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Synthesis and hydrogen-evolution activity of tungsten selenide thin films deposited on tungsten foils

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ABSTRACT

Thin films of WSe_2 have been deposited onto a conductive substrate (tungsten foil) using a relatively simple chemical-vapor-transport technique. X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, X-ray powder diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy indicated that the films consisted of micron-sized single crystals of WSe_2 that were oriented perpendicular to the surface of the tungsten foil substrate. Linear sweep voltammetry was used to assess the ability of the WSe_2 films to catalyze the hydrogen-evolution reaction and chronopotentiometry was used to gauge the temporal stability of the catalytic performance of the films under cathodic conditions. A 350 mV overpotential (η) was required to drive the hydrogen-evolution reaction at a current density of -10 mA cm^{-2} in aqueous 0.5 M H_2SO_4, representing a significant improvement in catalytic performance relative to the behavior of macroscopic WSe_2 single crystals. The WSe_2 thin films were relatively stable under catalytic conditions, with the overpotential changing by only ~10 mV after one hour and exhibiting an additional change of ~5 mV after another hour of operation.

1. Introduction

The successful development of a stable photoelectrochemical device comprised of only earth-abundant materials and capable of efficiently capturing and using the energy of sunlight to split water into its elements (H_2 and O_2) would represent significant progress toward the development of a technology to convert, store and effectively utilize solar energy [1]. A photoelectrochemical water-splitting device would employ one or multiple semiconductors to collect and convert incident photons into electron–hole pairs, which would then be transported in opposite directions to liquid interfaces by the electric fields inside the semiconductors. The cathode would contact a catalyst for the hydrogen-evolution reaction (HER, Eq. (1)) while the anode would contact a catalyst for the oxygen-evolution reaction (OER, Eq. (2)). Although noble metals, such as Pt, are highly active HER catalysts [2], the development of catalysts that are both stable for extended periods of time under cathodic conditions and composed only of earth-abundant materials, requirements for an economical and globally scalable technology, has proved challenging.

$$\text{Cathode (reduction)}: 2H^+_{(aq)} + 2e^- \rightarrow H_{2(aq)} \quad E^\circ = 0.00\ \text{V} \tag{1}$$

$$\text{Anode (oxidation)}: 2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \quad E_{ox} = -1.23\ \text{V} \tag{2}$$

Photoelectrochemical studies of the Group VI dichalcogenides have focused on the optical absorption properties and electronic properties of macroscopic single crystals, which have been shown to yield high (~17% for n-type WSe_2) solar-to-electrical energy-conversion efficiencies [3] and exceptional stability in acidic environments [4,5]. In contrast, recent electrochemical studies have focused on the ability of the transition-metal dichalcogenides to catalyze the hydrogen-evolution reaction [6]. The electrocatalytic activity of small polycrystalline samples of WSe_2 is substantially greater than that of macroscopic WSe_2 single crystals, and the step edges of the crystals are believed to be the active catalytic sites [6].

Although a variety of methods for preparation of WSe_2 have been published, those methods have involved multiple steps and, until recently, have relied on the use of non-conductive substrates [7–12]. A simple method that allows deposition of catalytically active samples of WSe_2 directly onto conductive substrates would facilitate studies of the electrocatalytic properties of WSe_2 and the potential future use of WSe_2 as a catalyst in photoelectrochemical water-splitting devices. Herein we describe a relatively simple,

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single-step method for the preparation of robust WSe_2 thin films capable of catalyzing proton reduction. The single-step method utilizes a chemical-vapor transport (CVT) approach that allows the thin films to be deposited directly onto conductive (W foil) substrates which can be used directly as robust electrodes for electrochemical studies.

2. Experimental

2.1. Synthesis of WSe_2 thin films by chemical-vapor transport

All chemicals were used as received and were stored under ambient conditions prior to use, unless noted otherwise. WSe_2 powder was prepared by sealing elemental W and Se in an evacuated quartz ampoule (10^{-4} Torr) and heating the ampoule in a tube furnace for 24 h at 900 °C. The powder was stored under an inert atmosphere prior to use. Thin films were then formed by loading 1.25 g of the WSe_2 powder, 0.18 g of particles of elemental Se (Sigma Aldrich, 99.99% pure), and 0.38 g of WO_2Cl_2 (Sigma Aldrich, 99.00% pure) into the sealed end of a custom-built quartz ampoule that had been soaked in a base bath for at least 12 h, rinsed with distilled H_2O, and dried with a flame prior to loading (see Fig. S1 in the Supplemental information). Strips (2.0 cm × 1.0 cm) of W foil (Sigma Aldrich) that were used as substrates for the WSe_2 deposition were placed along the length of the tube and were separated from each other by 5-mm spaces. A 3.0-cm diameter quartz tube was placed into the open end of the ampoule, which was then evacuated to 10^{-3} Torr. The open end of the ampoule was then heated until the quartz tube fused with and sealed the ampoule. The sealed ampoule was loaded into a three-zone tube furnace (Mellen Company, Concord, NH) that was then heated with the center-zone temperature set to 800 °C and the side-zone temperatures set to 700 °C. After remaining inside the furnace for two days, the ampoule was gradually cooled to room temperature. Under ambient conditions, the ampoule was then broken, and the strips of film-coated foil were removed. Unless specified otherwise, the thin film samples were used with the W foil intact for support.

2.2. Morphology and elemental analysis of the WSe_2 thin films

X-ray diffraction (XRD) patterns for the WSe_2 thin films were obtained using an X'pert powder diffractometer (PANalytical, Westborough, MA) with Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images of the thin films and energy dispersive X-ray spectroscopy (EDS) data were obtained using a Nova NanoSEM 450 (FEI, Hillsboro, OR) operating at an accelerating voltage of 20 kV. AZtecTEM software (Oxford Instruments, Santa Barbara, CA) was used to interpret the EDS spectra.

For high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) measurements, foil-supported samples in 2-propanol were gently sonicated to produce a suspension of platelets. The suspension was transferred by pipette onto 300-mesh carbon-coated Cu grids (SPI Supplies) and the solvent was allowed to evaporate. HRTEM and SAED images of the deposited WSe_2 platelets were then collected using a Tecnai F30ST system (FEI, Hillsboro, OR) operating at an accelerating voltage of 300 kV.

X-ray photoelectron spectroscopy (XPS) was performed on the thin films using an M-probe spectrometer (VG-Surface Science Instruments, Pleasanton, CA) controlled by Hawk Capture and Analysis software (V7.03.04; Service Physics, Bend, OR). The XPS chamber contained a monochromatic Al Kα (1486.6 eV) X-ray source operated at a nominal base pressure of $\sim 10^{-9}$ Torr. The 800 × 1500 μm elliptically focused beam was incident at an angle of 35° with respect to the sample surface plane. The emitted photoelectrons were filtered using a retarding energy of 154.97 eV and were collected at a 35° take-off angle by a hemispherical energy analyser.

2.3. Measurement of catalytic activity and stability

Samples of thin films grown on a W foil that had been scratched to expose striations of metallic W were mounted on a coiled Cu wire using Ag paint for adhesion as well as ohmic contact. The rear surface, the edges, and a portion of the front face of the electrode were covered with Hydrosol epoxy adhesive (Henkel Corporation, Irvine, CA). The exposed area of the electrodes was measured by an optical scanner to be 0.5 cm^2.

Linear sweep voltammetry (-50 mV s^{-1}) and chronopotentiometry (at a constant current density of -10 mA cm^{-2}) were obtained in a custom-built three-electrode cell controlled by a SP-200 potentiostat (BioLogic, Knoxville, TN). A Ag wire in 1 M KCl(aq) (CH Instruments, Austin, TX) was used as a reference electrode and a graphite rod (Alfa Aesar) served as the counter electrode. The 0.50 M H_2SO_4 (Sigma Aldrich, St. Louis, MO) electrolyte was prepared using 18.2 MΩ cm (EMD Millipore, Billerica, MA) resistivity H_2O, and $H_2(g)$ was bubbled through the stirred electrolyte during the electrochemical measurements.

3. Results and discussion

The XRD, EDS, and XPS survey-scan data (see Supplemental information) confirmed the presence of W and Se in the films. Additionally, C and O were detected at levels consistent with contamination resulting from exposure to the ambient environment between removal of the samples from the quartz ampoule and collection of the spectroscopic data.

SEM images (Fig. 1A) of a WSe_2 thin film indicated that the terraces of the WSe_2 platelets were oriented perpendicularly with respect to the substrate. HRTEM showed a hexagonal arrangement of atoms on the highly ordered terrace of a WSe_2 platelet and a somewhat disordered region at the edge of the platelet (Fig. 1B). The lattice distance of 2.8 Å observed on the terraces is attributable to the (1 0 0) planes of 2H-WSe_2. The left section of Fig. 1B is darkest because this region was the thickest portion of the film, and electron transmission through this region therefore encountered additional layers of WSe_2. The visible Moiré pattern in Fig. 1B indicates that the layers were incommensurate [13], as would be expected for WSe_2. A bright-field TEM image (Fig. 1C) of an isolated, and typical, micron-sized WSe_2 platelet indicated that the platelets ranged from 0.5 to 5.0 μm in size. The SAED patterns (Fig. 1D) obtained along the [0 0 1] zone axis were exceedingly sharp, consistent with crystalline WSe_2.

Fig. 2A shows the linear potential sweep current density versus the electrode potential of WSe_2 on W. The onset of hydrogen evolution occurred at -540 mV versus the Ag/AgCl reference electrode used for the experiment, which corresponds to an onset potential of ~300 mV relative to the reversible hydrogen electrode (RHE). The overpotential, η, required to drive the HER at a current density of -10 mA cm^{-2} was 350 mV for the CVT-prepared WSe_2 samples. As shown in Fig. 2B, η changed by 10 mV after 1 h of chronoamperometric operation, but η changed only by an additional 5 mV at the end of a second hour of operation.

Except for one recent account [7], previous reports for the preparation of WSe_2 crystals have relied on the use of non-conductive substrates [14]. In contrast, the CVT method allows the WSe_2