



Short communication

# Layered rhenium sulfide on free-standing three-dimensional electrodes is highly catalytic for the hydrogen evolution reaction: Experimental and theoretical study



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## ABSTRACT

Hydrogen evolution reaction is the key for clean energy utilization. Recently, molybdenum disulfide ( $\text{MoS}_2$ ) was suggested as a replacement for the most efficient catalyst to date for such reaction, which is platinum. We show here that electrodes based on layered rhenium sulfide ( $\text{ReS}_2$ ) catalyst show dramatic improvement when compared to  $\text{MoS}_2$ . We have shown by DFT calculations that  $\text{ReS}_2$  possesses metallic character of surface states which together with a higher position of Fermi level facilitates electron transfer and pronounced electrochemical activity of this surface.  $\text{ReS}_2$  has great potential for hydrogen evolution reaction applications.

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## 1. Introduction

Hydrogen evolution reaction (HER) is of utmost technological importance for the electrochemical production of hydrogen, which is a  $\text{CO}_2$ -free fuel [1]. Although Pt is the most efficient and widely used catalyst for HER, its limited availability on a truly large scale has encouraged an intensive search for alternative non-Pt catalysts with easily available, low-cost and comparable catalytic properties towards HER. Recently, numerous reports have appeared on the utility of layered transition metal dichalcogenides (TMDs), such as  $\text{MoS}_2$  [2–6],  $\text{MoSe}_2$  [7–10],  $\text{WS}_2$  [11,12],  $\text{WSe}_2$  [7], or misfit layered systems [13], which can act as efficient catalysts for HER. Most of the mentioned literature focused on the two-dimensional layer electrode assembly of TMDs [14,15]. However, for truly industrial-scale hydrogen evolution, a large catalyst surface area is required to ensure high turnover.

There is very limited literature on  $\text{ReS}_2$  properties [16]. Very recently, its optical properties were studied and it was found that, from bulk to monolayer, rhenium sulfide is a direct band gap semiconductor. [17]. In addition  $\text{ReS}_2$  exhibits anisotropic optical properties [17]. Up to now, the electrochemical properties of  $\text{ReS}_2$  have not been studied. We will show that  $\text{ReS}_2$  is a highly efficient catalyst for HER.

We have synthesized both  $\text{ReS}_2$  and  $\text{MoS}_2$  on free-standing, three-dimensional reticulated vitreous carbon foams (porosities of 100 PPI,

80 PPI, and 45 PPI) using thermal decomposition of ammonium tetrathiorhenate and ammonium tetrathiomolybdate in a nitrogen atmosphere at elevated temperature. Bare carbon free-standing 3D foam, 3D  $\text{MoS}_2$ , and 3D  $\text{ReS}_2$  electrodes were characterized by scanning electron microscopy (SEM), by energy-dispersive spectroscopy (EDS) for elemental composition, X-ray photoelectron spectroscopy (XPS) for elemental composition and bonding information, and by voltammetry for electrocatalytic properties.

## 2. Materials and methods

### 2.1. Materials

Ammonium molybdate tetrahydrate, dimethylformamide (DMF), and ammonia were purchased from PENTA, Czech Republic. Ammonium perrhenate and chloroplatinic acid hexahydrate were obtained from Alfa Aesar, Germany. Nitrogen (99.9999%) and hydrogen sulfide (99.9%) were obtained from SIAD, Czech Republic. Reticulated vitreous carbon foams of various porosities were obtained from K. R. Reynolds, USA.

### 2.2. Apparatus

A JEOL 7600F field emission scanning electron microscopy (JEOL, Japan) was used to obtain SEM images. EDX was obtained via Oxford instruments x-stream2 and micsf+. X-ray photoelectron spectroscopy

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(XPS) samples were prepared by compacting a uniform layer of the material on a carbon tape. The XPS samples were measured by use of a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer in order to obtain survey and high-resolution Re4f, Mo3d, and S2p spectra.

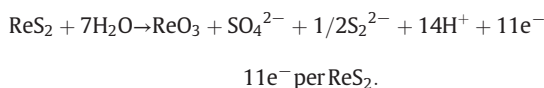
Voltammetric experiments were performed on Autolab PGSTAT 101 electrochemical analyzer (Eco Chemie, The Netherlands). Electrochemical experiments were performed in a voltammetric cell using a three-electrode configuration. The 3D samples were connected by a copper tape to the Autolab and used as working electrodes directly, a platinum electrode as an auxiliary electrode, and an Ag/AgCl electrode as a reference electrode. X-ray diffraction was carried out at a Bruker D8 Discoverer diffractometer in Bragg–Brentano parafocusing geometry. A CuK $\alpha$  radiation was used.

### 2.3. Calculations

The band structures and total energies of ReS<sub>2</sub> in a bulk form and two slabs with surfaces parallel (8 ReS<sub>2</sub> layers) and perpendicular (8 Re planes with different distance from the surface) to basal planes were calculated within density functional theory (DFT) using APW + lo basis set and generalized gradient approximation (GGA, PBE96 parametrization scheme) [18] for exchange correlation potential as implemented in the Wien2k software package [19]. The plane wave cut-off energy of 220 eV and the respective k-meshes 12  $\times$  13  $\times$  5, 12  $\times$  13  $\times$  1 and 1  $\times$  13  $\times$  5 for the bulk, basal plane slab and edge plane slab calculation were used. The two-dimensional character of the surface slabs was simulated by introducing a 15 Å thick vacuum in the corresponding direction ([001] and [100], respectively). All calculations were performed as non-spin polarized. The structure data for the bulk ReS<sub>2</sub> were adopted from Murray et al. [20]

Conversion of measured current to H<sub>2</sub> turnover (assuming 100% Faradaic efficiency) yields to H<sub>2</sub> turnover is 1.81  $\times$  10<sup>16</sup> H<sub>2</sub> s<sup>-1</sup> cm<sup>-2</sup> at -0.124 V. The anodic dissolution peak is shown in Fig. 2B, and a baseline corrected plot of the oxidation peak is present in Fig. 2C. Integral of peak of the LSV in Fig. 2B is 11.13 mC/cm<sup>2</sup>.

Assuming the reaction was:



Number of active sites:

$$(11.13 \text{ mC/cm}^2)(1\text{C}/1000\text{mC}) \left( \frac{6.241 \times 10^{18} \text{e}^-}{1\text{C}} \right) (1\text{ReS}_2/11\text{e}^-)$$

$$= 6.31 \times 10^{15} \text{ReS}_2/\text{cm}^2.$$

TOF at -0.124 V (5.81 mA/cm<sup>2</sup>)

$$(\text{Hturnover})(\text{cm}^2/6.31 \times 10^{15} \text{ReS}_2) = (1.81 \times 10^{16} \text{H}_2 \text{s}^{-1} \text{cm}^{-2})(\text{cm}^2/6.31 \times 10^{15} \text{ReS}_2)$$

$$= 2.87 \text{H}_2 \text{s}^{-1} \text{Re}^{-1}.$$

Assuming the random orientation of ReS<sub>2</sub> on GC electrode, we can calculate turnover frequency, assuming the monolayer coverage of ReS<sub>2</sub> on GC

$$(2.87 \text{H}_2 \text{s}^{-1} \text{Re}^{-1})(1\text{Re}_{\text{total}}/(1\text{Re}_{\text{surface}} \times 50\% \text{coverage})) = 5.74 \text{H}_2 \text{s}^{-1}/\text{Re}_{\text{surface}}.$$

### 2.4. Synthesis methods

Ammonium tetrathiomolybdate was prepared by passing hydrogen sulfide through a saturated solution of ammonium molybdate in concentrated ammonia. Crystals were separated by suction filtration and dried over KOH pellets in a vacuum desiccator. Vitreous carbon was soaked in 5 wt.% of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> in DMF and dried in vacuum

oven at 50 °C for 24 h. Ammonium tetrathiorhenate was prepared by passing hydrogen sulfide through 5 wt.% of NH<sub>4</sub>ReO<sub>4</sub> and 5 wt.% of ammonia for 12 h. Vitreous carbon foam was soaked in this solution and subsequently dried in a vacuum oven. Vitreous carbon foam coated with precursor was treated in a nitrogen atmosphere at 700 °C for 2 h. Platinum coated vitreous carbon foam was prepared by soaking in 5 wt.% solution of H<sub>2</sub>PtCl<sub>6</sub> and subsequent annealing at 700 °C for 2 h in a nitrogen.

## 3. Results and discussion

The morphology and elemental composition of carbon foam, 3D MoS<sub>2</sub> and 3D ReS<sub>2</sub> were studied by using SEM and EDS. As shown in Fig. 1, the micrographs present a free-standing 3D interconnected network of carbon foam for all samples (Figure A1–C1, and A2–C2). The SEM images of 3D MoS<sub>2</sub> and 3D ReS<sub>2</sub> exhibit bright surfaces, indicating the presence of MoS<sub>2</sub> and ReS<sub>2</sub> with an atomic number greater than that of carbon. EDS was used to obtain elemental maps and spectra of the samples, as shown in Fig. 1. The elemental maps for carbon foam, 3D MoS<sub>2</sub>, and 3D ReS<sub>2</sub> (Figure A3–C3) show the distribution of carbon, molybdenum, and rhenium. The results clearly show that rhenium and molybdenum are successfully coated onto the carbon foam. SEM/EDS spectra of individual electrodes are shown in Figure A4–C4. Fig. 1D shows photographs of the actual 3D electrodes. X-ray diffractogram of ReS<sub>2</sub> on GC foam is provided in Fig. 2A.

Both the composition and bonding information were obtained from XPS via survey spectra scan (Fig. 1E–G) and high-resolution spectra of Re4f, Mo3d and S2p (Fig. 1H–K) states. Compared with the carbon foam, 3D ReS<sub>2</sub> and 3D MoS<sub>2</sub> showed a Re4f peak around 43 eV, Mo3d peak around 230 eV, and S2p peak around 162 eV. For the high-resolution spectrum from 3D ReS<sub>2</sub>, the peaks shown at 41.9 eV (56.93 at.%) and 44.3 eV (43.04 at.%) are identified as Re4f<sub>7/2}^{4+}</sub> and Re4f<sub>5/2}^{4+}</sub>, respectively [21]; the peaks shown at 162.5 eV (61.9 at.%) and 163.7 eV (38.1 at.%) correspond to S<sup>2-</sup>. For 3D MoS<sub>2</sub>, the peaks shown at 229.4 eV (29.1 at.%) and 232.6 eV (28.2 at.%) are identified as Mo<sup>4+</sup> and the peaks at 232.9 eV (26.7 at.%) and 236 eV (21 at.%) as Mo<sup>6+</sup>. They also agreed with a previous study [22]. Additionally, from the wide scan of 3D MoS<sub>2</sub>, the ratio between Mo and S is 1:1.22 which also indicates that the prepared 3D MoS<sub>2</sub> might contain MoO<sub>x</sub>, where x = 2 or 3 depending on the oxidation state of Mo. Then, for the high-resolution S2p, the two peaks at 162.3 eV and 63.5 eV are caused by S<sup>2-</sup> for both 3D ReS<sub>2</sub> and MoS<sub>2</sub>.

The electrocatalytic properties of bare 3D glassy carbon, 3d MoS<sub>2</sub>, and 3D ReS<sub>2</sub> electrodes towards hydrogen evolution reaction (HER) were studied by linear sweep voltammetry (LSV). The voltammogram, shown in Fig. 1L, clearly indicates that the HER at 3D ReS<sub>2</sub> occurs at a much lower potential than that on 3D MoS<sub>2</sub> and carbon foam. We have recorded the potential at 10 mA/cm<sup>2</sup> for bare 3D glassy carbon foam, 3D MoS<sub>2</sub>, and 3D ReS<sub>2</sub> as -751 mV, -453 mV, and -336 mV, respectively. This indicates that 3D ReS<sub>2</sub> provides a lowering of overpotential by ~120 mV when compared to MoS<sub>2</sub>. When compared to Pt on 3D vitreous carbon foam (-185 mV), ReS<sub>2</sub> shows a slightly higher overpotential at current density of 10 mA/cm<sup>2</sup>. The ReS<sub>2</sub> electrode together with the Pt 3D electrode, exhibits the lowest overpotential for HER while the glassy carbon foam electrode exhibits the highest overpotential for HER. Assuming the random orientation of ReS<sub>2</sub> in the film coated on GC electrode, we can calculate turnover frequency, assuming the monolayer coverage of ReS<sub>2</sub> on GC [23], which yields 5.74 H<sub>2</sub> s<sup>-1</sup>/Re<sub>surface</sub> (see Fig. 2 and material and methods section). There is slight pre-wave at ReS<sub>2</sub> electrode, starting ~+200 mV. This pre-wave is reproducible and is present even after several reduction cycles. Interestingly, similar effects were previously observed in case of other 3D electrodes covered with WS<sub>2</sub> and MoS<sub>2</sub>; however, origin of such pre-wave is not known [24,25].

In order to get insight into the behavior of ReS<sub>2</sub>, we carried out DFT calculations. Compared to other TM dichalcogenides adopting CdCl<sub>2</sub>

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