



Full Length Article

A straight forward approach to electrodeposit tungsten disulfide/poly(3,4-ethylenedioxythiophene) composites onto nanoporous gold for the hydrogen evolution reaction



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ABSTRACT

1.1 nm tungsten disulfide/poly(3,4-ethylenedioxythiophene) (PEDOT) was successfully electrodeposited on the surface of dealloyed nanoporous gold (NPG) surface to form uniform nanocomposites and offers an excellent electrocatalysis for the electrochemical dihydrogen evolution reaction (HER) in acidic media. The approach is straight forward and does not require any expensive equipment or intensive energy. The morphology and composition of the nanocomposites were structurally mapped by high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrometry (FTIR). The roles of both the NPG substrate and PEDOT in the observed enhanced HER activity compared to planar Au-electrode surfaces and pure single-component WS₂ have been deconvoluted experimentally. PEDOT itself is inert for the HER, but was found to improve significantly the conductivity and operating stability of the WS₂ catalyst. The prepared nanocomposites reach the best in 2D WS₂ catalyst family, exhibiting excellent electrochemical catalytic activity for the HER. The optimal electrode showed an onset potential of −164 mV vs. reversible hydrogen electrode (RHE), an apparent exchange current density as high as 0.04 mA cm^{−2}, and a very low Tafel slope of 53 mV dec^{−1}. These catalysts are promising electrocatalysts for generation a large amount of H₂ from water.

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1. Introduction

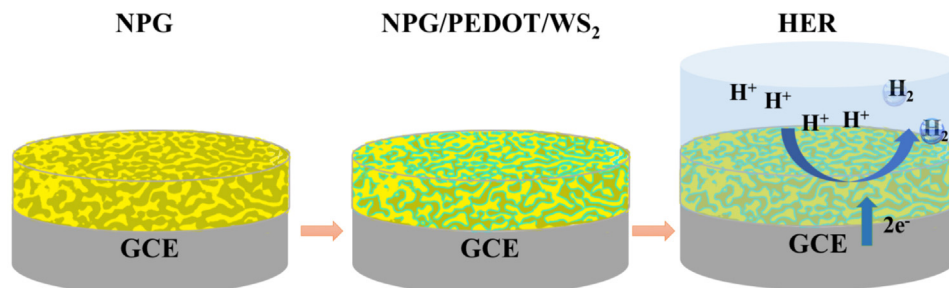
Hydrogen is appealing as a clean and sustainable energy carrier with a strong perspective in future energy systems [1]. The electrochemical dihydrogen evolution reaction (HER) [2,3] offers a controllable approach to generate clean H₂ but requires efficient and cheap catalysts. Pt and noble metal containing materials have been considered hitherto as the most effective HER electrocatalysts, but suffer from high cost and low abundance [3,4]. As economically feasible replacements, transition metal sulfides (TMSs), including molybdenum and tungsten disulfides (MoS₂ and WS₂), are attractive [2,5–7]. To enhance the electrocatalytic efficiency of MoS₂ or WS₂, two main strategies are broadly employed: (1) Fabrication of various forms of dispersed and nanostructured

particles that increase the number of exposed active sites [6–11]; (2) Incorporation of TMSs into highly conducting matrices that offer facile electron transfer (ET) pathways between the active sites and the supporting electrodes [12–16]. So far, three-dimensional (3D) hybrids of WS₂/graphene/Ni foam exhibited the best electrocatalytic performance (a ~0.1 V overpotential and a Tafel slope of ~43 mV per decade) among the WS₂ catalyst family [17]. The preparation procedure required expensive equipment and intensive energy for graphene growth and elevated temperature annealing.

In situ electrodeposition of amorphous molybdenum or tungsten disulfide films prepared from [MoS₄]^{2−} or [WS₄]^{2−} is another approach to obtain active HER catalysts immobilized on the electrodes [18,19], avoiding the usage of Nafion[®] films for drop-casting [20]. In contrast to other sophisticated preparation protocols, electrodeposition operates in a facile and scalable manner at room temperature without any ultra-high vacuum environment. The electrochemically generated film thickness can further be tuned by controlling the deposition conditions [21]. Hu et al. reported

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Scheme 1. Methodology of NPG based HER.

electrodeposition of amorphous MoS_2 or MoS_3 films by adjusting the scanned potential window [18]. WS_2 /reduced graphene oxide (GO) hybrids generated electrochemically on the electrode in electrolytes with $[\text{WS}_4]^{2-}$ and GO, is recently reported [19]. Particle aggregation resulting in activity loss of the catalysts, can in principle be suppressed by dispersing the particles on/in a support [22].

Combining MoS_2 and WS_2 with conducting polymers (CPs) [23–25], e.g. polyaniline (PANI)[26], polypyrrole (PPy) [27] and their derivatives [22], can increase their conductivities and alleviate catalyst aggregation [22]. In the presence of both CP monomers and the precursor $[\text{MoS}_4]^{2-}$, co-electrodeposition provides an efficient approach for controlled distribution of catalyst particles in the polymer matrix [28]. Electrochemically generated MoS_x/PPy exhibits good HER activity with an onset potential of 0 V vs. the reversible hydrogen electrode (RHE), i.e. close to the equilibrium potential of RHE. Such performance is comparable to commercial Pt/C catalysts, however the catalysts show rather poor stability on long-term testing [27].

Dealloyed nanoporous metals (NPMs) [29] offer unique conductivity and very large surface areas [30]. NPMs have emerged as promising substrates for loading of MoS_2 [13], resulting in layered MoS_2 with significant out-of-plane lattice strains [31]. Moreover, the pores inside the NPMs confine the supported catalysts, thus improving their operational stability [21]. In our previous work, electrodeposition of both homogeneous poly(3,4-ethylenedioxythiophene) (PEDOT) films [32] and of tungsten sulfides [21] onto nanoporous gold (NPG) [33,34] was achieved successfully. In the present work, we combine these two elements together to develop stable organic/inorganic hybrid catalysts and explore their potential as electrocatalysts for the HER, Scheme 1. NPG is used as a NPM representative for the comparison of porous and planar electrode surfaces in the HER. The synergy of these factors in the resulting hybrids yielded excellent HER activity both with a Tafel slope as low as 53 mV dec^{-1} , and with high durability.

2. Experimental

2.1. Reagents

Ammonium tetrathiotungstate ($(\text{NH}_4)_2\text{WS}_4$, 99.9%) was purchased from J&K Scientific Ltd. (Beijing, China). Lithium perchlorate (99.9% metals basis), 3,4-ethylenedioxythiophene (EDOT), polyethylene glycol (PEG) 20,000, sulfuric acid (H_2SO_4 , 98%) and nitric acid (HNO_3 , 65%) were from Shanghai Sinopharm Chemical Co., Ltd. (Shanghai, China). All chemicals were used as received. Ultrapure water (resistivity $>18.25 \text{ M}\Omega \text{ cm}$) was obtained from the UPH-IV ultrapure water purifier (Chengdu Ultrapure Technology Co., Ltd, China).

2.2. Synthesis of NPG supported tungsten sulfide composites

NPG sheets were fabricated, via a well-established protocol [35], 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 . Such conditions led to NPG with a typical pore size of ca. 30 nm (Fig. S1). After careful cleaning in ultrapure water, the NPG films were transferred onto pre-polished glassy carbon electrodes (GCE) with a diameter of 4 mm. Prior to use, cyclic voltammetry (CV, between -0.2 and 1.65 V , 100 mV s^{-1}) of NPG in $1 \text{ M H}_2\text{SO}_4$ was carried out to create clean surfaces of NPG.

Electrolyte for electrodeposition containing 20 mM EDOT, 20 mM LiClO_4 , 2.5 mM $(\text{NH}_4)_2\text{WS}_4$ and 1.0 mM PEG was prepared and allowed to age overnight before use. The optimization of the precursor concentration ratio is given in Fig. S2. Electrodeposition was performed by cycling the potential between -0.7 and 1.0 V (vs. Ag/AgCl) at 100 mV s^{-1} for a certain number of cycles. The thickness of the deposition layer depends on the number of the cycles. For comparison, WS_2 films were also deposited on the surface of GCE and standard polycrystalline gold (polyAu) electrodes with a diameter 3 mm.

2.3. Characterization

Microstructures of the WS_2 composites on NPG were observed by high-resolution transmission electron microscope (HRTEM, FEI Titan) at DTU fitted with a spherical aberration corrector on the condenser lens system operated at 300 kV. X-ray photoelectron spectroscopy (XPS) of composites deposited on gold foils (thickness: 0.1 mm, purity: 99.9%) was carried out on the MatLine beamline at the ASTRID2 synchrotron facility of Aarhus University, with a multipole wiggler as light source and the photoelectrons collected by a SCIENTA (SES 200) analyzer. XPS data analyses were fitted with the similar full width at half maximum (FWHM) for the particular component. For S 2p spectra, area ratios of 2:1 and energy separation of 1.1 eV were used to obtain optimal fitting. Fourier transform infrared (FTIR) analysis was performed on a Perkin Elmer Spectrum 100 interferometer.

2.4. Electrochemical measurements

All electrochemical studies were performed using a CHI660E electrochemical workstation (Shanghai, China) in a standard three-electrode setup with a specific NPG supported tungsten sulfide working electrode, a saturated calomel electrode (SCE) as reference, and a platinum (Pt) foil as counter electrode. A graphite rod (diameter 3 mm) was also tested as a counter electrode for HER. No significant difference between graphite and Pt counter electrodes was found. The electrocatalytic activity towards the HER was examined by polarization curves using linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ at room

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