation of platinum nanoparticles prepared by microemulsion: how to clean them without loss of crystalline surface structure. Journal of Electroanalytical Chemistry, 491: 69-77.

[13] Inaba M., Ando M., Hatanaka A., Nomoto A., Matsuzawa K., Tasaka A., Kinumoto T., Iriyama Y. and Ogumi Z. (2006) Controlled growth and shape formation of platinum nanoparticles and their electrochemical properties. Electrochimica Acta, 52: 1632-8.

[14] Gong K., Vukmirovic M. B., Ma C., Zhu Y. and Adzic R. R. (2011) Synthesis and catalytic activity of Pt monolayer on Pd tetrahedral nanocrystals with CO-adsorption-induced removal of surfactants. Journal of Electroanalytical Chemistry, 662: 213-8.

[15] Song H., Kim F., Connor S., Somorjai G. A. and Yang P. (2005) Pt Nanocrystals: Shape Control and Langmuir−Blodgett Monolayer Formation. The Journal of Physical Chemistry B, 109: 188-93.

[16] Han S.-B., Song Y.-J., Lee J.-M., Kim J.-Y. and Park K.-W. (2008) Platinum nanocube catalysts for methanol and ethanol electrooxidation. Electrochemistry Communications, 10: 1044-7.

[17] Rodes A., Zamakhchari M. A., El Achi K. and Clavilier J. (1991) Electrochemical behaviour of Pt(100) in various acidic media: Part I. On a new voltammetric profile of Pt(100) in perchloric acid and effects of surface defects. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 305: 115-29.

[18] Martinez-Rodriguez R. A., Vidal-Iglesias F. J., Solla-Gullon J., Cabrera C. R. and Feliu J. M. (2014) Synthesis of Pt Nanoparticles in Water-in-Oil Microemulsion: Effect of HCl on Their Surface Structure. Journal of the American Chemical Society, 136: 1280-3.

[19] Berlin E., Garbarino S., Guay D., Solla-Gullon J., Vidal-Iglesias F. J. and Feliu J. M. (2013) Electrodeposited platinum thin films with preferential (100) orientation: Characterization and electrocatalytic properties for ammonia and formic acid oxidation. Journal of Power Sources, 225: 323-9.

[20] Liu J., Fan X., Liu X., Song Z., Deng Y., Han X., Hu W. and Zhong C. (2017) Synthesis of Cubic-Shaped Pt Particles with (100) Preferential Orientation by a Quick, One-Step and Clean Electrochemical Method. Acs Applied Materials & Interfaces, 9: 18856-64.

[21] Serrano-Ruiz J. C., Lopez-Cudero A., Solla-Gullon J., Sepulveda-Escribano A., Aldaz A. and Rodriguez-Reinoso F. (2008) Hydrogenation of alpha, beta unsaturated aldehydes over polycrystalline, (111) and (100) preferentially oriented Pt nanoparticles supported on carbon. Journal of Catalysis, 253: 159-66.

[22] Herrero E., Franaszczuk K. and Wieckowski A. (1994) Electrochemistry of Methanol at Low Index Crystal Planes of Platinum: An Integrated Voltammetric and Chronoamperometric Study. The Journal of Physical Chemistry, 98: 5074-83.

[23] Lu L. L., Yin G. P., Wang Z. B. and Gao Y. Z. (2009) Electro-oxidation of dimethyl ether on platinum nanocubes with preferential \{100\} surfaces. Electrochemistry Communications, 11: 1596-8.

[24] Neurock M., Janik M. and Wieckowski A. (2009) A first principles comparison of the mechanism and site requirements for the electrocatalytic oxidation of methanol and formic acid over Pt. Faraday Discussions, 140: 363-78.

[25] Safo I. A. and Oezaslan M. (2017) Electrochemical Cleaning of Polyvinylpyrrolidone-capped Pt
Nanocubes for the Oxygen Reduction Reaction. Electrochimica Acta, 241: 544-52.

[26] Housmans T. H. M. and Koper M. T. M. (2003) Methanol Oxidation on Stepped Pt[n(111) × (110)] Electrodes: A Chronoamperometric Study. The Journal of Physical Chemistry B, 107: 8557-67.

[27] Solla-Gullon J., Vidal-Iglesias F. J., Lopez-Cudero A., Garnier E., Feliu J. M. and Aldaza A. (2008) Shape-dependent electrocatalysis: methanol and formic acid electrooxidation on preferentially oriented Pt nanoparticles. Physical Chemistry Chemical Physics, 10: 3689-98.

[28] Markarian M. Z., El Harakeh M. and Halaoui L. I. (2005) Adsorption of Atomic Hydrogen at a Nanostructured Electrode of Polyacrylate-Capped Pt Nanoparticles in Polyelectrolyte. The Journal of Physical Chemistry B, 109: 11616-21.

[29] Narayanan R. and El-Sayed M. A. (2005) Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Nanoparticle Shape Dependence and Stability. The Journal of Physical Chemistry B, 109: 12663-76.

[30] Nguyen Viet L., Ohtaki M., Nogami M. and Tong Duy H. (2011) Effects of heat treatment and poly(vinylpyrrolidone) (PVP) polymer on electrocatalytic activity of polyhedral Pt nanoparticles towards their methanol oxidation. Colloid and Polymer Science, 289: 1373-86.

[31] Solla-Gullon J., Rodriguez P., Herrero E., Aldaz A. and Feliu J. M. (2008) Surface characterization of platinum electrodes. Physical Chemistry Chemical Physics, 10: 1359-73.

[32] Sheng T., Tian N., Zhou Z.-Y., Lin W.-F. and Sun S.-G. (2017) Designing Pt-Based Electrocatalysts with High Surface Energy. Acs Energy Letters, 2: 1892-900.