



A simple electrochemical method for conversion of Pt wires to Pt concave icosahedra and nanocubes on carbon paper for electrocatalytic hydrogen evolution

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ABSTRACT In the controlled synthesis of noble metal nanostructures using wet-chemical methods, normally, metal salts/complexes are used as precursors, and surfactants/ligands are used to tune/stabilize the morphology of nanostructures. Here, we develop a facile electrochemical method to directly convert Pt wires to Pt concave icosahedra and nanocubes on carbon paper through the linear sweep voltammetry in a classic three-electrode electrochemical cell. The Pt wire, carbon paper and Ag/AgCl (3 mol L⁻¹ KCl) are used as the counter, working and reference electrodes, respectively. Impressively, the formed Pt nanostructures exhibit better electrocatalytic activity towards the hydrogen evolution compared to the commercial Pt/C catalyst. This work provides a simple and effective way for direct conversion of Pt wires into well-defined Pt nanocrystals with clean surface. We believe it can also be used for preparation of other metal nanocrystals, such as Au and Pd, from their bulk materials, which could exhibit various promising applications.

Keywords: noble metals, electrochemical conversion, concave nanostructures, electrocatalysis, hydrogen evolution

INTRODUCTION

Noble metals including Pt have been widely used for energy storage and conversion because of their excellent electrocatalytic activity towards the hydrogen evolution, and the oxygen reduction and evolution [1–7]. Due to the scarcity and high cost of noble metals, improvement of their utilization efficiency becomes extremely important. The catalytic performance of noble metal nanocrystals is highly dependent on their size, shape, composition, crystal facet, crystal phase, etc. Besides the recently de-

veloped crystal-phase controlled synthesis of noble metal nanocrystals [8–13], lots of efforts have been devoted into the shape-controlled synthesis of noble metal nanostructures with high-index facets [14–22]. However, most of the reported noble metal nanostructures with unique morphologies are prepared *via* the traditional wet-chemical methods in which metal salts or complexes are used as precursors, and surfactants or ligands are used to tune/stabilize their morphologies [23–27]. Until now, to the best of our knowledge, there is no report on direct preparation of noble metal nanocrystals with controlled morphologies and clean surfaces in solution from their bulk materials.

As known, electrochemical synthesis is one of the simple and efficient methods for preparing noble metal nanostructures [28]. In order to control the morphology of noble metal nanostructures using the electrochemical method, anodic aluminum oxide membranes or mesoporous silicon templates are normally used [29–32]. However, further process is required to remove these templates in order to purify noble metal nanomaterials used for various applications including electrocatalysis. Recently, Sun and co-workers [14,17,33–35] developed a square-wave potential based method to directly synthesize Pt and Pd polyhedra with high-index facets on glassy carbon electrode (GCE) using noble metal salts, i.e., K₂PtCl₆ and PdCl₂, respectively, as precursors.

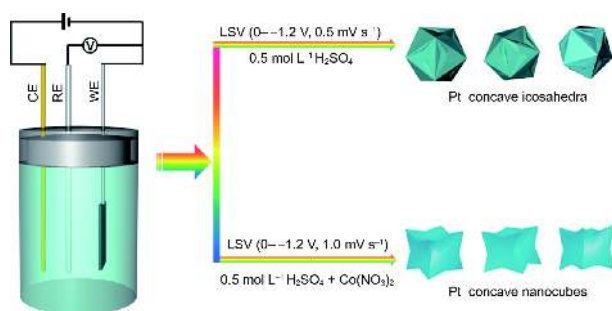
In this study, different from previously reported methods, we develop a facile electrochemical method for preparation of Pt concave icosahedra and nanocubes from Pt wire. As shown in Scheme 1, the electrochemical synthesis of Pt concave icosahedra and nanocubes can be

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Scheme 1 Schematic illustration of electrochemical setup for conversion of Pt wire into Pt concave icosahedra and nanocubes on carbon paper. CE: Pt wire; RE: Ag/AgCl (3 mol L⁻¹ KCl); WE: carbon paper.

achieved in a three-electrode electrochemical cell with carbon paper, Ag/AgCl (3 mol L⁻¹ KCl) and Pt wire as working electrode (WE), reference electrode (RE) and counter electrode (CE), respectively. Linear sweep voltammetry (LSV) scanning was carried out to directly convert the Pt wire into Pt concave icosahedra on carbon paper in 0.5 mol L⁻¹ H₂SO₄ aqueous solution. When cobalt nitrate was added in the aforementioned electrochemical synthesis solution, Pt concave nanocubes were obtained. Note that no surfactants or ligands were used in the aforementioned reactions. Therefore, the surface of obtained Pt nanostructures is clean. As a proof-of-concept application, the Pt concave icosahedra and nanocubes on carbon paper were used as electrocatalysts for the hydrogen evolution reaction (HER), which exhibited higher electrocatalytic activity in 0.5 mol L⁻¹ H₂SO₄ aqueous solution compared to the commercial Pt/C catalyst.

EXPERIMENTAL SECTION

Materials

Pt wires were purchased from the CH Instruments Ins. HClO₄, H₂SO₄ and Co(NO₃)₂·6H₂O were purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). Milli-Q water (Millipore, 18.2 MΩ cm) was used in all experiments.

Preparation of Pt concave icosahedra and nanocubes from Pt wires

Pt concave icosahedra were prepared in 10.0 mL of 0.5 mol L⁻¹ H₂SO₄ solution by repeated LSV scanning (25 times) from 0 to -1.2 V (*vs.* Ag/AgCl (3 mol L⁻¹ KCl)) at scan rate of 0.5 mV s⁻¹ using a three-electrode electrochemical cell with carbon paper as the WE, Ag/AgCl (3 mol L⁻¹ KCl) as the RE, and Pt wire as the CE. Pt concave nanocubes were prepared on carbon paper by

repeated LSV scanning (25 times) from 0 to -1.2 V (*vs.* Ag/AgCl (3 mol L⁻¹ KCl)) at scan rate of 1.0 mV s⁻¹ after adding 100 μL of cobalt nitrate (3 mmol L⁻¹) into the aforementioned 10 mL of 0.5 mol L⁻¹ H₂SO₄ aqueous solution.

Electrocatalytic hydrogen evolution of Pt concave icosahedra and nanocubes

Pt concave icosahedra or Pt concave nanocubes on carbon paper were directly used as the WE to evaluate their electrocatalytic activity for hydrogen evolution reaction (HER). The amount of Pt of the prepared Pt concave icosahedra and nanocubes was measured by the inductive coupled plasma-optical emission spectroscopy (ICP-OES). Electrochemical active surface areas (ECSAs) of Pt concave icosahedra and nanocubes on carbon paper were evaluated by cyclic voltammetry (CV) in N₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution at scan rate of 50 mV s⁻¹. ECSA = Q_H/(m×210), where Q_H (μC) is the charge of hydrogen absorption on catalysts, 210 (μC cm⁻²) is the charge associated with monolayer adsorption of hydrogen on the surface of Pt, and *m* (g) is the loading amount of Pt per cm² geometric area of electrode. HER measurements were carried out in H₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution by LSV method at scan rate of 5 mV s⁻¹ using Ag/AgCl (3 mol L⁻¹ KCl) and graphite rod as RE and CE, respectively. As a comparison, the commercial Pt/C suspension with the same amount of Pt loading as Pt concave icosahedra or Pt concave nanocubes was dropped onto carbon paper for CV and LSV measurements. The Ag/AgCl (3 mol L⁻¹ KCl) electrode was calibrated with respect to the reversible hydrogen electrode (RHE) in the H₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution. As shown in Fig. S1, *E* (*vs.* RHE) = *E* (*vs.* Ag/AgCl (3 mol L⁻¹ KCl)) + 0.246 V.

Characterization

Pt concave icosahedra and nanocubes on carbon paper were directly used for scanning electron microscopy (SEM, JSM-7600F, JEOL). Samples for transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEOL JEM-2100F) characterizations were prepared by sonicating carbon paper-supported Pt concave icosahedra or nanocubes in ethanol and then dropping the formed Pt concave icosahedron or nanocube ethanol suspension on copper grids, which were dried at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on a XPS spectrometer (QUANTUM 2000, Physical electronics,

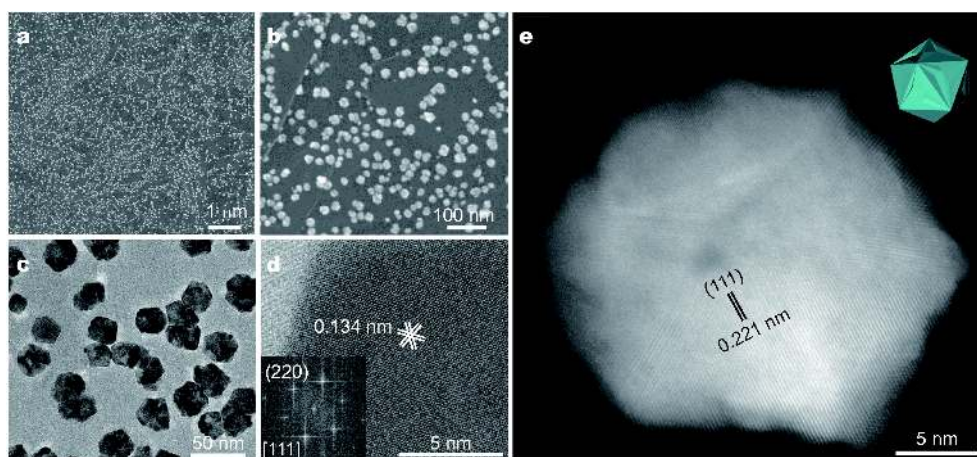


Figure 1 (a, b) SEM images of the formed Pt concave icosahedra on carbon paper. (c) TEM and (d) HRTEM images of the formed Pt concave icosahedra. Inset: The corresponding fast fourier transform (FFT) pattern of the Pt concave icosahedron in (d). (e) HAADF-STEM image taken from a typical Pt concave icosahedron along a five-fold symmetry axis. Inset: 3D model of a Pt concave icosahedron.

USA) using a monochromatic Al K α as the X-ray source. The binding energies were calibrated by the C 1s peak at 284.6 eV. ICP-OES was performed on a Dual-view Optima 5300 DV ICP-OES system to determine the amount of Pt element of the prepared Pt concave icosahedra and nanocubes on carbon paper.

RESULTS AND DISCUSSION

As shown in Scheme 1, Pt concave icosahedra were formed on carbon paper through the repeated LSV scanning (25 times) from 0 to -1.2 V (*vs.* Ag/AgCl (3 mol L $^{-1}$ KCl)) at scan rate of 0.5 mV s $^{-1}$ in 10 mL of 0.5 mol L $^{-1}$ H $_2$ SO $_4$ aqueous solution. The obtained Pt concave icosahedra were characterized by SEM, TEM, HRTEM and XPS. As shown in Fig. 1a, b, most of Pt concave icosahedra are highly dispersed on carbon paper with the size of 21.5 ± 7.9 nm (Fig. S2 in Supplementary information). TEM image (Fig. 1c) shows the concave icosahedral shape of Pt nanocrystals. HRTEM image (Fig. 1d) of a single Pt concave polyhedron displays the lattice fringes with interplanar spacing of about 0.134 nm along the [111] zone axis (Fig. 1d, inset), corresponding to the (220) plane of face-centered-cubic (fcc) Pt [36]. The characteristic five-fold symmetry axis of Pt concave icosahedron with the exposed (111) plane is observed from a high-angle annular dark-field scanning TEM (HAADF-STEM) image (Fig. 1e), which matches well with the three-dimensional (3D) model of icosahedron (inset in Fig. 1e) [37–41]. The XPS survey spectrum of Pt concave icosahedra (Fig. S3a) shows the characteristic peak of Pt at 68–77 eV. High-resolution Pt 4f XPS spectrum of Pt

concave icosahedra (Fig. S3b) shows two peaks at 71.2 and 74.4 eV, corresponding to Pt 4f $_{7/2}$ and Pt 4f $_{5/2}$ of zero-valent Pt, respectively [42].

Interestingly, after adding 100 μ L of cobalt nitrate (3 mmol L $^{-1}$) into the aforementioned 10 mL of 0.5 mol L $^{-1}$ H $_2$ SO $_4$ aqueous solution, Pt concave nanocubes were formed on carbon paper by the repeated LSV scanning (25 times) from 0 to -1.2 V (*vs.* Ag/AgCl (3 mol L $^{-1}$ KCl)) at scan rate of 1.0 mV s $^{-1}$. As shown in Fig. 2a, b, well-dispersed Pt concave nanocubes with the size of 22.6 ± 7.4 nm (Fig. S4) can be observed. TEM image (Fig. 2c) displays the shape of Pt concave nanocubes. HRTEM image (Fig. 2d) of a single Pt concave nanocube presents the lattice fringes with interplanar spacing of 0.196 nm along the [100] zone axis (Fig. 2d, inset), corresponding to the (200) plane of fcc Pt [15]. A HAADF-STEM image shows the shape of typical Pt concave nanocube with the exposed (200) plane (Fig. 2e), matching very well with its 3D model (inset in Fig. 2e). Moreover, the XPS survey spectrum of Pt concave nanocubes (Fig. S5a) shows the characteristic peak of Pt, and no peak ascribed to Co is observed, indicating the formation of pure Pt nanostructures. In the high-resolution Pt 4f XPS spectrum of Pt concave nanocubes (Fig. S5b), two peaks at 71.2 and 74.5 eV, assignable to Pt 4f $_{7/2}$ and Pt 4f $_{5/2}$ of zero-valent Pt, respectively, are observed [42].

Noble metal concave nanostructures have been proven to be highly active catalysts for electrocatalysis, such as oxygen reduction reaction [18], electrochemical oxidation of ethanol [43] and formic acid [16], and HER [44]. In this work, as a proof-of-concept application, Pt concave

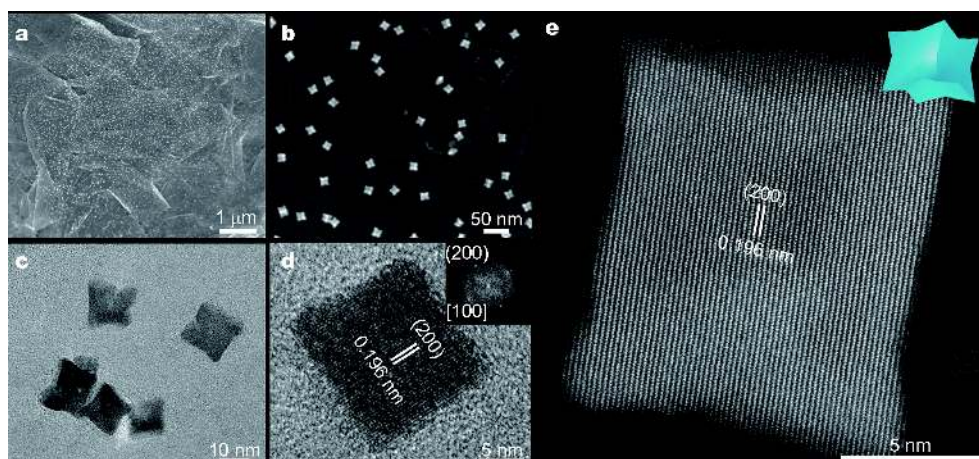


Figure 2 (a, b) SEM images of the formed Pt concave nanocubes on carbon paper. (c) TEM and (d) HRTEM images of the formed Pt concave nanocubes. Inset: The corresponding FFT pattern of Pt concave nanocube in (d). (e) HAADF-STEM image of a typical Pt concave nanocube. Inset: 3D model of a Pt concave nanocube.

icosahedra and nanocubes on carbon paper are used as highly efficient electrocatalysts for hydrogen evolution due to their exposed active facets and clean surface. The commercial Pt/C catalyst is used for comparison. ECSAs of Pt/C, and Pt concave icosahedra and nanocubes were evaluated by their CV curves in N_2 -saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ aqueous solution (Fig. 3a). As shown in Fig. 3b, the ECSAs of Pt concave icosahedra ($107.5 \text{ m}^2 \text{ g}^{-1}$) and Pt concave nanocubes ($134.9 \text{ m}^2 \text{ g}^{-1}$) are much greater than that of Pt/C ($34.1 \text{ m}^2 \text{ g}^{-1}$). Polarization curves of Pt/C, Pt concave icosahedra and nanocubes are shown in Fig. 3c, indicating that Pt concave icosahedra and nanocubes give better electrocatalytic activity towards hydrogen evolution compared to the commercial Pt/C catalyst. As shown in Fig. 3d, the mass activities of Pt concave icosahedra ($0.81 \text{ mA } \mu\text{g}^{-1}_{\text{Pt}}$) and Pt concave nanocubes ($1.05 \text{ mA } \mu\text{g}^{-1}_{\text{Pt}}$) for electrochemical hydrogen evolution at working potential of -0.05 V (vs. RHE) are about 2.3 and 2.9 times that of commercial Pt/C catalyst ($0.36 \text{ mA } \mu\text{g}^{-1}_{\text{Pt}}$), respectively. All the aforementioned results confirm that the Pt concave icosahedra and nanocubes synthesized by our electrochemical method have higher electrocatalytic activities for HER compared to the commercial Pt/C catalyst. Furthermore, the durability tests show that the commercial Pt/C showed 9.2% decrease of current density for HER at -0.1 V (vs. RHE) after 20,000 potential cycles from 0.248 to -0.152 V in H_2 -saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ aqueous solution (Fig. S6a), while the polarization curves of Pt concave icosahedra and nanocubes for HER display no obvious change after 20,000 potential cycles (Fig. S6b, c), indicating the better electrocatalytic stabilities of Pt

concave icosahedra and nanocubes compared to the commercial Pt/C.

The superior electrocatalytic activities of Pt concave icosahedra and nanocubes for HER might arise from their concave and stepped surface morphologies, exposed high-active facets, no surfactants or ligands on the Pt surface, and good contact between the prepared Pt nanostructures and carbon paper. First, Pt concave icosahedra and nanocubes present atomic steps and kinks with low coordination numbers, which have been proved to be beneficial for electrocatalysis such as hydrogen adsorption and evolution [45–47]. Second, small Pt nanoparticles on the commercial Pt/C catalyst are usually enclosed by (200) and dominant (111) facets (Fig. S7) [48], while the Pt concave icosahedra and nanocubes possess high-index facets exposed on their surface [45,47], which are more active for hydrogen evolution than the (111) facet [49,50], resulting in the better electrocatalytic HER activity of Pt concave icosahedra and nanocubes compared to the commercial Pt/C. Third, the directly electrodeposited Pt concave icosahedra and nanocubes on carbon paper are free of surfactants and ligands. Their clean surfaces and good contact with carbon paper result in the easier hydrogen adsorption and electron transfer in the process of HER [14,33].

CONCLUSIONS

In conclusion, a simple electrochemical method has been developed for conversion of Pt wires to Pt concave icosahedra and nanocubes on carbon paper in a classic three-electrode electrochemical system, in which Pt wire,

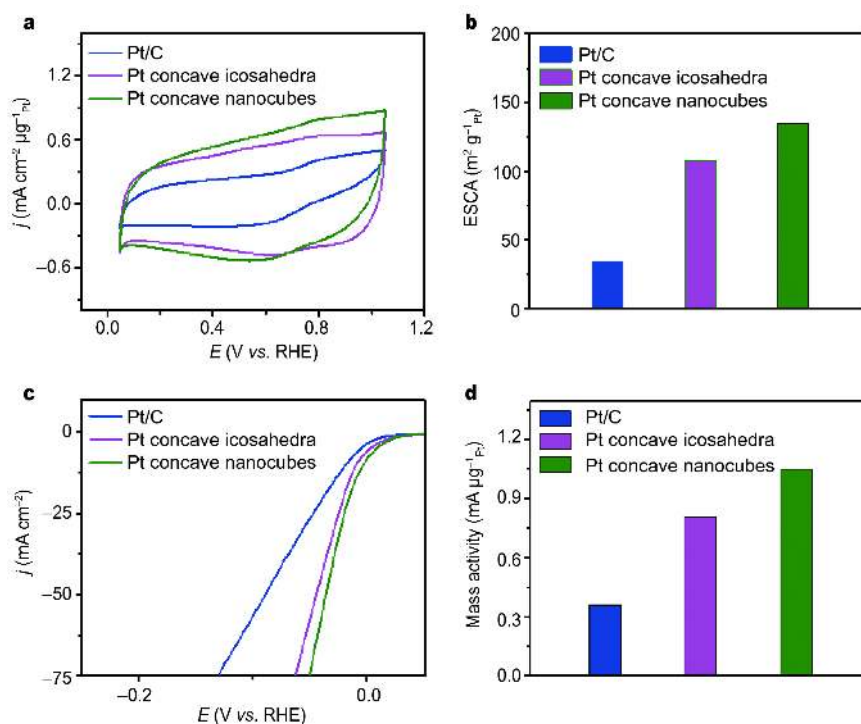


Figure 3 (a) Cyclic voltammograms of Pt/C, and Pt concave icosahedra and nanocubes on carbon paper in N₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution at scan rate of 50 mV s⁻¹. (b) ECSAs of Pt/C, and Pt concave icosahedra and nanocubes on carbon paper. (c) Polarization curves of Pt/C, and Pt concave icosahedra and nanocubes for electrocatalytic hydrogen evolution in H₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution. (d) The mass activities of Pt/C, and Pt concave icosahedra and nanocubes for electrocatalytic hydrogen evolution at working potential of -0.05 V (vs. RHE).

carbon paper and Ag/AgCl (3 mol L⁻¹ KCl) are used as the counter, working and reference electrodes, respectively. The surface of as-prepared high-active Pt concave icosahedra and nanocubes is clean since no surfactants or ligands were used in the synthesis process. The prepared Pt concave icosahedra and nanocubes on carbon paper used as electrocatalysts for HER show better electrocatalytic activity in comparison with the commercial Pt/C catalyst. Our simple method provides a new and effective way to directly convert Pt wire into well-defined Pt nanocrystals for highly efficient electrocatalysis, which might be further used to prepare well-defined nanocrystals (unpublished results), such as Au, Pd, Rh, Ru and Cu, from their bulk metals for various applications.

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Author contributions All authors contributed to the discussion and preparation of the manuscript. The final version of the manuscript was approved by all authors.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting figures and calibration curve of Ag/AgCl (3 mol L⁻¹ KCl) reference electrode are available in the online version of the paper.



Zhimin Luo is currently a professor at Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications. He received his bachelor degree from Fujian Normal University in 2002 and completed his PhD in 2013 under the supervision of Prof. Lianhui Wang. He worked as a postdoctoral fellow in Prof. Hua Zhang's group in the School of Materials Science and Engineering at Nanyang Technological University in Singapore from 2013 to 2018. His research interests include the synthesis and applications of advanced catalysts such as two-dimensional metal dichalcogenides and noble metal nanostructures.



Hua Zhang obtained his bachelor and master degrees at Nanjing University in 1992 and 1995, respectively, and completed his PhD with Prof. Zhongfan Liu at Peking University in 1998. As a Postdoctoral Fellow, he joined Prof. Frans C. De Schryver's group at Katholieke Universiteit Leuven (Belgium) in 1999, and then moved to Prof. Chad A. Mirkin's group at Northwestern University in 2001. After he worked at NanoInk Inc. (USA) and Institute of Bioengineering and Nanotechnology (Singapore), he joined Nanyang Technological University in July 2006. His current research interests focus on the (crystal-)phase engineering of nanomaterials and controlled epitaxial growth of heterostructures, including the synthesis of ultrathin two-dimensional nanomaterials (e.g. metal nanosheets, graphene, metal dichalcogenides, metal-organic frameworks, covalent organic frameworks, etc.), novel metallic and semiconducting nanomaterials, novel amorphous nanomaterials and their hybrid composites, for various applications such as catalysis, clean energy, (opto-)electronic devices, nano- and biosensors, and water remediation.

电化学方法把铂丝转化到碳布上形成铂二十面体和纳米立方体并用于电催化产氢

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摘要 湿化学法可控合成贵金属纳米结构通常需要金属盐或金属配合物作为前体, 并利用表面活性剂和配体来调节和稳定纳米结构的形貌. 本文通过一种简单的电化学方法(线性扫描伏安法), 在三电极体系中直接把铂线转化到碳布表面形成铂二十面体和纳米立方体. 在三电极体系中, 铂线、碳布和Ag/AgCl(3 mol L⁻¹ KCl)分别作为对电极、工作电极和参比电极. 与商业Pt/C催化剂相比, 制备的铂二十面体和纳米立方体展现出优越的电催化活性. 该方法简单、有效, 可拓展到其他贵金属纳米结构的合成和应用研究. 如通过这种电化学方法直接将Au、Pd等块体材料转化成具有各种潜在应用的Au、Pd等纳米结构.