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# Ni<sub>0.85</sub>Se as an efficient non-noble bifunctional electrocatalyst for full water splitting

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## ABSTRACT

In this letter, we reported hexagonal phase Ni<sub>0.85</sub>Se as a new bifunctional electrocatalyst for full water splitting, which was prepared through electrodeposition. The as-synthesized Ni<sub>0.85</sub>Se films supported on graphite substrate exhibited excellent activities for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). It needs overpotentials of 200 and 302 mV to drive 10 mA cm<sup>-2</sup> for HER and OER in 1.0 M NaOH, respectively, and shows competitive activity among non-noble electrocatalysts with strong durability. The marvellous performance of cost-effective Ni<sub>0.85</sub>Se in HER and OER enables it to serve as competitive bifunctional electrode in alkaline water electrolyzer.

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## Introduction

As the ever increasing energy consumption and continuous concerns for the environment, it is highly desirable to explore green and sustainable energy resources as alternatives to traditional fossil fuels [1]. Hydrogen is expected to be an ideal future fuel for its high heat of combustion and high energy capacity [2]. Moreover, the electrochemical water splitting reaction provides a convenient chemical method to directly convert electricity into chemical energy stored by hydrogen fuel [3], which makes electrochemical water splitting a potentially commercial application. The widely recognized optimal catalysts for water splitting are all noble metals and their ramifications, for example, platinum shows the best activity towards hydrogen evolution reaction (HER) and Ir/Ru oxides are the most efficient catalysts for oxygen evolution reaction (OER), but their wide-scale applications are limited

due to the scarcity and high cost [4–6]. Thus, it is of great significance to develop cost-effective counterparts as alternatives to precious HER and OER catalysts, particularly those based on earth-abundant elements.

Employing a bifunctional OER and HER catalyst in the water electrolyzer can simplify the system and lower the cost. Moreover, the low overpotential of the bifunctional electrocatalyst enhances the potential application of water electrolysis cell in large-scale production of hydrogen fuel. However, few bifunctional electrocatalysts have been investigated for overall water splitting. The metal oxides such as NiO [7], MnO<sub>x</sub> [8], Co<sub>3</sub>O<sub>4</sub> [9,10], ZnCo<sub>2</sub>O<sub>4</sub> [11], complex graphene–MnO<sub>2</sub>–NiCo<sub>2</sub>O<sub>4</sub> framework [12], MnCo<sub>2</sub>O<sub>4</sub> [13] and LiCoO<sub>2</sub> [14] show good catalytic activity and corrosion stability toward electrochemical OER in basic media, but poor activity toward HER. Many inexpensive catalysts consisting of earth-abundant elements have been considered as promising alternatives for HER catalyst [15,16]. Transition metal alloys

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have showed great potential [17,18], such as NiMo alloy, which is probably the most efficient HER electrocatalysts in alkaline solution [19]. Some transition metal derivatives also exhibit incredible HER performance, for example. CoPS has been recently reported as best HER catalyst in acid electrolyte [20]. However, very few of them have shown potential for harsh OER. It is thus necessary to develop a noble-metal-free bifunctional efficient catalyst for both HER and OER.

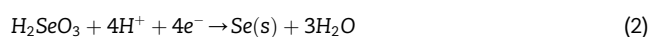
Consequently, various strategies have been pursued to develop inexpensive efficient bifunctional catalysts. (1) Fabricating electrocatalysts with nanocomposites and complex structures. CoMnO@CN superlattice was developed by a solvent evaporation-induced self-assembly method, where the ordered superlattice structure is beneficial to enhance reactive sites and charge transfer [21]. (2) Synthesizing composite catalysts with complex multicomponent, such as Bi<sub>2</sub>Te<sub>3</sub>@CoNiMo [22], N-doped graphene–NiCo<sub>2</sub>O<sub>4</sub> [23], Zn<sub>0.76</sub>Co<sub>0.24</sub>S/CoS<sub>2</sub> [24]. Those ternary compounds are benefited from synergetic effects of these transition metals. (3) Improving electrochemical active surface areas. Ni<sub>3</sub>S<sub>2</sub> arrays possess 3D nanostructure on large specific surface area support, which results in a higher number of exposed electrocatalytically active sites per unit geometric area [25–27]. These strategies have enriched bifunctional electrocatalysts for overall water splitting in basic media, but it is still highly significant to fabricate earth-abundant catalysts via simple and low cost approaches [28].

Transition metal chalcogenides (TMDs) catalysts have been reported as a group of high-performance HER catalysts based on earth abundant elements [29], many of them are not only benefit from their active metal sites, but also the distinct crystal phases. 1T metal phase MoS<sub>2</sub> and WS<sub>2</sub> are much more active for HER than their 2H semiconducting phase [30,31]. FeS<sub>2</sub>, NiS<sub>2</sub> and CoS<sub>2</sub> are typical metal pyrites with the metal atoms octahedrally bonded to neighbouring sulphur atoms, they exhibit activity toward HER as their general electrocatalytic properties [32,33]. For the specific nickel selenide family, cubic NiSe<sub>2</sub> [34–37] and related phases such as rhombohedral Ni<sub>3</sub>Se<sub>2</sub> [38], trigonal NiSe [39] have been discovered as favourable HER catalysts or even bifunctional catalysts. However, there are few reports on the electrocatalytic performance of hexagonal phase catalysts. Herein, in this letter, hexagonal phase Ni<sub>0.85</sub>Se directly grown on graphite substrate was successfully synthesized via the electrodeposition method. The Ni<sub>0.85</sub>Se catalyst had superior catalytic activity and durability for both HER and OER in strongly basic media. It achieved the current density of 10 mA cm<sup>-2</sup> for HER and OER in 1.0 M NaOH with the overpotentials at about 200 and 302 mV, respectively. The excellent catalytic activity is probably attribute to the metal vacancies in their hexagonal structure [40]. As a bifunctional catalyst, Ni<sub>0.85</sub>Se served as cathode and anode in a two-electrode system for overall water splitting in alkaline solution. The potential of 1.73 V was required to reach 10 mA cm<sup>-2</sup>, and it can maintain stable for over 48 h.

## Experimental

The Ni<sub>0.85</sub>Se catalyst was directly grown on graphite substrate (GS) by potentiostatic electrodeposition method. The

deposition bath was a 100 mL aqueous solution that consisted of 10 mM nickel (II) chloride, 10 mM selenium dioxide and 50 mM potassium chloride. The GS were used as working electrode, platinum wire and saturated calomel (SCE) served as counter electrode and reference electrode, respectively. The potentiostatic electrodeposition technology was conducted at -0.7 V vs SCE for 60 min. The deposition process was the following reactions (Eqs. (1)–(4)) [41,42]:



The synthesis process is illustrated in Fig. 1a. Firstly, the SeO<sub>2</sub> is hydrolysed to H<sub>2</sub>SeO<sub>3</sub> in the aqueous solution, then the H<sub>2</sub>SeO<sub>3</sub> is reduced to Se<sub>x</sub><sup>2-</sup> under the applied voltage. The Ni<sup>2+</sup> ions gather around the electrode surface and bond with Se<sub>x</sub><sup>2-</sup> ions to form amorphous NiSe<sub>x</sub> on the graphite surface. After the deposition, the NiSe<sub>x</sub>/GS was alternately washed with ultrapure water and ethyl alcohol, then dried under vacuum. Finally, the Ni<sub>0.85</sub>Se/GS sample was obtained after calcination of NiSe<sub>x</sub>/GS at 250–500 °C under N<sub>2</sub> atmosphere.

## Results and discussion

We chose typical Ni<sub>0.85</sub>Se/GS sample calcined at 400 °C to serve as representative example for further investigation, which showed stable crystal structure and best catalytic activity. The crystal structure and morphology of nickel selenide products were confirmed by XRD, SEM and TEM characterizations (see Supplementary Fig. S1 and Fig. S5a for SEM images and XRD patterns of NiSe<sub>x</sub> calcined at different temperatures). XRD patterns of Ni<sub>0.85</sub>Se/GS synthesized at 400 °C is shown in Fig. 1b. The diffraction peaks at 33.1, 44.9, 50.5, 60.2, 61.8 and 69.7° can be indexed to the (101), (102), (110), (103), (201), and (202) planes of Ni<sub>0.85</sub>Se (JCPDS 18-0888), respectively, which suggest the formation of Ni<sub>0.85</sub>Se with hexagonal structure [43,44]. Fig. 1c shows the morphology of Ni<sub>0.85</sub>Se grown on graphite substrate characterized by SEM. The graphite surface is fully covered with a porous film (Fig. S3). The average thickness of the Ni<sub>0.85</sub>Se film is about 7 μm (Fig. S2). TEM characterization was employed for further structural characterization in the low and high-resolution magnifications in Fig. 1d and e, respectively, along with the fast Fourier transformation pattern as inset. In Fig. 1d, it was found that the dispersed Ni<sub>0.85</sub>Se particles were about one hundred nanometers in diameter. In Fig. 1e, the well-resolved lattice fringe with interplanar distance of 2.70 Å can be indexed to the (101) plane of Ni<sub>0.85</sub>Se [45], thus the high resolution TEM image is in accord well with XRD data.

The XPS measurements were taken to confirm the valence and chemical composition of Ni<sub>0.85</sub>Se/GS sample synthesized at 400 °C. The XPS survey spectrum (see Supplementary Fig. S6) demonstrate the composition of Ni<sub>0.85</sub>Se with the peaks of C, O, Se and Ni. The peak located at around 285.0 eV is

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