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# Self-assembled CNT/$Ni_{0.85}Se$-$SnO_2$ networks as highly efficient and stable electrocatalyst for hydrogen evolution reaction

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ABSTRACT

For the first time, a novel porous and conductive $Ni_{0.85}Se$-based electrocatalyst, CNT/$Ni_{0.85}Se$-$SnO_2$ networks (CNSN), has been synthesized utilizing a facile solvothermal method. The CNSN exhibit much better hydrogen evolution reaction (HER) performance than bare $Ni_{0.85}Se$-$SnO_2$ nanoparticles (NSP) and bare $Ni_{0.85}Se$, with ultra-low Tafel slope of 33.2 mV $dec^{-1}$, which is comparable to that of commercial Pt/C electrocatalysts, a large cathode current density of 28.4 mA $cm^{-2}$ (at ~ −270 mV vs RHE), which is over 4 and 10 times larger than those of NSP (7.1 mA $cm^{-2}$), and bare $Ni_{0.85}Se$ (2.7 mA $cm^{-2}$), respectively. It also shows outstanding electrocatalytic stability even after 1500 CV cycles. The superior HER performances of CNSN can be attributed to its well-designed unique nanoarchitecture with high conductivity and rich porosity. $Ni_{0.85}Se$-$SnO_2$ nanoparticles are anchored on the porous networks constructed with highly conductive CNT, and adjacent $Ni_{0.85}Se$-$SnO_2$ nanoparticles are tightly connected to each other. As a result, it can not only guarantee strong reactive activity and abundant active sites due to its large specific surface area and rough surface, but also facilitate the charge transfer, resulting in the enhancement of electrocatalytic activity and stability. This work provides a rational structural design and a low-cost, facile synthesis method of transition-metal chalcogenide based electrocatalysts with good stability and high efficiency for hydrogen evolution reaction.

## 1. Introduction

Owing to the finite of fossil fuel, it is urgent to search for a resource-rich and eco-friendly energy [1–3]. Hydrogen is a good alternative and renewable clean energy [4,5]. Thus, as an efficient method of producing hydrogen, hydrogen evolution reaction (HER) has become a research hotspot [6]. It is well-known that the platinum (Pt) has outstanding electrocatalytic performance. However, the preciousness and scarcity of Pt have hindered industrial scale production of hydrogen, making it a great challenge to search a suitable candidate with comparable catalytic performances [7–10].

The transition-metal compounds (TMCs), such as FeP [11,12], CoP [13,14], $CoSe_2$ [15–20], $NiSe_2$ [21–24], $MoSe_2$ [5], $PtSe_2$ [25], $WSe_2$ [26,27], $WS_2$ [28], $ReS_2$ [29] and $ReSe_2$ [30] have caused great concern in academia [31]. Recently, many experimental researches have confirmed that Nickel selenides (NiSe and $NiSe_2$) are efficient electrocatalysts for HER [21,23,24]. As an important member of nickel selenides, $Ni_{0.85}Se$ also exhibits promising electrocatalytic potential due to its particular electronic configuration and plentiful unsaturated atoms, indicating that it has many electrocatalytic active sites and fast charge-transfer channels [22,32]. However, there are rare reports on electrocatalytic performance of $Ni_{0.85}Se$. In addition, in order to further improve the HER kinetics, $MX_2$ grown on a variety of materials including graphene oxide have been studied [15,16,33–39]. Meanwhile, the CNTs with ultra-high conductivity and great chemical stability has been broadly applied to optimize the electrocatalytic performance [19,21,40]. However, it is still challengeable to design a rational nanoarchitecture with high conductivity and abundant catalytic sites to further improve the

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HER performance of $Ni_{0.85}Se$-based electrocatalysts.

Herein, for the first time, the CNT/$Ni_{0.85}Se$-$SnO_2$ networks (CNSN) has been synthesized via a facile solvothermal method. The CNSN is constructed with $Ni_{0.85}Se$-$SnO_2$ nanoparticles embedded in CNT networks. Because of its special structure, CNSN display a great HER catalytic activity with an ultra-high electric current density of 28.4 mA cm$^{-2}$ (at ~ −270 mV vs RHE), a low onset potential of ~190 mV (vs RHE) and long-term stability. Particularly, the CNSN has a small Tafel slope of 33.2 mV dec$^{-1}$, which is much lower than those of previously reported $Ni_{0.85}Se$-based HER catalysts. In light of its excellent catalytic activity, the CNSN is promising as highly efficient electrocatalysts for hydrogen evolution reaction.

## 2. Experimental

### 2.1. Synthesis of the CNT@NiSn(OH)$_6$ nanocubes precursor

All the reagents are of analytical grade and used without further purification. A typical synthesis procedure of CNT@NiSn(OH)$_6$ precursor was prepared as follows. First, the CNTs were acidized via previous procedures. 400 mg acid-treated CNT was dispersed in 400 ml deionized (DI) water. Then, 3.16 g $SnCl_4\cdot 5H_2O$ and 2.04 g NaOH were added to above CNTs solution and stirred for 20 min at 70 °C, followed by the addition of 56 ml ammonia with stirring. After that, 200 ml solution of 0.045 M $NiCl_2\cdot 6H_2O$ was added into obtained solution with vigorous stirring for 20 min at 90 °C. After the mixture cooled down slowly at ambient temperature and stirred for 5 h. The precipitate was rinsed by centrifugation with ethanol and DI water, then dried by vacuum freeze drying for 12 h to obtain the precursor of CNT@NiSn(OH)$_6$. The synthesis procedure of bare NiSn(OH)$_6$ nanocubes was similar as that CNT@NiSn(OH)$_6$ except that the CNTs solution is replaced by DI water.

### 2.2. Synthesis of CNT/$Ni_{0.85}Se$-$SnO_2$ network

All the reagents are of analytical grade and used without further purification. 0.5 g CNT@NiSn(OH)$_6$ precursor was dispersed in 60 ml DI water and sonicated for 10 min. After that, 1 g Sodium selenite and 5 ml Hydrazine hydrate were added to above solution and stirred for 30 min. Then, the mixed solution was transferred into a 100 ml of Teflon-lined autoclave and kept at 140 °C for 22 h. After cooling to ambient temperature, the black precipitate was collected by centrifugation, washed with DI water and dried under vacuum at 60 °C for 12 h. Finally, the CNT/$Ni_{0.85}Se$-$SnO_2$ Network was harvested. The synthesis procedure of $Ni_{0.85}Se$-$SnO_2$ nanoparticles was similar as that CNT/$Ni_{0.85}Se$-$SnO_2$ except that the CNT@NiSn(OH)$_6$ precursor is replaced by NiSn(OH)$_6$ nanocubes.

### 2.3. Characterization

The crystal structure of CNSN was analyzed through X-ray diffraction (XRD, Rigaku diffractometer, 35 kV, 25 mA, 10° min−1 from 10° to 80°). The crystal morphology, size and structure were tested by transmission electron microscopy (TEM, Tecnai F20 at 200 kV) and field emission scanning electron microscopy (FESEM, JSM-7000F, JEOL). The Raman spectra was obtained from Raman microscopy (532 nm, Renishaw). In addition, the chemical compositions of CNSN and NSP were performed via X-ray photoelectron spectroscopy (XPS, Kratos XSAM 800, AI K$\alpha$ radiation).

### 2.4. Measurement of electrocatalytic properties

All hydrogen evolution reaction measurements, including cyclic voltammogram (CV), linear sweep voltammetry (LSV), electrochemical double-layer capacitances ($C_{dl}$) and electrochemical impedance spectroscopy (EIS) were performed in 0.5 M $H_2SO_4$ electrolyte by electrochemical station (CHI 660D). The saturated calomel electrode (SCE) as the counter and the graphite rod as the reference electrodes, respectively. Before the electrochemical measurements, the 0.5 M $H_2SO_4$ electrolyte was saturated with $N_2$ for 1 h. To prepare the tested electrode, 4 mg of CNSN was uniformly dispersed in 1 ml of ethanol/water (1:4), and the above solution was ultrasonicated for 20 min. After that, 60 μL Nafion (5% w/w in water and 1-propanol, Sigma-Aldrich) was added into the mixed solution with 30 min sonication. Then 5 μL of the above ink was dropped onto polished glassy carbon electrode with 3 mm in diameter. The NSP, bare $Ni_{0.85}Se$, bare $SnO_2$ samples and commercial 20 wt % Pt/c catalysts were prepared in same way as a comparison. The loading of the CNSN and other catalysts was about 0.285 mg cm$^{-2}$. All of the measurement potentials have been calibrated to reversible hydrogen electrode (RHE), $E$(RHE) = $E$ (RHE) + 0.255 V [15,28,41,42]. In this work, the onset potential is defined at the current density of 0.5 mA cm$^{-2}$ [15].

## 3. Results and discussion

The synthetic strategy of CNSN by a facile solvothermal method is schematically illustrated in Fig. 1. The crystalline structures of CNT@NiSn(OH)$_6$ and bare NiSn(OH)$_6$ precursors, the CNSN, NSP, bare $Ni_{0.85}Se$ and bare $SnO_2$ were performed by the X-ray diffraction (XRD) patterns. Fig. 2 (a) shows the patterns of the NiSn(OH)$_6$ nanocubes and CNT@NiSn(OH)$_6$ precursor. The XRD patterns reveals a typical NiSn(OH)$_6$ (PDF card 20−0795) phase with eleven typical peaks, which indicated that the result is consistent with the standard NiSn(OH)$_6$ nanocubes [43]. The (002) peak of CNT appears at 25.6° in CNT@NiSn(OH)$_6$. Fig. 2 (b) shows the patterns of the CNSN, NSP, bare $Ni_{0.85}Se$ and bare $SnO_2$. The XRD patterns of CNSN and NSP indicate that both the Sederholmite structure of $Ni_{0.85}Se$ (PDF card No.18−0888) and Cassiterite structure of $SnO_2$ (PDF card No.41−1445) can be corresponded. The XRD patterns have six characteristic peaks at 32.97°, 44.5°, 50.25°, 59.63°, 61.6° and 69.12°, corresponding to (101), (102), (110), (103), (201) and (202) of the Sederholmite structure of $Ni_{0.85}Se$ respectively [22]. The characteristic diffraction peaks are located at 26.49°, 33.77°, 37.85°, 38.88°, 51.67°, 54.66°, 57.72°, 64.63°, 65.86° and 71.17°, corresponding to (110), (101), (200), (111), (211), (220), (002), (112), (301) and (202) of the Cassiterite structure $SnO_2$, respectively [44]. In addition, the XRD diffraction peaks of CNTs cannot be obviously observed in the CNSN due to the characteristic peaks of CNTs are covered by that of $SnO_2$.

As shown in Fig. 3, the scanning electron microscopy (SEM) pictures exhibit the morphologies of CNSN, NSP and the precursor of bare NiSn(OH)$_6$ (Fig. S1 (a,b)) and CNT@NiSn(OH)$_6$ (Fig. S1 (c,d)). Fig. 3 (a−b) shows the synthesized NSP with particles size about of 300 nm. The SEM picture of CNSN is shown in Fig. 3 (c−d), and the CNSN show microsphere structure with particles size around of 100 nm and connects with the nearby NSP through the CNT in the form of conductive network. The CNT in the CNSN not only guarantee the outstanding electronic conductivity between adjacent NSP but also a good dispersity of NSP. The $Ni_{0.85}Se$-$SnO_2$ is present in CNSN in the form of smaller nanoparticles, which is beneficial to expose more HER active sites.

The precise crystal microstructure of CNSN was further tested by high-resolution transmission electron microscopy (HRTEM). As shown in Fig. 4 (a−b), the images clearly show that the NSP embedded in CNT networks, and the NS nanoparticles with a size about of 100 nm, which is consistent with observation from previous SEM images of CNSN. The HRTEM images of CNSN are showed in Fig. 4 (c−d). The lattice spacing of 0.27 and 0.336 nm are assigned to the (101) crystal plane of the Sederholmite structure $Ni_{0.85}Se$ and