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Short communication

Ru-modified silicon nanowires as electrocatalysts for hydrogen evolution reaction

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ABSTRACT

Ruthenium nanoparticles modified on silicon nanowires (Ru/SiNWs) were prepared by directly reducing Ru ions with Si–H bonds. The composites with different contents of Ru (denoted as Ru/SiNW-x, x means the relative molar ratio of Ru to SiNW) were evaluated as electrocatalysts for the hydrogen evolution reaction (HER). Ru/SiNW-42.9 showed an excellent electrocatalytic activity in the oxygen-free 0.5 M H_2SO_4 medium. The Tafel slope of Ru/SiNW-42.9 was 81 mV/decade, indicating that its catalytic effect was even better than pure Ru particles. SiNWs modified with proper content of Ru may be a promising electrocatalyst for HER.

1. Introduction

In recent years, increasing interest has been paid to renewable energy sources because of energy crisis and environmental contaminant. Fossil fuels currently supply most of the energy needs. However their long-term resource utilization is unacceptable. Hydrogen as a fundamental energy source, primarily derived from water, can address issues of sustainability, environmental emissions, and energy security [1–3].

Electrochemical hydrogen evolution reaction (HER) [4] occupies a special position in hydrogen production. To achieve the best efficiency, the high-performance electrocatalysts play a key role in the HER. As is well-known, platinum group metal nanostructures, for example platinum and ruthenium nanoparticles, have been regarded as the most efficient catalysts [5,6].

During the fabrication process, introducing carriers is a crucial step to obtain high efficient catalysts due to the agglomeration tendency of nanoparticles. They may also provide vast surface area to accelerate charge transfer and reduce the usage amount of noble metals. The materials of carriers usually include graphene [6], polymer templates [7–9], carbon [10], alumina [11] and silica [12]. Nowadays, silicon nanowires (SiNWs), a widely used one-dimensional nanostructure, have attracted much attention as a new catalyst carrier [13].

SiNWs have been synthesized via various methods [14–17]. They are widely used in the experimental process because they offer a number of advantages such as high surface to volume ratio [18] and easy modification with numerous metal particles [19,20].

In this work, Ru nanoparticles were directly reduced and grown on SiNWs (Ru/SiNWs) at room temperature. The composites with different contents of Ru (denoted as Ru/SiNW-x, x means the relative molar ratio of Ru to SiNW) were employed as electrocatalysts for HER in acidic medium, where Ru nanoparticles worked as an active composition and SiNWs as the catalyst carrier. The Ru nanoparticles were grown in-situ on the surface of SiNWs, helping confine the particles' size and prevent agglomeration during the catalytic process. The electrochemical results showed that Ru/SiNW-49.2 exhibited excellent HER electrocatalytic performance with low overpotential and small Tafel slope, which are better than Ru/SiNW-5.8 and pure Ru particles.

2. Experimental

2.1. Synthesis of Ru nanoparticles modified on SiNWs

SiNWs obtained via the high temperature method [15] were etched with 5 mL 5% HF aqueous solution for 1 min to form Si–H bonds on their surface. The etched-SiNWs were rinsed with distilled water, and then immersed in different 10 mL concentrations of $RuCl_3$ aqueous solution with stirring for 30 min to form Ru/SiNW composites with different contents of Ru. Ru/SiNW-5.8 and Ru/SiNW-42.9 were picked up to investigate their catalysis to the HER. The content was evaluated by semi-quantitative calculation of X-ray diffraction (XRD). The as-prepared Ru/SiNW-42.9 was added to excessive 5% HF aqueous solution to etch the residual SiNWs to ultimately obtain pure Ru particles.

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2.2. Characterization

The phase and crystallography of samples were characterized by XRD (Philips X'pert PRO MPD diffractometer) equipped with Cu Kα radiation (λ = 0.15406 nm). The morphology of samples was examined by scanning electron microscopy (SEM, FEI-quanta 200 scanning electron microscope) equipped with EDAX, using Cu sheet as a substrate. Transmission electron microscope (TEM) image and high resolution TEM (HRTEM) image were recorded using a FEI Tecnai F20 transmission electron microscope with an accelerating voltage of 200 kV.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in a conventional three-electrode cell connected with a Princeton VersaSTAT4 electrochemistry workstation. A platinum plate with an area of 2 cm^2 was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode and a bare or modified glass carbon electrode (GCE) as the work electrode.

For a typical fabrication of the work electrode, 2 mg catalysts were dispersed in 1 mL of 5: 1 v/v water-isopropanol mixed solvent with 100 μL 0.5 wt.% Nafion solution, and ultrasonically stirred for at least 30 min to become homogeneous suspension. Then 10 μL of the suspension was loaded onto a GCE with diameter of 3 mm (loading ~ 0.257 mg/cm^2). Finally, the as-prepared catalyst film was dried at room temperature.

3. Results and discussion

The SEM image of high density SiNWs is shown in Fig. 1a. There is only Si and O elements in the EDS spectrum of SiNWs. Fig. 1b presents the SEM image of Ru/SiNW-42.9, where the nanoparticles are clearly observed. Meanwhile the signal of Ru element can be perceived in EDS spectrum, revealing the presence of Ru and Si elements. The SEM image of pure Ru particles is presented in Fig. 1c, showing the pure Ru particles without supporting of SiNWs. And the corresponding EDS spectrum just shows Ru element. All the copper peaks and carbon peaks in the EDS spectra come from the substrate of copper sheet and air, respectively.

The structure details of Ru/SiNW-42.9 are studied by TEM in Fig. 1d. SiNWs are ca. 50 nm in diameter and wrapped by blocky Ru nanoparticles. The corresponding HRTEM image is inserted in Fig. 1d, which demonstrates that the Ru nanoparticles are embedded in the SiNW. The lattice spacings of 0.241 and 0.322 nm are corresponding to the (100) interplanar distance of hexagonal Ru and the (111) interplanar distance of cubic Si, respectively.

The XRD pattern of pristine SiNWs (Fig. 1e) is consistent with JCPDS data No. 27-1402. SiNWs usually have a thin oxide layer covering the surface. It would be coated with Si–H bonds when the oxide was removed by HF solution. The Si–H bonds own the ability to reduce noble metal ions [21]. Therefore, Ru nanoparticles can grow on SiNWs. The XRD pattern of Ru/SiNW-42.9 is also shown in Fig. 1e. All the diffraction peaks can be well indexed as Ru (JCPDS data No. 89-4903) and Si (JCPDS data No. 27-1402), respectively.

Ru/SiNW composites that have distinct compositional and structural engineering may be suitable to electrocatalysis. Thus the catalytic activity of the composites is investigated by studying the electrochemical hydrogen evolution reaction in acids, which served as hydrogen donor. Two compositions with different contents of Ru, pure Ru particles, commercial 20 wt.% Pt/C catalyst and SiNWs are fabricated onto GCE for linear sweep voltammetry (LSV) tests in oxygen-free 0.5 M H_2SO_4 (refer to experimental details and Fig. 1f).

Fig. 2a shows their LSV curves within a cathodic potential window. The Pt/C exhibits excellent HER performance with hydrogen evolution

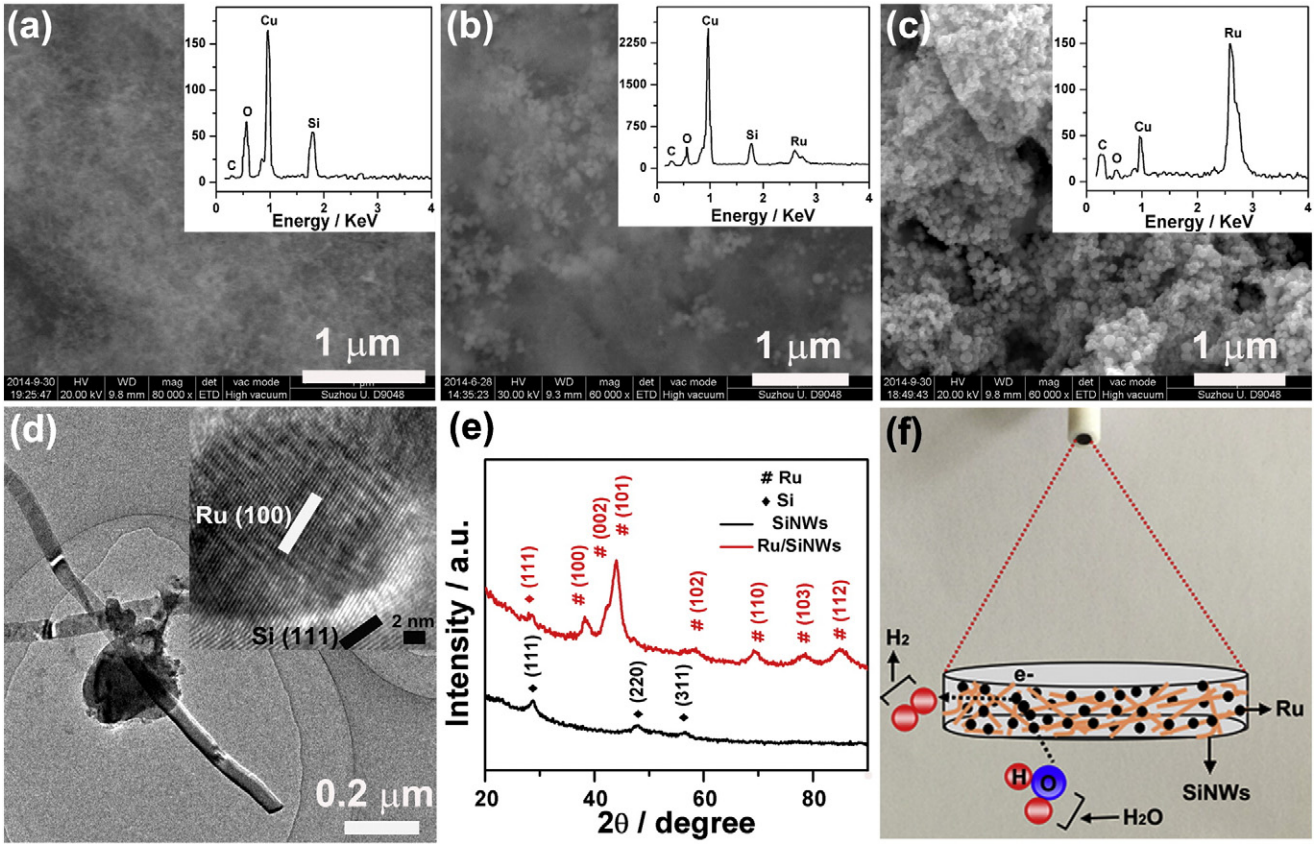

Fig. 1. SEM images and corresponding EDS spectra of (a) SiNWs, (b) Ru/SiNW-42.9 and (c) pure Ru particles; (d) TEM and HRTEM images of Ru/SiNW-42.9; (e) the XRD patterns of SiNWs and Ru/SiNW-42.9; and (f) optical photograph of the Ru/SiNW catalysts coated on GCE and corresponding schematic representation of the constructed film.