



Platinum nanocuboids supported on reduced graphene oxide as efficient electrocatalyst for the hydrogen evolution reaction



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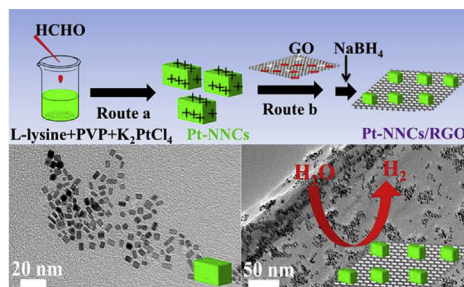
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HIGHLIGHTS

- Pt nanocuboids (Pt-CNSs) are achieved through L-lysine-assisted hydrothermal reduction route.
- Pt-CNSs can self-assemble on graphene oxide (GO) surface to generate Pt-CNSs/GO.
- Pt-CNSs/GO can be reduced to generate Pt-CNSs/RGO nanohybrids.
- Pt-CNSs/RGO display excellent electrocatalytic performance for hydrogen evolution reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Active and stable electrocatalysts for the hydrogen evolution reaction (HER) are highly desirable for hydrogen production. Herein, the cuboid-like platinum nanocrystals (Pt-CNSs) are achieved through a facile L-lysine-assisted hydrothermal reduction method. Then, reduced graphene oxide (RGO) supported Pt-CNSs (Pt-CNSs/RGO) nanohybrids are obtained through the self-assembly of Pt-CNSs on graphene oxide (GO) and followed by NaBH₄ reduction. The resulting Pt-CNSs/RGO nanohybrids are characterized by transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, thermogravimetric analysis and Raman, showing that the well-defined Pt-CNSs with 5.8 nm length and 3.0 nm width are uniformly and firmly attached on the RGO surface. Electrochemical tests demonstrate that Pt-CNSs/RGO nanohybrids have superior electrocatalytic activity and stability for the HER than pure Pt-CNSs, demonstrating RGO is an excellent cathode support materials for Pt-CNSs. Meanwhile, the present results indicate that the as-prepared Pt-CNSs/RGO nanohybrids have great potential application in HER.

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1. Introduction

With the rapid increase of energy demand and the depletion of fossil fuel reserves, research on new environment-friendly energy sources and their practical applications has drawn great attention in the past decades [1–3]. Among the proposed clean energy

sources, hydrogen has been considered as one of the most promising power vectors because of its high energy density, high efficiency, and low pollutant emission [4–12], which was powered by renewable energy sources, such as water- or solar-based technologies. The hydrogen evolution reaction (HER), a clean and regenerative approach to hydrogen production through the splitting of water with the aid of specialized photocatalysts or electrocatalysts, has attracted widespread attention for this purpose [4–12].

Platinum (Pt) is considered as the archetypal base metal for the electrocatalysis of HER in acid media [13–15]. When Pt is used

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as an electrocatalyst, however, the limited reserve in nature, high-cost, and growing consumption in the automobile industry hinder its commercial use. To effectively minimize the use of precious Pt, decrease the aggregation of Pt nanocrystals, and improve the electrocatalytic activity of Pt nanocrystals, one of the efficient strategies is to load Pt nanocrystals on various carbon nanomaterials, such as carbon black, carbon nanotubes, carbon nanofibers and graphene, etc.

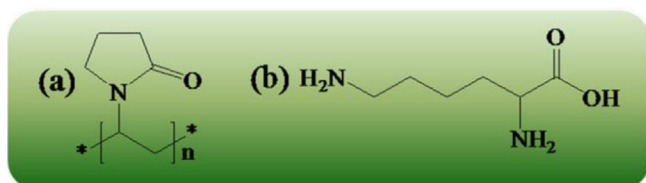
Compared with other carbon nanomaterials, two-dimensional graphene has been considered as an ideal support due to its exceptional properties, including the quantum hall effect, high carrier mobility, good optical transparency, high surface area, excellent thermal conductivity and electric conductivity, and strong mechanical strength [16,17]. Based on non-covalent interactions (i.e., the electrostatic interaction or van der Waals interaction), the self-assembly technique has been successfully developed to fabricate graphene-supported noble metal nanohybrids [18–24], which can effectively anchor metal nanocrystals with the intended shape on the graphene surface. Although the self-assembly route is a highly versatile and powerful strategy for synthesis of the graphene-based nanohybrids, it is difficult to attach metal nanocrystals on the graphene substrates firmly. Thus, it is crucial to select a suitable chemical material as an adhesion agent. For instance, Niu's group demonstrated that citrate protected negatively-charged AuPd hollow nanoparticles could make efficient the self-assembly on the surface of positively-charged reduced graphene oxide (RGO) [24].

Proteins are complex amphiphilic biopolymers, featuring hydrophobic and hydrophilic patches on their surfaces, which makes them well-known for their adhesiveness to graphene oxide (GO) surfaces, generating an extremely versatile and highly efficient self-assembly platform to construct graphene/noble metal nanohybrids [25,26]. For example, Qu's group synthesized GO/Au nanohybrids through the self-assembly between GO and protein-stabilized Au nanoclusters [26]. In this work, L-Lysine, as a basic structural unit of protein, was used to synthesize positively-charged cuboid-like Pt nanocrystals (Pt-CNSs), and then glued them on the negatively-charged GO surface via electrostatic interaction, accompanied with a followed chemical reduction. The as-prepared Pt-CNSs/RGO nanohybrids exhibited excellent electrocatalytic activity and stability for HER, indicating that the Pt-CNSs/RGO nanohybrids might serve as an ideal candidate in regenerative H₂–O₂ fuel cells.

2. Experimental

2.1. Reagents and chemicals

Poly(vinyl pyrrolidone) (PVP, MW = 30,000, Scheme 1a), L-Lysine (Scheme 1b), potassium tetrachloroplatinate(II) (K₂PtCl₄) and formaldehyde solution (HCHO, 40%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Graphene oxide (GO) was purchased from Nanjing XFANO Materials TECH Co., Ltd. Other reagents were of analytical reagent grade and used without further purification.



Scheme 1. Molecule structures of (a) PVP and (b) L-Lysine.

2.2. Preparation of Pt-CNSs/RGO nanohybrids

The overall synthetic route of Pt-CNSs/RGO nanohybrids is illustrated in Scheme 2. Firstly, 1.0 mL of 0.05 M K₂PtCl₄ solution, 0.5 mL of 0.5 M L-Lysine, and 50 mg PVP were added into 8.0 mL deionized water. After adjusting the solution's pH to 9.0, 1.0 mL of HCHO solution was rapidly added into the mixture solution, and heated at 160 °C for 4 h to achieve Pt-CNSs [27], as shown in route a. After being cooled to room temperature, 9.75 mg of GO sheets were added into the above Pt–CNS's suspension with ultrasonic treatment for 0.5 h and constant stirring for 2 h at 30 °C to generate Pt-CNSs/GO nanohybrids, as shown in route b. The self-assembly of Pt-CNSs on GO surface is ascribed to the electrostatic force and van der Waals force between Pt-CNSs and GO sheets: (i) L-lysine-stabilized Pt-CNSs (zeta potential of the L-lysine-stabilized Pt-CNSs aqueous solution is at pH 7.0 + 48 mV) can anchor easily onto the GO sheets (zeta potential of the GO aqueous solution is –48 mV at pH 7.0) through the electrostatic interaction [26]; (ii) The van der Waals force interaction between L-lysine and GO sheets facilitates the anchorage of Pt-CNSs on GO surface [28]. Afterwards, 4 mL of NaBH₄ solution (1 mg mL⁻¹) was dropwise added into Pt-CNSs/GO nanohybrids solution. Finally, the obtained Pt-CNSs/RGO nanohybrids were separated by centrifugation, washed several times with water, and then dried in a vacuum dryer.

2.3. Physical characterizations

Standard and high resolution transmission electron microscopy (TEM and HRTEM) were carried out on a JEOL JEM-2100F transmission electron microscopy. Scanning electron microscopy (SEM) images were taken on a JSM-2010 microscopy. X-Ray diffraction (XRD) was performed on a D/max-rC X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo ESCALAB 250 with an Al anode. The composition of the catalysts was determined by the energy dispersive spectrum (EDS) technique and inductively coupled plasma-atomic emission spectrometer (ICP-AES, X Series 2, Thermo Scientific USA). Thermogravimetric analysis (TGA) was performed on a Perkin Elmer thermogravimetric analyzer under an air atmosphere over a temperature range of 20–1000 °C with a ramp rate of 10 °C min⁻¹. Raman spectra were recorded on a Labram HR 800 UV Raman spectrometer. The zeta potential measurement was performed on a Malvern Zetasizer Nano ZS90 analyzer at room temperature.

2.4. Electrochemical measurements

All electrochemical experiments were performed on CHI 660 C electrochemical analyzer at 30 °C. A standard three-electrode system was used, which consisted of a Pt wire as the auxiliary electrode, a saturated calomel reference electrode (SCE), and a catalyst modified glassy carbon electrode as the working electrode. All potentials in this study were reported with respect to the reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) and durability tests were conducted in a Gamry's Rotating Disk Electrode (RDE710) in order to avoid the interference produced by hydrogen bubbles [29,30].

Before the preparation of working electrode, Pt-CNSs/RGO nanohybrids were irradiated with the UV irradiation (185 and 254 nm) in air for 4 h to remove the capping agents by the photosensitized oxidation process [31–34]. The catalyst ink was prepared by an ultrasonic mixture of 10 mg catalyst and 5 mL H₂O for 30 min, and 6 μL of the resulting suspension was drop-cast onto the glassy carbon electrode with a diameter of 5 mm. After drying at room temperature, 3 μL of Nafion solution (5 wt. %) was covered on the modified electrode surface and allowed to dry again

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