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Hydrogen evolution at nanoporous gold/tungsten sulfide composite film and its optimization

Xinxin Xiao [a], Christian Engelbrekt [b], Zheshen Li [c], Pengchao Si [a,*]

[a] Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, School of Materials Science and Engineering, Shandong University, Jinan 250061, People's Republic of China
[b] Department of Chemistry, DTU Chemistry, Building 207, Kemitorvet, Technical University of Denmark, DK 2800 Kongens Lyngby, Denmark
[c] ISA, Department of Physics, Aarhus University, 8000 Aarhus, Denmark

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ABSTRACT

Development of efficient and economical electrochemical systems for water splitting is a key part of renewable energy technology. Amorphous films of tungsten sulfide have been deposited by electrochemical reduction of tetrathiotungstate ions (WS_4^{2-}) on dealloyed nanoporous gold (NPG) for electrochemical hydrogen evolution reaction (HER). The electrocatalytic performance has been proved to be sensitive to the thickness of the deposited layer, with an optimal deposition time of 600 s identified. The bi-continuous nanoporous morphology of the composites has been confirmed by transmission electron microscopy (TEM), and is beneficial for high exposure of catalytic sites and electrolyte access to the electrode surface. High-resolution TEM (HRTEM) has been employed to characterize the strong adhesion between the ultrathin film (less than 1 nm) and gold skeleton, allowing rapid charge transfer and long-term stability. The measured Tafel slope of 74 mV dec^{-1} implies an underlying Volmer-Heyrovsky HER mechanism.

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1. Introduction

Constructing a sustainable energy system is a crucial strategy to eliminate the threat of environmental issues and dependency on non-renewable energy (coal, oil, natural gas, etc.), by substituting the current energy carrier mix with hydrogen [1]. Implementation of the hydrogen economy [1] is now driving research towards efficient, reliable and sustainable H_2 production technologies to replace the widespread use of steam methane reforming that still consumes fossil fuels. Electro- [2] and photo-electrocatalytic [3] water splitting are compelling and consist of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The core challenge, which impedes the commercialization of water splitting, is the development of inexpensive and competitively efficient catalysts. At present, Pt and Pt-group composite materials are the most capable catalysts, but limited for practical applications by their high cost and low abundance.

A so-called volcano plot [4] of the HER activity as a function of free energy of hydrogen adsorption, with the Pt family at the top, can serve as a guide to find alternative catalysts. Identification of the low-cost transition metal sulfides (TMSs), including molybdenum sulfides (MoS_x) and tungsten sulfides (WS_x), has indicated a new path in this area [5,6]. Generally, bulky TMSs are not highly efficient for HER but show promising catalytic capabilities as nanostructured materials, suggesting an increase in active site concentration. Structure-function relations have been proposed when TMS catalysts were comprehensively studied in the petroleum and chemical industry, e.g. hydrodesulfurization [7]. The rim/edge model was developed at that time, predicting that unstacked and monolayered TMS catalysts possess the best selectivity towards hydrogenation. Now computational [8] and experimental [9,10] results have indicated that metallic edges of TMS crystals are electrocatalytically active for HER. By elaborately designing TMSs at the nanoscale with different morphologies (i.e. nanoparticles [9], nanosheets [10,11], nanoribbons [12], nanowires [13], nanoflowers [14], nanospheres [15], double-gyroid [16] etc.), more active sites can be exposed, reactant diffusion optimized and HER kinetics improved, thus moving upward in the volcano plot.

Another avenue is to couple semiconducting TMS catalysts with highly conductive substrates to accelerate the electron transport between the active sites and electrodes. Accordingly, MoS_2 nanoparticles grown on reduced graphene oxide (rGO) sheets [17], low crystalline MoS_2 nanosheet coated carbon nanotubes (CNTs) [18], two-dimensional hybrid nanosheets of tungsten

* Corresponding author.
E-mail address: pcsi@sdu.edu.cn (P. Si).

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disulfide and rGO [19], MoS_x grown on graphene-protected three-dimensional Ni foams [20] and MoS_2 on ordered mesoporous carbon nanospheres [21] have been fabricated for HER. Apart from introducing an excellent electron pathway between substrate electrode and catalyst, the nanostructured support also provides a large surface area for facile contact with the electrolyte and homogeneous dispersion of catalysts free from aggregation. From this viewpoint, dealloyed nanoporous gold (NPG) [22] is a good candidate for catalysts support due to its unique bi-continuous nanoporous character, single crystalline features and stability in acidic media. Moreover, NPG can be easily functionalized with transition metal oxides [23], noble metals [24], conducting polymers [25] and thiol-conjugates [26] for energy devices and biosensors. It has been demonstrated that NPG provides excellent contact between MnO_2 and gold ligaments, which greatly improves the electrical conductivity of the hybrid materials [23]. Most recently, amorphous molybdenum sulfide@NPG hybrids have been fabricated via a chemical plating procedure, showing excellent catalytic behavior [27]. In this work, we stabilize amorphous tungsten sulfide thin films onto NPG by an electrochemical route, which is more controllable than chemical plating. The abundance of structurally unsaturated sites on the amorphous thin layer, large specific surface area, fast electron transfer at the interface of NPG and active catalyst, and their unique synergetic effects make this nanocomposite a promising electrode system for HER.

2. Experimental Section

2.1. Reagents

Ammonium tetrathiotungstate ($(NH_4)_2WS_4$) was purchased from J&K Scientific Ltd. (Beijing, China). Potassium chloride (KCl, 99.99%), sulfuric acid (H_2SO_4, 98%) and nitric acid (HNO_3, 65%) were ordered from Shanghai Sinopharm Chemical Co., Ltd. (Shanghai, China). All chemicals were used as received without any further purification. Ultrapure water with a resistivity >18.25 M Ω cm^{-1} was obtained from a UPH-IV ultrapure water purifier (Chengdu Ultrapure Technology Co., Ltd China).

2.2. Synthesis of NPG supported tungsten sulfide composites

NPG sheets were fabricated by dealloying 100 nm thick Au/Ag leaf alloy (12-carat, Sepp Leaf Products, New York) in concentrated HNO_3 for 30 min at 30 °C. After carefully cleaning with ultrapure water, the NPG films were placed onto pre-polished glassy carbon electrodes (GCE) with a diameter of 4 mm. Prior to use, cyclic voltammetry (CV) of NPG in 1 M H_2SO_4 were carried out to create high surface areas. Electrodeposition of tungsten sulfide was performed by applying a constant potential of −0.9 V (vs. SCE) to NPG electrodes for different time in 0.1 M KCl solution containing 5 mM $(NH_4)_2WS_4$. Finally, 3.0 μL 0.05% Nafion solution was dropped on the electrode surface and left to dry naturally. For comparison, tungsten sulfide films were also deposited onto GCE and standard polycrystalline gold (polyAu).

2.3. Characterization

Scanning electron microscopy (SEM) images were recorded by a Hitachi SU-70 microscope, equipped with an energy dispersive X-ray spectroscopy (EDX) system. Microstructures of deposited materials were observed by scanning transmission electronic microscope (STEM) and transmission electron microscope (TEM, FEI Tecnai G2 F30) at an acceleration voltage of 300 kV. Further characterization was carried out with high-resolution TEM (HRTEM, FEI Titan) fitted with a field-emission electron source and a spherical aberration corrector on the condenser lens system operated at 300 kV. X-ray photoelectron spectroscopy (XPS) was carried out on the MatLine beamline at the ASTRID2 synchrotron facility of Aarhus University, with a multipole wiggler as light source. The photon electrons were collected by SCIENTA (SES 200) analyzer.

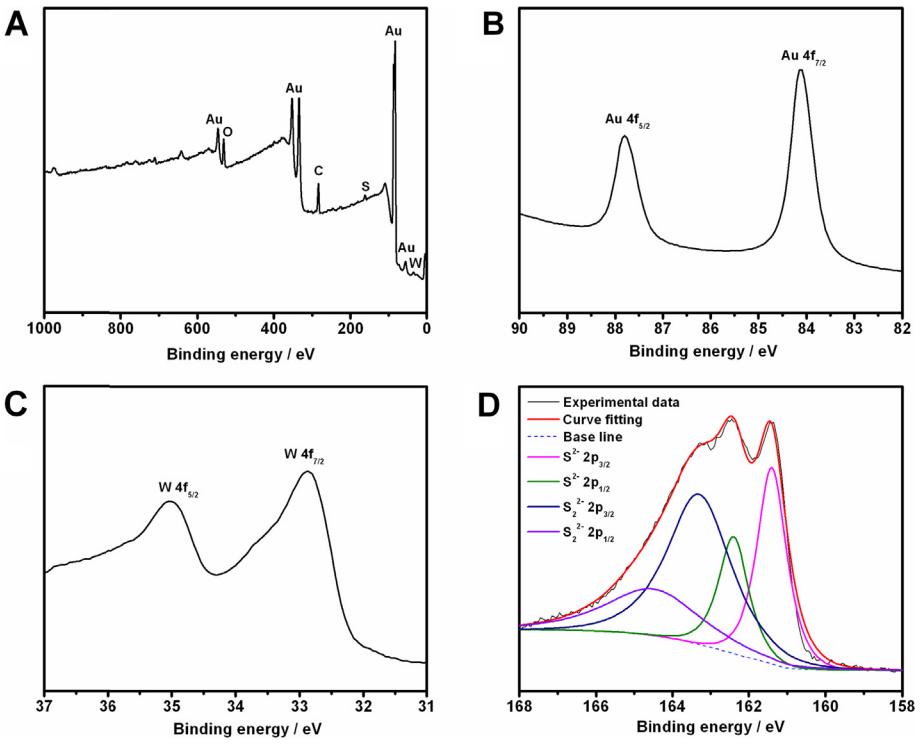

Fig. 1. XPS spectra of NPG/WS_x (600 s). (A) Survey spectrum. (B) Au 4f spectrum. (C) W 4f spectrum. (D) S 2p spectrum.

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