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Polyallylamine-Rh nanosheet nanoassemblies – carbon nanotubes organic-inorganic nanohybrids: A electrocatalyst superior to Pt for the hydrogen evolution reaction

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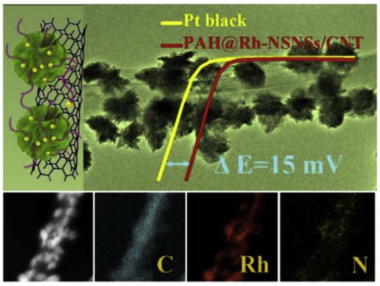
HIGHLIGHTS

- PAH@Rh-NSNSs/CNT are synthesized by a facile hydrothermal method.
- Polyallylamine molecules play an important role for the formation of nanosheets.
- PAH@Rh-NSNSs/CNT show the excellent HER activity in acidic media.
- PAH molecules act as proton carriers to enhance the HER activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Rationally tailoring the surface/interface structures of noble metal nanostructures emerges as a highly efficient method for improving their electrocatalytic activity, selectivity, and long-term stability. Recently, hydrogen evolution reaction is attracting more and more attention due to the energy crisis and environment pollution. Herein, we successfully synthesize polyallylamine-functionalized rhodium nanosheet nanoassemblies-carbon nanotube nanohybrids via a facile one-pot hydrothermal method. Three-dimensionally branched rhodium nanosheet nanoassemblies are consisted of two dimensionally atomically thick ultrathin rhodium nanosheets. The as-prepared polyallylamine-functionalized rhodium nanosheet nanoassemblies-carbon nanotube nanohybrids show the excellent electrocatalytic activity for the hydrogen evolution reaction in acidic media, with a low onset reduction potential of -1 mV, a small overpotential of 5 mV at 10 mA cm^{-2}, which is much superior to commercial platinum nanocrystals. Two dimensionally ultrathin morphology of rhodium nanosheet, particular rhodium-polyallylamine interface, and three-dimensionally networks induced by carbon nanotube are the key factors for the excellent hydrogen evolution reaction activity in acidic media.

1. Introduction

The clean and renewable energies have drawn great attention due to the shortage of energy and environmental crises. Hydrogen (H_2) has been identified as a highly promising alternatives for the traditional fossil fuels due to carbon-free, high energy density, and recyclability, but free H_2 does not exist naturally. For hydrogen production, electrochemical water splitting driven by renewable wind and solar energy

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is a green and efficient technology [1,2]. Due to the overpotential (η) in hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$), the suitable electrocatalysts are necessary for the high hydrogen production efficiency. So far, platinum (Pt) and Pt-based nanostructures are best electrocatalysts for the HER in acid media, which have near-zero η value and superior corrosion resistance [3–5]. Unfortunately, Pt metal suffers from the expensive cost and scarcity, which limits its large-scale application.

Till now, numerous efforts have been devoted to developing non-Pt electrocatalysts for the HER, including transition metals-based sulfides [6,7], carbides [8], phosphides [9], nitrides [10], selenides [11], and oxides [12,13], as well as various carbon nanomaterials [14–17]. However, in acidic media, the HER performance of these non-noble metal nanomaterials still lacks the enough competitive power relative to Pt-based electrocatalysts. This fact indicates the cost can't be the sole selection criterion for the electrocatalysts. Rhodium (Rh), one of the Pd-group Pt-group elements (Pt, Pd, and Rh), has physical/chemical properties similar to Pt. Very recently, rhodium (Rh) and Rh-based nanostructures have emerged as the promising non-Pt electrocatalysts for the HER due to their high activity, which may originates from the similar physical/chemical properties between Pt and Rh [18–21]. It is well known that the stability of electrocatalysts is very important for their practical applications. In particular, Rh metal has extreme resistivity for the various acids (including aqua regia) [22,23], which will import Rh-based electrocatalysts with excellent electrochemical stability in acidic electrolyte. Obviously, excellent electrochemical stability of Rh-based electrocatalysts can extend the working life of the water splitting equipment, which is favorable for the commercialization of the water splitting equipment. Although the Rh price abnormally exceeds Pt price at 2017 year due to unknown reason (Fig. S1), the high stability of Rh-based electrocatalysts will be a big advantage for the commercial applications in the water splitting equipment.

Apart from chemical composition, size, and morphology controls, tailoring the interfacial property of noble metal nanostructures with functional molecules is also an efficient strategy for improving their catalytic/electrocatlytic activity and selectivity [24–29]. For example, ethylenediamine functionalized ultrathin Pt nanowires show high selectivity for the hydrogenation of nitroaromatics due to the electronic effect induced by ethylenediamine modifications [24]; The cucurbit [6] uril functionalization imparts Pt nanocrystals with excellent anti-poisoning capability for the methanol oxidation reaction due to the strong interaction between cucurbit [6]uril molecule and CO-like intermediate [26]; The protic ionic liquid functionalized Pt_3Ni nanocrystals show improved catalytic activity for the oxygen electroreduction compared to Pt_3Ni nanocrystals due to the electronic and steric effects [27]. Although chemical functionalized Pt and Pd nanostructures reveal the wide applications in catalysis/electrocatalysis [24–29], the application of chemical functionalized Rh nanostructures in electrocatalysis has not yet been reported.

In this work, we developed a water-based one-pot route to synthesize polyallylamine-functionalized Rh nanosheet nanoassemblies-carbon nanotube (PAH@Rh-NSNSs/CNT) nanohybrids using polyallylamine hydrochloride (PAH) as a complexant and shape directing agent. The morphology, composition, and interfacial property of PAH@Rh-NSNSs/CNT nanohybrids were characterized by various physical techniques. When used as HER electrocatalyst in acidic media, PAH@Rh-NSNSs/CNT nanohybrids displayed enhanced electrocatalytic performance for the HER compared to commercial Pt nanocrystals from Johnson Matthey Corporation (Pt-JM NCs).

2. Experimental

2.1. Reagents and chemicals

Polyallylamine hydrochloride (PAH, Scheme S1, molecular weight: 5000) was purchased from Nitto Boseki Co. Ltd (Tokyo, Japan). Rhodium (III) chloride hydrate ($RhCl_3{\cdot}3H_2O$), formaldehyde solution (HCHO, 40%) were obtained from Aladdin Industrial Co. (Shanghai, China). The carboxylated carbon nanotube (CNT, outer diameter 110–170 nm) was purchased from Sigma-Aldrich (USA). Commercial Pt nanocrystals from Johnson Matthey Corporation (Pt-JM NCs) was obtained from Shanghai Hesen Electric Co. Ltd (Shanghai, China).

2.2. Synthesis of PAH@Rh-NSNSs/CNT nanohybrids

Typically, 5.0 mL of 0.05 M $RhCl_3$ and 15 mL of 0.5 M PAH were added into 45 mL of water to generate the soluble PAH–Rh^{III} complex by coordination [30]. After adjusting the solution pH to 7.0, 19.5 mg of CNT was dispersed in the PAH–Rh^{III}complex solution by ultrasonic treatment for 1 h. After addition of 1.3 mL of HCHO, the mixture was transferred to a 20 mL Teflon-lined stainless-steel autoclave, and was then heated at 120 °C for 6 h. After reaction, PAH@Rh-NSNSs/CNT nanohybrids were separated by centrifugation at 5000 rpm for 10 min, washed several times with water to remove the remaining reagents, and then dried at 60 °C for 5 h in a vacuum dryer.

For comparison, Rh nanoparticles-CNT nanohybrids (Rh-NPs/CNT) were synthesized in the absence of PAH under the same experimental conditions. PAH-functionalized Rh nanosheet nanoassemblies (Rh-NSNSs@PAH) were synthesized in the absence of CNT under the same experimental conditions. The irregular Rh nanocrystals (Rh-irNCs) were achieved in the absence of PAH and CNT under the same experimental conditions.

2.3. Electrochemical measurements

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) tests were performed on CHI 660 D electrochemical analyzer at 30 ± 1 °C. An electrocatalyst modified glassy carbon electrode (3 mm diameter), a carbon rod with 3 mm, and a saturated calomel electrode were used as working electrode, auxiliary electrode and reference electrode respectively. The area of glassy carbon electrode was calculated to be $0.0707\ cm^2$, which was used to determine the current density in LSV curves. All potentials in this study were referenced to the reversible hydrogen electrode (RHE), which was obtained using the following equation ($E_{RHE} = E_{SCE} + 0.059\ pH + 0.2412$). The electrocatalyst ink was obtained by mixing 10 mg of electrocatalyst and 5 mL water containing 25 μL of 5 wt % Nafion under strong sonication for 20 min. Then, 4 μL of $2\ mg\ mL^{-1}$ electrocatalys ink was carefully deposited on the surface of clean glassy carbon electrode and allowed to dry at room temperature. The metal loading on working electrode is ca. $\sim 52\ \mu g\ cm^{-2}$. The HER polarization curves were evaluated by sweeping the potential from 0.35 to −0.19 V at a scan rate of $5\ mV\ s^{-1}$ with 1000 rpm in N_2-saturated 0.5 M H_2SO_4 solution using a Gamry RDE710 rotating disk electrode with 95% iR drop compensation. The EIS tests were obtained from 0.02 ~ 100, 000 Hz at 0.06 V with a modulation amplitude of 10 mV.

2.4. Instruments

Scanning electron microscopy (SEM) images were taken on a model SU-8020 instrument. Standard and high resolution transmission electron microscopy (TEM and HRTEM) images, selected area electron diffraction (SAED), and energy-dispersive X-ray (EDS) maps were obtained from a TECNAI G2 F20 transmission electron microscopy. X-Ray diffraction (XRD) was performed on a DX-2700 X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on AXIS ULTRA spectrometer. The composition of sample was determined by the energy dispersive spectrum (EDS) technique. The surface charge measurement was investigated by Nano ZS90 zeta potential analyzer. Thermogravimetric analysis (TGA) was taken on a Q600 systems thermoanalyzer under air atmosphere. Atomic force