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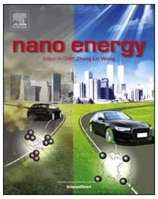

Iron diselenide nanoplatelets: Stable and efficient water-electrolysis catalysts

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ABSTRACT

The development of efficient water-electrolysis catalysts plays a key role in clean and sustainable energy sources. In this work, 2D $FeSe_2$ nanoplatelets have been successfully synthesized via a hydrothermal reduction route, which exhibit extraordinarily high catalytic activities and stability for oxygen evolution reaction (OER). The remarkable electrocatalytic performance of $FeSe_2$ nanoplatelets (e.g., overpotential: 2.2 times higher than that of commercial RuO_2 at 500 mV; Tafel slope: 48.1 mV/dec; steady-state current densities remain constant after 70 h) can be attributed to highly exposed active sites associated with (210) crystal faces; the 2D nanostructure could also facilitate improvement of kinetics of water oxidation. Furthermore, the changes of energy level, band structure and water adsorption ability of $FeSe_2$ under different bias were further understood based on density functional theory calculation. Therefore, this work provides the first example of $FeSe_2$ nanoplatelets as OER application, which may open a new avenue to design and explore other Fe-based nanostructures as efficient catalysts for renewable energy.

1. Introduction

Hydrogen (H_2) is regarded as one of the most potential clean energy in the 21st century [1–3]. However, currently, more than 90% of hydrogen energy is obtained from fossil fuels [4–6]. As is known to all the burning of fossil fuels will highly increase the pollution of the environment and the crisis of global warming [7]. From a clean and sustainable perspective, water splitting is a low-cost and environmentally-friendly way to obtain hydrogen energy [8]. Generally, water electrolysis consists of two half reactions: 1) water oxidation and 2) proton reduction. The first half reaction is usually considered as the critical bottleneck in developing efficient electrolysis of water due to the inherent sluggish oxygen evolution reaction (OER) kinetics [9–12]. Thus, it is highly desirable to develop efficient electrocatalysts for OER, which has already attracted worldwide attention in recent years. To date, IrO_2 and RuO_2 are commonly considered as the most effective catalysts for OER in industry [13,14]. However, the low natural abundance and high cost have restricted the use of noble metal oxides in large scale water splitting technologies. Therefore, the development of earth-abundant OER electrocatalysts has become the new trend. Moreover, it was well-recognized that the interface and micro/nanostructures of the electrocatalysts have great effect on OER performance. i.e., the exposure of high catalytically active sites plays an important role in OER process.

Recently, the use of 2D layered nanostructures as OER catalysts has been paid much attention. For example, Sun et al. showed that the 2D $g\text{-}C_3N_4$ nanosheets with same catalyst loading give a higher current density (10.5 mA/cm^2) than bulk $g\text{-}C_3N_4$ [15], since the 2D nanosheets have higher specific surface area than bulk $g\text{-}C_3N_4$, thereby exposing more active sites for catalytic reaction. Song and Hu confirmed that the exfoliated 2D nickel iron and nickel cobalt layered double hydroxides nanosheets exhibit obvious higher activity and stability than the commercial iridium dioxide catalyst in oxygen evolution [16]. Xie et al. have developed 2D $CoSe_2$ nanosheets, which give a lower Tafel slope of 64 mV/dec, since the Co^{2+} ions are exposed on the surface and serve as the catalytically active sites [17]. Therefore, several 2D layered nanostructures present advantages of high-efficiency OER catalytic activity, due to the fully utilization of catalytic species and effective electron transfer at the interface/surface of electrocatalysts during water-splitting process.

From an elemental composition perspective, iron (Fe) has become one of the most promising non-noble metals for the design of robust OER catalysts [18,19], especially Fe-based 2D materials (such as metal hydroxide [20–22] and mixed-metal oxides [23]). Besides abundance and low cost, the excellent performance of Fe-based compounds derives from the intrinsic semiconductor/metal characters and unique

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electronic structures, which could improve the electrical conductivity and the adsorption of H_2O. For example, Driess et al. [23] reported the 2D cobalt iron oxides material could achieve obviously higher catalytic performance in the kinetics regime, in terms of onset potential and diffusing limiting current density. Dai et al. have reported a 2D nickel–iron layered double hydroxide (NiFe-LDH)–carbon nanotube (CNT) complex with higher OER catalytic activity and stability than commercial Ir-based catalysts [20]. The high catalytic activity can be attributed to the formation of ultrathin 2D nanoplates of a highly OER-active NiFe-LDH structure. Therefore, the design of idealized 2D Fe-based catalysts with high exposure of active sites could be a facile strategy to develop high-efficiency water electrolysis.

In the meantime, very recently, several bulk metal selenides (such as NiSe and $CoSe_2$ materials) with good OER catalytic performance are reported [24–26]. To combine the advatanges of Fe-based 2D materials and metal selenides, herein, iron diselenide ($FeSe_2$) nanocrystals have been selected as the model system, which can be synthesized via a hydrothermal reduction route. The as-prepared $FeSe_2$ nanocrystals present highly tunable micro/nano-sized morphologies, which were further transferred onto a nickel substrate as OER catalysts. $FeSe_2$ nanoplatelet-based electrocatalyst shows a much lower overpotential (of 330 mV to achieve 10 mA/cm^2). At 500 mV overpotential, the current density of $FeSe_2$ nanoplatelets is 70 mA/cm^2, which is 2.2 times higher than that of commercial RuO_2, strongly demonstrating the high electrocatalytic activity of 2D $FeSe_2$ nanoplatelets. Furthermore, the steady-state current densities of the $FeSe_2$ still remain constant even after 70 h at high potential (1.67 V), and the linear sweep voltammetry (LSV) curve of $FeSe_2$ nanoplatelets almost has no decrease. In addition, the changes of energy levels and electronic structures of $FeSe_2$ under different bias were further analyzed based on the theoretical studies. To the best of our knowledge, this is the first example of $FeSe_2$ nanoplatelets towards high-efficiency OER application.

2. Experimental section

2.1. Synthesis of $FeSe_2$ and $CuSe_2$

The synthesis of MSe_2 (M=Fe and Cu) was based on a mild solution approach: Mixing aqueous solutions consisting of Se powder and metal chlorides were made according to stoichiometric ratios ($FeSe_2$: 0.03 g of Se and 0.06 g of $FeCl_3{\cdot}6H_2O$; $CuSe_2$: 0.0240 g of Se powders and 0.08 g of $CuCl_2{\cdot}6H_2O$). The total volume of reagent solution was adjusted to 70 mL by adding deionized water. 5 mL of hydrazine hydrate (98 wt%) was then dropped into the above solution. After vigorous agitating for 10 min, the reactant was transferred into a 100 mL of Teflon–lined autoclave, which was sealed and maintained at different temperatures (120 °C; 150 °C; 180 °C; 210 °C for $FeSe_2$, and 180 °C for $CuSe_2$) for 24 h and then naturally cooled to room temperature. The final product was collected and washed with distilled water and absolute ethanol for many times, and dried in vacuum at 60 °C overnight for further characterization.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of all the samples were carried out using a graphite-filtered Cu Kα radiation operating at 40 kV and 30 mA, λ=0.15418 nm (Rigaku X-ray diffractometer). X-ray photoelectron spectrometry (XPS) was recorded using Al Kα radiation (Thermo VG ESCALAB MK II). The positions of all binding energies were calibrated by using the C 1 s line at 284.8 eV. Scanning electron microscopy with an accelerating voltage of 20 kV (SEM, ZeissSUPRA 55) was applied for detailed morphology analyses. TEM and EDS mappings were taken using microscopy (JEOL JEM-2010F) combined with an EDX (Oxford X-MaxN 80-TLE) spectroscopy.

2.3. Preparation of RuO_2 electrodes

A homogeneous catalyst was obtained by sonication of 2 mg RuO_2, 0.5 mL water, 30 µL 5 wt% Nafion solution, and 0.5 mL ethanol for 30 min. Then, 5 µL of the dispersion (containing 10 µg of catalyst) was loaded on the surface of a nickel piece (surface area: 1 cm^2). Consequently, the overall RuO_2 electrode loads amount of 10 µg cm^{-2}.

2.4. Electrochemical measurements

All electrochemical measurements were carried out on the electrochemical workstation (CHI 660 C, CH Instrument Co. USA). Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. Typically, 2 mg of catalyst and 30 µL Nafion solution (Sigma Aldrich, 5 wt%) were dispersed into 1 mL water-ethanol solution with volume ratio of 1:1 by sonicating for at least 0.5 h to form a homogeneous ink. Then, 5 µL of the dispersion (containing 10 µg of catalyst) was loaded onto a 1×1 cm^2 pure nickel piece (the pure nickel piece was cleaned by sonication with acetone for 30 min firstly, then sonicated by hydrochloric acid (30wt%) for 2 min. Linear sweep voltammetry with a scan rate of 10 mV/s was conducted in 1 M KOH. The KOH electrolyte was degassed by bubbling oxygen for 30 min. All of the potentials were calibrated to a reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) was performed at various scan rates (4, 40, 80, 120, 160 and 200 mV/s, etc) in 0.61–0.74 V vs. RHE region. The double-layer capacitance (C_{dl}) was estimated by plotting the Δj (j_a-j_c) at 0.67 V vs. RHE against the scan rates, in which the j_a and j_c are the anodic and cathodic current density, respectively. The slope is twice that of the double-layer capacitance C_{dl}. For water splitting, $FeSe_2$ and $CuSe_2$ electrocatalyst were used as working electrode in a three-electrode system. The Faradaic efficiency was calculated by comparing the amount of gas theoretically calculated and experimentally measured. To assess the Faradic efficiency, we collected O_2 by water-gas displacing method, and calculated the mole values of O_2 generated from the water splitting. And then we calculated the theoretical amount of O_2 with I–t curve by applying the Faraday law.

2.5. Calculated details

Periodic density functional theory (PDFT) calculations of the electronic properties for idealized $FeSe_2$ model (Scheme S1a) under different bias potentials (0–0.182 V/nm: corresponding to 0–2 V in experiment conditions considering the thickness of 11 nm for the $FeSe_2$ nanoplatelets) were performed using Dmol3 [27,28] module in Material Studio software package.[29] The geometric configuration was optimized by Perdew-Wang (PW91) [30] generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP). The core electrons for metals were treated by effective core potentials (ECP). SCF converged criterion was within 1.0×10^{-5} hartree/atom and the converged criterion of structure optimization was 1×10^{-3} hartree/bohr. The Brillouin zone is sampled by 1×1×1 k-points, and test calculations reveal that the increase of k-points does not influence the results. For calculations of adsorption energy of water, the (210) crystal face of $FeSe_2$ (Scheme S1b, with three atomic layers) were modeled with vacuum widths of 15 Å.

3. Results and discussion

The hydrothermal synthesis process of $FeSe_2$ was performed at different temperatures, in which hydrated iron chloride was employed to supply Fe source, and aqueous hydrazine ($N_2H_4{\cdot}H_2O$) was used as reducing agent (Fig. 1). As shown in Fig. 2a and Fig. S1, all the X-ray diffraction (XRD) peaks of the obtained powder samples are consistent with the $FeSe_2$ phase (JCPDS Card No. 21-0432), which can be indexed as orthorhombic crystal system (*Pnnm* space group and *mmm* point