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Jingyun Jiang,<sup>a</sup> Chuanyu Yan,<sup>a</sup> Xinhui Zhao,<sup>a</sup> Hongxia Luo,<sup>a</sup> Zhimin Xue,<sup>b</sup> and Tiancheng Mu<sup>\*a</sup>

As ionic liquids analogues or quasi-ionic liquids, deep eutectic solvents (DESs) have been applied in many fields in the past few years. Herein, a noval PEGylated DES composed of PEG 200 and thiourea was formed for the first time and was used for solvothermal synthesis of nickel cobalt sulfides. The structure and composition of the as-synthesized sulfides can be tuned by adjustment of the ratio of the reactants. The PEGylated DES plays multiple roles as solvent, shape-control agent, and sulfur source in the synthesis of the sulfides. Compared with traditional sulfuration routes, this proposed route is costeffective and energy-efficient by combining solvothermal synthesis and sulfuration process. The prepared sulfides were used as catalysts for electrochemical water oxidation and they exhibited excellent oxygen evolution reaction (OER) performance, especially for NiCo<sub>2</sub>S<sub>4</sub> with hierarchical pores. The demanding overpotential ( $\eta$ ) was 337 mV for the current density reaching 10 mA·cm<sup>-2</sup> and the Tafel slope was 64 mV·dec<sup>-1</sup> in an alkaline medium (1 M KOH) for NiCo<sub>2</sub>S<sub>4</sub>. In addition, NiCo<sub>2</sub>S<sub>4</sub> demonstrated a long-term stability with little deactivation after either thirty hours continuous operation or two thousand cycles and high Faradic efficiency of 95.8 %. Synergistic effects including relatively high Brunauer-Emmett-Teller area, abundant active sites, easy diffusion of electrolytes and oxygen gas, and strong structure integrity contribute to the high activity and long-term stability of the catalyst for OER. This study provides a new way for the synthesis of hierarchically structured metal sulfides for energy conversion and storage applications.

# Introduction

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Ionic liquids have been widely used in nanomaterials synthesis because of their unique physical and chemical properties, such as low volatility, low flammability, wide electrochemical window, high thermal stability, and extended hydrogen network.<sup>1-5</sup> As ionic liquids analogues or quasi-ionic liquids, deep eutectic solvents (DESs) can be prepared by mixing two components (usually the hydrogen bond donors and hydrogen bond acceptors) through the self-association effects. The melting points of the formed DESs are usually far below those of the individual components.<sup>6</sup> Prior to ionic liquids, DESs are particularly tractable, cheap, biodegradable and noncytotoxic.<sup>7</sup> Materials synthesis in DESs sometimes can result in interesting structures which are not easy to be obtained from other conventional fabrication routes.<sup>8,9</sup> Through the synthesis process, DESs could play multiple roles.<sup>10-12</sup> However, the synthesis of nanomaterials in DESs is less studied.

As a mimic of solar-to-chemical energy conservation

through photosynthesis in natural system, water splitting has attracted numerous attentions.<sup>13-17</sup> A typical water splitting reaction can be divided into two half reactions: the hydrogen evolution reaction (HER) at cathode and oxygen evolution reaction (OER) at anode; and the multi-electron transfer process associated with the breakdown of O-H bond and the formation of O-O bond in the OER limits the overall efficiency of water splitting.<sup>18-20</sup> Because of large overpotentials derived from the two half reactions, the electrochemically water splitting process is rarely used in industrial applications until now.<sup>21</sup> Thus, developing earth-abundant water oxidation catalyst for the OER with low overpotential, high energy efficiency, durability, and cost effectiveness is of great importance and has attracted tremendous research attention.<sup>20, 22-25</sup> Traditionally, commercially available Ru- and Ir-based oxides are considered as the state-of-the-art OER catalyst which can efficiently lower the overpotential and increase the reaction rate.<sup>14</sup> However, the high price and low natural abundance prevent their large scale production for the industrial scale electrolysis system. To reduce or even eliminate the use of the precious metal-based catalysts, considerable efforts have been made to synthesizing nonprecious metal catalysts with high efficiency for OER.<sup>26</sup> The promising alternatives for OER including oxides, hydroxides, sulfides, carbides, nitrides, and phosphides of first-row transition metal (such as Fe,<sup>22</sup> Co,<sup>20, 23, 27</sup> Ni,<sup>23, 28</sup> Mn,<sup>29</sup> and Cu<sup>30,</sup> <sup>31</sup>) and their alloys<sup>26, 32</sup> are usually prioritized because of their high activities. In particular, the multi-metal catalysts are

<sup>&</sup>lt;sup>a.</sup> Department of Chemistry, Renmin University of China, Beijing 100872, China. Tel: 86-10-6251492, E-mail: <u>tcmu@ruc.edu.cn</u>.

<sup>&</sup>lt;sup>b.</sup> Beijing Key Laboratory of Lignocellulosic Chemistry, College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China

Electronic Supplementary Information (ESI) available: IR spectra of DES; XRD pattern, morphology images, and N<sub>2</sub> absorption-desorption isotherms of the synthesized sulfides; polarization curve of the bare GC electrode; Chronoamperometry test; and other supplementary figures and tables. See DOI: 10.1039/x0xx00000x

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believed to be more active and stable due to the tailored electronic and surface properties of the host structure by introducing secondary metal ion.<sup>27</sup> Among the multi-metal based OER catalysts, Ni and Co-based samples have already been applied as OER catalysts because they are highly resistant to corrosion in alkaline aqueous solution and they have sufficient variable valence states.<sup>24, 33</sup>

Recently, nanostructured metal sulfides have been widely used in energy conversion, supercapacitors, and lithium storage devices for their excellent electrochemical activities.<sup>34</sup> Moreover, nickel cobalt sulfides are believed to have much higher conductivity than the related ternary nickel cobalt oxides because of their smaller band gap.<sup>35, 36</sup> Although the cobalt sulfides reported nickel exhibit promising electrochemical activities, the synthesis of those sulfides usually needs a complicated process, and the components of the fabricated sulfides are often complex, which leads to extra risk of uncertainty. Usually, nickel cobalt sulfides were synthesized by a two-step hydrothermal method including the formation of nickel cobalt oxides or carbonate hydroxides and further sulfurization by reacting with additional sulfide sources (sodium sulphide,<sup>36-38</sup> thiourea,<sup>39</sup> thioacetamide,<sup>40</sup> etc.). It is desirable to combine the two steps (solvothermal synthesis and sulfuration process) to reduce cost.

Liquid poly(ethylene glycol)s (PEGs, molecular weight < 800 g·mol<sup>-1</sup>) have been used as green solvents in various fields.<sup>41, 42</sup> We have developed PEGylated quasi-ionic liquid electrolytes and used as media for efficient electrodeposition of aluminum.<sup>43</sup> PEG 200 is an efficient shape-control agent for nanoparticles formation because its two –OH groups which can be selectively adsorbed on certain faces to increase the growth rate of these faces, and the steric hindrance effect to obtain the well assembled secondary and tertiary branches on the longer trunk.<sup>33, 44</sup> In addition, thiourea works as not only the sulfur source but also a bidentate ligand to form relatively stable metal-thiourea through the M-S bonds.<sup>39, 44</sup>

Herein, a novel PEGylated DES was developed and used for cost-effective one-step solvothermal synthesis of nickel cobalt sulfides (Fig. 1). The unique adaptability and flexibility of PEGylated DES make it possible for providing a powerful route for synthesizing metal sulfides and the composition and structure of the as-synthesized sulfide can be tuned. The synthesized nickel cobalt sulfides, especially NiCo<sub>2</sub>S<sub>4</sub>, exhibited excellent OER performance, long-term stability and a high Faradic efficiency. Deep eutectic solvothermal synthesis of hierarchically structured metal sulfides with the cheap and environment benign PEGylated DES acts as simultaneously solvent, shape-control agent, as well as sulfur source may support a new possibility in the development of highly efficient sulfides used for OER.



Fig. 1 Schematic representation of the formation of  $NiCo_2S_4$  in the multifunctional DES composed of PEG 200 and thiourea in the molar ratio of 2:1.

# **Results and discussion**

The PEGylated DES was obtained by simple mixing PEG 200 and thiourea in the molar ratio of 2:1 at room temperature. The formation of the PEGylated DES was confirmed by the Fourier Transform Infrared Spectroscopy (FTIR) analysis (Fig. S1a), <sup>1</sup>H NMR spectroscopy analysis (Fig. S1b) and differential scanning calorimetry (DSC) experiment (Fig. S1c). The characteristic absorption peaks of C-O-C, -OH, and -CH<sub>2</sub> stretching vibration derived from PEG 200,45 and -NH<sub>2</sub>, C-N stretching vibration derived from thiourea<sup>46</sup> were observed in the PEGylated DES (Fig. S1a). The slight shifts of -OH and -NH<sub>2</sub> stretching vibration peaks further prove the existence of interaction between PEG 200 and thiourea. In addition, as depicted in Fig. S1b, the chemical shift of hydroxyl hydrogen atoms on PEG moved downfield, which is attributed to the hydrogen bonding between the thiourea and the terminal alcoholic groups from PEG.<sup>43, 47</sup> DSC analysis (Fig. S1c) was used to assess the effect of adding thiourea to the PEG 200. The endotherms at 178  $^{\circ}\text{C}$  for thiourea and -58  $^{\circ}\text{C}$  for PEG 200 showed the onset melting point of thiourea and PEG 200, respectively. The onset melting point of the synthesized DES (PEG 200 : thiourea = 2 : 1) is -87  $^{\circ}$ C , lower than both PEG 200 and thiourea, which further proved the formation of DES.<sup>11, 48</sup> For better understanding the PEGylated DES, the viscosity (170.2 mPa·s<sup>-1</sup>) and conductivity (6.8  $\mu$ S·cm<sup>-2</sup>) were determined at 298.15 K. Nickel cobalt sulfides were synthesized through a one-step solvothermal synthesis in the synthesized DES composed of PEG 200 and thiourea in the molar ratio of 2:1. The detailed synthesis procedure can be found in the experimental section. Specially, the composition of sulfides can be tuned simply adjusting the ratio of the reactants (Table S1). In the synthesis process of the sulfides, PEG 200 is an efficient surfactant to control the shape of sulfides and thiourea is a sulfur source for in situ sulfuration. The metal chelate ions of thiourea with Ni<sup>2+</sup> and Co<sup>2+</sup> contribute to a high monomer concentration after the nucleation stage for further growth. The synergistic effects of PEG 200 and thiourea promote the special structure of sulfides. For comparison, ternary nickel cobalt oxide was synthesized in PEG 200 but without thiourea.

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To evaluate the crystallographic structure and phase purity of the prepared sulfides, X-ray diffraction (XRD) analysis was carried out and the results were shown in Fig. 2a and Fig. S2. The products are different with the variation of the precursor ratio, which could be verified by the XRD pattern. As depicted in Fig. 2a, at the molar ratio of  $Ni(NO_3)_2$  and  $Co(NO_3)_2$ of 1:2, the diffraction peaks of the product locate at 20 of 26.9°, 31.6°, 38.4°, 50.6°, and 55.3° which could be well indexed to the (220), (311), (400), (511), and (440) planes of the cubic NiCo<sub>2</sub>S<sub>4</sub> phase, respectively, which are in agreement with the standard XRD pattern of the cubic NiCo<sub>2</sub>S<sub>4</sub> phase (JCPDS card No. 43-1477).<sup>49</sup> The absence of other impurity peaks could be ascribed to the high purity of the sample. While at equimolar quantities of Ni(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub>, the diffraction peaks could be indexed to the mixture of Ni<sub>2</sub>CoS<sub>4</sub> (JCPDS card No. 24-0334)<sup>50</sup> and CoS<sub>2</sub> (JCPDS card No. 65-3322)<sup>51</sup>. In this regard, binary cobalt sulfide CoS<sub>2</sub> appears easier formation compared with nickel sulfide NiS<sub>2</sub>. Further increasing the molar ratio of  $Ni(NO_3)_2$  and  $Co(NO_3)_2$  to 2:1, the diffraction peaks could be indexed to Ni<sub>2</sub>CoS<sub>4</sub> (JCPDS card No. 24-0334).<sup>36, 40</sup> Likewise, single component Ni(NO<sub>3</sub>)<sub>2</sub> or Co(NO<sub>3</sub>)<sub>2</sub> in the DES could be indexed to the formation of the corresponding binary metal sulfides NiS<sub>2</sub> (JCPDS card No. 03-0734)<sup>52</sup> or CoS<sub>2</sub> (JCPDS card No. 65-3322), respectively (Fig. S2). Therefore, the formation of crystalline and highly purity nickel cobalt sulfides was proved by the XRD results. In addition, with the molar ratio of Ni(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> in PEG 200 of 1:2, the diffraction peaks were well in agreement with ternary metal oxide NiCo<sub>2</sub>O<sub>4</sub> (JCPDS card No. 02-1074).<sup>33</sup> Therefore, the prepared catalysts were named as NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, NiCo<sub>2</sub>S<sub>4</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> according to their composition, respectively.



**Fig. 2** a) XRD pattern of the hierarchically structured NiCo<sub>2</sub>S<sub>4</sub>, and XRD data was indexed to JCPDS (43-1477); XPS spectra of the prepared NiCo<sub>2</sub>S<sub>4</sub> sample: b) Co 2p, c) Ni 2p and d) S 2p. The XPS spectra were fitted according to the Gaussian fitting method.

To further study the near surface chemical compositions and oxidation states of  $NiCo_2S_4$ , X-ray photoelectron spectroscopy (XPS) analyses were performed. The existence of

# Co, Ni, and S elements in the sample was verified by full XPS spectrum in the 0–1000 eV range. The $CO^{2}p_{0}^{0.1}N^{3}2p_{0}^{-7}and^{1}2^{1}2p$ spectra are presented in Fig. 2b, 2c, and 2d, respectively. According to the Gaussian fitting method, two spin-orbit doublets (which can be contributed to the characteristic of Co<sup>2+</sup> and Co<sup>3+</sup>) and two shake-up satellites (Sat.) are observed in Fig. 2b. The peak located at 795.6 eV can be ascribed to Co $2p_{1/2}$ with a satellite at 800.9 eV, while the peak at 784.2 eV is related to Co $2p_{3/2}$ with a satellite at 779.3 eV.<sup>49, 53</sup> The spinenergy separation of Co 2p<sub>1/2</sub> and Co 2p<sub>3/2</sub> is higher than 15 eV which also proved the existence of Co<sup>2+</sup> and Co<sup>3+, 54</sup> Similarly, two spin-orbit doublets including peaks located at 855.6 eV and 873.1 eV are fitted to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ which can be owned to the characteristic of Ni<sup>2+</sup> and Ni<sup>3+</sup>, and two shakeup satellites are obtained from the Ni 2p spectra (Fig. 2c).55 Additionally, the S 2p spectra can be fitted to two main peaks and one shake-up satellite (Fig. 2d). The peak located at 163.6 eV is characteristic peak of metal-sulfide bonds, and the peak located at 161.2 eV is owned to the $S^{2-}$ in the low coordination. $^{35, 55, 56}$ According to the XPS analysis, $\mathrm{Co}^{2+}, \, \mathrm{Co}^{3+},$ $Ni^{2+}$ , $Ni^{3+}$ and $S^{2-}$ were observed in the near-surface of the synthesized NiCo<sub>2</sub>S<sub>4</sub> sample, which was consist with NiCo<sub>2</sub>S<sub>4</sub>.

The morphologies and structures of synthesized samples were investigated by scanning electron microscopy (SEM). As depicted in Fig. 3a, the as-prepared NiCo<sub>2</sub>S<sub>4</sub> is consisted of spherical sea urchin-like nanostructure with diameters around 1.9  $\mu$ m. The sea urchin-like morphology is composed of uniformly interconnected nanorods (uniform diameter around 70 nm and length of 300 nm) radially grown from the center (Fig. 3b). It could be speculated that the unique morphology might have a high surface area owing to the hierarchical structures. To recognize the components of NiCo<sub>2</sub>S<sub>4</sub>, elemental mapping was performed with energy-dispersive X-ray spectrometer (EDX) attached to the SEM instrument and the corresponding EDX elemental mapping (Fig. 3c) confirmed the presence of evenly dispersed Ni, Co, and S elements.



Fig. 3 SEM images of the sea urchin-like  $NiCo_2S_4$  at low magnification a) and high magnification b); c). EDX elemental mapping of Ni, Co, and S

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elements; d). TEM image of an individual NiCo<sub>2</sub>S<sub>4</sub>; e). HRTEM image of hierarchically structured NiCo<sub>2</sub>S<sub>4</sub> collected from the marked area in d); and f). HRTEM image and the corresponding lattice fringes of NiCo<sub>2</sub>S<sub>4</sub>.

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The detailed morphology and hierarchically structured NiCo<sub>2</sub>S<sub>4</sub> can be confirmed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), as shown in Fig. 3d-3f. An individual sea urchin like-NiCo<sub>2</sub>S<sub>4</sub> with a diameter of about 1.9  $\mu$ m is depicted in Fig 3d, which is in accordance with the SEM result. Afterwards, from the HRTEM image in Fig. 3e, the sea urchin-like NiCo<sub>2</sub>S<sub>4</sub> has hierarchically porous structure ranging from 1 nm to 20 nm. In addition, an HRTEM image taken from Fig. 3e (shown in the inset of Fig. 3f) confirmed the crystalline nature of NiCo<sub>2</sub>S<sub>4</sub>. The lattice fringes displayed in Fig. 3f including 0.241 nm and 0.235 nm could be, respectively, indexed to the (311) and (400) crystal planes, suggesting the formation of NiCo<sub>2</sub>S<sub>4</sub>. The special interconnected nanorod structure and the resulting mesoporous and microporous structures may create plentiful catalytic sites and promote the mass transportation in OER.<sup>57</sup>

The morphology of other samples was also studied by SEM and HRTEM, and the related results are given in Fig. S3-S7. Flower-like ternary metal oxide NiCo<sub>2</sub>O<sub>4</sub> with a mean diameter of about 3 µm was observed (Fig. S3a). And the petals of the flowers are made up of porous 2D nanosheets (Fig. S3b). The hierarchically structured NiCo<sub>2</sub>O<sub>4</sub> could be further confirmed by HRTEM images (Fig. S3c-3d). The as-synthesized Ni<sub>2</sub>CoS<sub>4</sub> is composed of nanorods with 100-150 nm wide and up to about 450 nm in length (Fig. S4). In addition, nanorods and nanoparticles were shown in the synthesized mixture of Ni<sub>2</sub>CoS<sub>4</sub> and CoS<sub>2</sub> (Fig. S5). Unlike ternary metal sulfides, the hierarchically structured binary metal sulfide (NiS<sub>2</sub> and CoS<sub>2</sub>) are composed of rough-surfaced spherical particles with similar sizes (Fig. S6-S7). The mean diameter of NiS<sub>2</sub> and CoS<sub>2</sub> was 150 nm and 240 nm, respectively. The lattice fringes depicted in the HRTEM images were well consistent with the former XRD pattern.

 $N_2$ absorption-desorption isotherms and the corresponding pore size distribution plots of the synthesized samples are displayed in Fig. 4 and Fig. S8-12. As shown in Fig. 4, NiCo<sub>2</sub>S<sub>4</sub> presents a type IV isotherm according to the rules set by Union of Pure and Applied Chemistry (IUPAC),<sup>58</sup> suggesting the nature of mesoporous material. And the sample has a relatively high Brunauer-Emmett-Teller (BET) surface area of 33.1  $\text{m}^2 \cdot \text{g}^{\text{-1}}$  with mean pore diameter of 8.93 nm. Besides, the absorption-desorption curve was used to introduce the pore size distribution by the BJH method and the result shows that the size of the pores ranges from 1 nm to 20 nm, which is in accordance with HRTEM image (Fig. 3e). The hierarchical porous NiCo<sub>2</sub>S<sub>4</sub> including mesopore and micropore may be in favor of the diffusion of the active species and release of gas.<sup>39, 59</sup> The N<sub>2</sub> absorption-desorption isotherms of other five samples are depicted in Fig. S8-12 and the corresponding parameters including BET area and mean pore diameter are shown in Table S1. Interestingly, it was observed that the BET area, the mean pore size and distribution of the hierarchical porous sulfides were associated with the

precursor of metal ion. For sulfide based samples, the BET area decreases in the following order: NiCo<sub>2</sub>S<sub>4</sub><sup>O|>1</sup>NiS<sub>2</sub><sup>39</sup>CNi<sub>2</sub>CoS<sub>4</sub><sup>2</sup> > CoS<sub>2</sub> > Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>. In addition, the pore distribution of all the samples is well consistent with the sizes of pores shown in HRTEM results.



**Fig. 4** Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of the NiCo<sub>2</sub>S<sub>4</sub>.

The electrocatalytic OER performance of the samples was determined in 1 M KOH solution at 5 mV·s<sup>-1</sup> using a three electrode electrochemical configuration with Ag/AgCl (3M KCl) as the reference electrode and platinum wire as the counter electrode. It should be noted that the working electrodes were obtained by the modification of the as-prepared samples (catalysts) on the simple glassy carbon (GC) electrode (not on metal foam, carbon cloth, or carbon paper electrodes with large supportive surface areas high non-Faradaic background current) utilizing the drop-casting method, respectively. For comparison, the OER performance of other four samples was also tested under the same conditions. Because of the effect of ohmic resistance, the as-measured reaction currents did not directly reflect the intrinsic performance of catalysts.<sup>19</sup> We applied an iR correction to all the original data for further analysis (Fig. 5).



Fig. 5 a) Polarization curves and b) Overpotentials of  $NiCo_2O_4$ ,  $NiS_2$ ,  $CoS_2$ ,  $NiCo_2S_4$ ,  $Ni_2CoS_4 + CoS_2$ , and  $Ni_2CoS_4$  modified GC electrodes in 1

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NiCo<sub>2</sub>S<sub>4</sub>@N/S

doped-rGO

 $Ni_1Co_1$ 

Co<sub>9</sub>S<sub>8</sub>/S-C-

800<sup>1</sup>

 $NiCo_2O_4$ 

β-Ni(OH)<sub>2</sub>

N doped CG<sup>2</sup>-

CoO

Cu₂O-Cu

Co<sub>3</sub>O<sub>4</sub> MTA<sup>3</sup>

IrO<sub>2</sub>

0.1 M

кон

0.1 M

KOH

1 M

кон

1 M

кон

1 M

кон

1 M

КОН

1 M

KOH

1 M

кон

1 M

кон

GC

GC

Cu

foam

Ni

foam

Ni

foam

230

250

290

240

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M KOH at 5 mV·s<sup>-1</sup> utilizing Ag/AgCl (3M KCl) electrode and Pt wire as the reference and counter electrode, respectively; c) Tafel plots obtained from polarization curves in a); and d) Nyquist plot of NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, NiCo<sub>2</sub>S<sub>4</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> electrocatalysts for the OER carried out under potential of 1.51 V (vs. RHE) and the fitting result was shown as solid traces.

The linear sweep voltammetry (LSV) curves on a reversible hydrogen electrode (RHE, all potentials related in this work were vs. RHE unless stated otherwise) scale are presented in Fig. 5a. In each LSV measurement, the voltage applied to the working electrode was linearly swept from 1.00 to 1.65 V. Fig. 5a indicates that all the modified GC electrodes showed high performance toward OER, whereas the bare GC electrode showed negligible OER performance (Fig. S13, the current density reached 0.3 mA·cm<sup>-2</sup> by applying 1.65 V). The substrate of the GC contributes little to the OER activity, implying that the catalysts are mainly responsible for the OER activity. The onset potential (the current density reached 1  $mA \cdot cm^{-2}$ ) of NiCo<sub>2</sub>S<sub>4</sub> modified GC electrode was 1.45 V versus RHE, which was much smaller than NiCo<sub>2</sub>O<sub>4</sub> (1.54 V), NiS<sub>2</sub> (1.54 V), CoS<sub>2</sub> (1.53 V), Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub> (1.52 V), and Ni<sub>2</sub>CoS<sub>4</sub> (1.55 V). In other words, the NiCo2S4 exhibited the lowest onset potential compared with other catalysts, suggesting its higher OER performance compared with other sulfides. Though hierarchical porous NiCo2O4 has larger BET areas, its OER performance was lower than NiCo2S4, which might be due to the bigger band gap existing in oxides.<sup>26</sup> Moreover, the higher activity of as-prepared NiCo2S4 is also evident from the smallest overpotential compared with recently reported metal oxides and sulfides at fixed current density. NiCo<sub>2</sub>S<sub>4</sub> exhibited an overpotential of 337 mV (Fig. 5b) at a fixed current density of 10 mA·cm<sup>-2</sup> which was lower than NiCo layered double hydroxide (367 mV),<sup>25</sup> N-doped 3D crumpled graphene-CoO (340 mV),  $^{60}$  and NiCo\_2O\_4 (360 mV).  $^{54}$  The synthesized NiCo\_2O\_4 required an overpotential of 377 mV to afford a current density of 10 mA·cm<sup>-2</sup>, which was 38 mV higher than that of NiCo<sub>2</sub>S<sub>4.</sub> A more detailed comparison was given in Table 1.

 Table 1 OER behaviors comparison between the synthesized catalysts

 and representative metal oxides and sulfides catalysts published in

 literature.

Catalysts	Electro	Subs-	${}^{4}\eta_{\text{onset}}$	⁵η	Tafel slope	Ref.
	-lytes	trate	(mV)	(mV)	(mV·dec⁻¹)	
NiCo <sub>2</sub> S <sub>4</sub>	1 M	GC	220	337	64.0	Ours
	КОН					
NiCo <sub>2</sub> O <sub>4</sub>	1 M	GC	333	377	91.0	Ours
	КОН					
NiS <sub>2</sub>	1 M	GC	296	413	94.0	Ours
	КОН					
CoS <sub>2</sub>	1 M	GC	308	428	103	Ours
	КОН					
Ni <sub>2</sub> CoS <sub>4</sub> +	1 M	GC	318	399	94.0	Ours
CoS <sub>2</sub>	КОН					
$Ni_2CoS_4$	1 M	GC	296	386	91.0	Ours
	КОН					

GC	-	<b>470</b> View Article Onli <b>[1</b> ] <sup>6</sup> DOI: 10.1039/C7GC01012E				
GC	-	399	87.3	[2] <sup>6</sup>		
GC	280	339	64.0	[3] <sup>6</sup>		
Ti foil	330	-	60.0	[4] <sup>5</sup>		

340

350

290

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[5]<sup>23</sup>

[6]<sup>60</sup>

[7]<sup>32</sup>

[8]<sup>20</sup>

[9]<sup>64</sup>

132

71.0

67.5

84.0

71.0

<sup>1</sup>S-C-800, S doped C obtained at calcination temperature of 800 °C; <sup>2</sup>Ndoped CG, N-doped 3D crumpled graphene; <sup>3</sup>MTA, microtube arrays; <sup>4</sup> $\eta_{onset}$ , onset overpotential, was donated as the overpotential at the current density of 1 mA·cm<sup>-2</sup>; <sup>5</sup> $\eta$ , overpotential at the current density of 10 mA·cm<sup>-2</sup>.

The superior OER performance of NiCo<sub>2</sub>S<sub>4</sub> could be attributed to several factors. Firstly, the closely packed arrays of large  $S^{2\text{-}}$  anions (larger than  $O^{2\text{-}}$  anions) with Ni and Co cations in various valence states ( $Ni^{2+}$ ,  $Ni^{3+}$ ,  $Co^{2+}$ , and  $Co^{3+}$ ) present in NiCo<sub>2</sub>S<sub>4</sub> (as shown in Fig. 2b-2d), resulting in more active site for efficient OER performance at a low activation potential.<sup>55</sup> Secondly, good electronic conductivity of Ni and Co facilitates electron transfer to the substrate. Thirdly, the hierarchically structure is beneficial for enhancing the OER performance because of the increasing active sites exposed in electrolyte and the easy release of O2 gas. In addition, the BET area of NiCo<sub>2</sub>S<sub>4</sub> was higher than that of other catalysts. Therefore, relatively high Brunauer-Emmett-Teller (BET) area, abundant active sites, easy diffusion of electrolytes and oxygen gas, and strong structure integrity contribute to the full use of the whole catalyst when performing the electrochemical reactions.

For better understanding the kinetics process, the corresponding Tafel plots of the catalysts were obtained from the polarization curves. Those Tafel plots were fitted to the equation:  $\eta = b \log j + a$ , where  $\eta$  is overpotential, j is the current density, and b is the Tafel slope. Sea urchin-like NiCo<sub>2</sub>S<sub>4</sub> possessed the lowest Tafel slope (64 mV·dec<sup>-1</sup>) compared with NiCo<sub>2</sub>O<sub>4</sub> (91 mV·dec<sup>-1</sup>), NiS<sub>2</sub> (94 mV·dec<sup>-1</sup>), CoS<sub>2</sub> (103 mV·dec<sup>-1</sup>), Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub> (94 mV·dec<sup>-1</sup>), and Ni<sub>2</sub>CoS<sub>4</sub> (91 mV·dec<sup>-1</sup>), and was even smaller than that of the reported IrO<sub>2</sub> (71 mV·dec<sup>-1</sup>), <sup>64</sup> implying its more favorable reaction kinetics for OER (Fig. 5c). The improved OER performance of NiCo<sub>2</sub>S<sub>4</sub> was originated from its short diffusion route and fast transportation for active species, and the easy release of the formed O<sub>2</sub> gas bubbles.

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Moreover, the reaction kinetics of these samples was investigated by electrochemical impedance spectroscopy (EIS) analyses and the corresponding results were displayed in Fig. 5d. The Nyquist plots were fitted with the simplified Randles equivalent circuit and presented in Fig. S14. The fitting impedance parameters including the uncompensated series resistance R<sub>s</sub>, the charge transfer resistance (R<sub>ct</sub>) which can be assigned to charge-transfer process of oxygen evolution at the catalyst interface, and the accompanying double-layer capacitance C<sub>dl</sub> were listed in Table S1. The R<sub>s</sub> values of the NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, NiCo<sub>2</sub>S<sub>4</sub>, CoS<sub>2</sub> + Ni<sub>2</sub>CoS<sub>4</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> were similar indicting that the experimental configuration was consistent. The R<sub>ct</sub> values increased in the following order: NiCo<sub>2</sub>S<sub>4</sub> (7.046 Ω·cm<sup>-2</sup>) < NiCo<sub>2</sub>O<sub>4</sub> (10.37 Ω·cm<sup>-2</sup>) < NiS<sub>2</sub> (17.70  $\Omega \cdot \text{cm}^{-2}$ ) < CoS<sub>2</sub> (32.68  $\Omega \cdot \text{cm}^{-2}$ ) < CoS<sub>2</sub> + Ni<sub>2</sub>CoS<sub>4</sub> (65.98  $\Omega \cdot \text{cm}^{-2}$ ) <  $Ni_2CoS_4$  (63.06  $\Omega$ ·cm<sup>-2</sup>). A fast charge transfer rate (which is characterized by the smallest R<sub>ct</sub> value) occurring at the NiCo<sub>2</sub>S<sub>4</sub> could be attributed to its abundant active sites and excellent electronic conductivity. This further led to the improvement of access of current on the electrode and the enhancement of the capability of charge transport.<sup>24</sup> The NiCo<sub>2</sub>S<sub>4</sub> had abundant electrocatalytic sites and large active surface area, which can be proved by the related double-layer capacitance (C<sub>dl</sub>). The data of C<sub>dl</sub> derived from the EIS analysis were listed in Table S1. The  $C_{dl}$  of NiCo<sub>2</sub>S<sub>4</sub> reaches 9.95  $\mu$ F·cm<sup>-2</sup>, which is higher than those of NiCo<sub>2</sub>O<sub>4</sub> (8.699  $\mu$ F·cm<sup>-2</sup>), NiS<sub>2</sub>  $(9,637 \ \mu F \cdot cm^{-2})$ ,  $CoS_2$   $(9.090 \ \mu F \cdot cm^{-2})$ ,  $Ni_2CoS_4$  +  $CoS_2$  (9.264) $\mu$ F·cm<sup>-2</sup>), and Ni<sub>2</sub>CoS<sub>4</sub> (9.008  $\mu$ F·cm<sup>-2</sup>) (shown in Table S1). Therefore, the NiCo<sub>2</sub>S<sub>4</sub> has more effective active sites for water oxidation compared with other mentioned electrocatalysts.<sup>28, 65, 66</sup>

In the view of practical application, long-term stability of the electrocatalysts is another important parameter. The chronopotentiometry (CP) experiment was used to evaluate the electrocatalytic durability of NiCo<sub>2</sub>S<sub>4</sub> for OER in 1 M KOH without iR compensation. As depicted in Fig. 6a, the overpotential of NiCo<sub>2</sub>S<sub>4</sub> was almost unchanged at the current density of 10 mA·cm<sup>-2</sup> for thirty hours, suggesting that the deep eutectic solvothermal synthesized NiCo<sub>2</sub>S<sub>4</sub> owned excellent stability for OER in alkaline media. The unique structure of hierarchical porous NiCo<sub>2</sub>S<sub>4</sub> ensured the easy release of the O<sub>2</sub> gas. As a result, the NiCo<sub>2</sub>S<sub>4</sub> behaved the necessary enhanced stability and durability for prolonged OER operation. After the CP test for thirty hours, the morphology of NiCo<sub>2</sub>S<sub>4</sub> was examined by SEM (Fig S15) and the result showed that its morphology was almost unchanged, indicting its structure stability. The long-term stability was further confirmed by the continuous cyclic votammogram scanning for two thousand cycles in 1 M KOH at a scan rate of 100 mV·s<sup>-1</sup> (Fig. 6b). As shown in Fig. 6b, there was only 4 % cathodic current loss, indicting the outstanding ability of  $NiCo_2S_4$  to endure accelerated electrochemical process. In addition, chronoamperometry (CA) test was performed at 1.6 V (vs. RHE) for five hours to obtain Faradic efficiency (FE) and the result indicated that NiCo2S4 modified GC electrode delivered stable OER current density of around 23 mA·cm<sup>-2</sup> (Fig. S16). The detailed calculation of FE is shown in the experimental section.

As shown in Figure 5f, the measured amount of oxygen washed good agreement with the theoretical amount calculated according to the transferred charge. The FE of 95.8% was obtained based on the experimental and theoretical amounts of the evolved  $O_2$  gas, implying that the produced charges were nearly consumed for OER (Fig. S17). CP and CA experiments of the other synthesized samples including NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> were performed and the results were displayed in Fig. S18. All the samples exhibited long-term stability.



Fig. 6 a) Chronopotentiometry test of OER by NiCo<sub>2</sub>S<sub>4</sub> modified GC electrode in 1 M KOH at a current density of 10 mA·cm<sup>-2</sup>; and b) Polarization curve of NiCo<sub>2</sub>S<sub>4</sub> modified GC electrode before (black line) and after 2000 cycles (red dashed line).

# Experimental

#### **Chemicals and Materials**

PEG 200, thiourea, nickel(II) nitrate hexahydrate, and cobaltous(II) nitrate hexahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd.. All chemicals were analytical grade and used as received without further purification. Milli-Q water of 18.2  $M\Omega \cdot cm^{-1}$  was used in all experiments.

# Synthetic procedures

Synthesis of NiCo<sub>2</sub>S<sub>4</sub>. In a typical synthesis process, the PEGylated DES was obtained by simply mixing polyethylene glycol 200 (PEG 200) and thiourea in the molar ratio of 2:1. Then, 10 mmol Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  (2.91 g) and 20 mmol Co(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  (5.82 g) were dissolved in 40 ml PEGylated DES to form a homogeneous solution. Following, the mixture was put into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was treated at 433.15 K and maintained for 16 h before cooling in air. The resulting precipitates were filtered and washed thoroughly with deionized (DI) water and ethanol for three times and then dried in air at 353.15 K for 12 h.

## Characterizations

The IR spectra were obtained by the couple of the attenuated total reflection (ATR-IR) equipment with the FTIR spectrometer (Prestige 21, Shimadzu, Japan, DTGS detector) in the range of 600 to 1500 cm<sup>-1</sup>. Solution 1H NMR experiments were performed on a Bruker DMX 300 NMR spectrometer (300 MHz) with d<sup>6</sup>-dimethyl sulfoxide as the standard. The data of chemical shifts were later processed by the MestReNova

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Program. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments-Waters LLC, USA) system at a heating rate of 10 °C·min<sup>-1</sup>. Thiourea was run in an aluminium pan in a sealed furnace from room temperature to 200 °C. PEG 200 was cooled to -70 °C before heating up to 20 °C, while, the prepared DES was cooled to -120 °C before heating up to 20 °C . The viscosity ( $\eta$ ) of the PEGylated DES was measured at 298.15 K using an Anton Paar DMA 5000M for five times and the average value was reported. The conductivity of the PEGylated DES was measured by using a conductivity meter (DDS-307A, Shanghai INESA Scientific Instrument Co., Ltd., China) for five times at 298.15 K. The deviation of the equipment was less than ± 0.5 %.

X-ray powder diffraction (XRD) measurements of the samples were performed with Shimadzu XRD-7000 X-ray diffractometer (Shimadzu, Japan) using Cu K radiation at a scanning rate of 1 °·s<sup>-1</sup>. The surface morphology and elemental composition of samples were analyzed by a field emission scanning electron microscopy (FESEM) (Hitachi SU8010, Hitachi High-technologies Corporation, Japan) equipped with an Oxford-Horiba Inca XMax50 energy dispersive X-ray (EDX) at an accelerating voltage of 5 keV and 15 keV, respectively. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted using a JEM-2100F field-emission TEM. For TEM and HRTEM experiments, the samples were prepared by dispersing the products in ethanol and dropping the suspension on a Cu microgrid. N<sub>2</sub> adsorption-desorption isotherms were obtained at 77 K on Belsorp-Mini II (BEL Japan Inc., Japan) after the sample was degassed in vacuum at 573 K for 4 h.

## Modification of electrode

The NiCo<sub>2</sub>S<sub>4</sub> modified glassy carbon (GC) electrodes were prepared by dispersing 1mg NiCo<sub>2</sub>S<sub>4</sub> in 0.5 mL water and 0.5 mL ethanol with 10  $\mu$ L Nafion solutions (5 %) to form homogeneous inks. Then, as prepared inks (5  $\mu$ L) was drop coating on GC electrode (3 mm) with a 0.07069 cm<sup>2</sup> area and then dried under the infrared lamp. This yielded a NiCo<sub>2</sub>S<sub>4</sub> powder loading weight of about 0.07 mg·cm<sup>-2</sup>. The bare GC electrode was polished with 10  $\mu$ m Al<sub>2</sub>O<sub>3</sub> powder, subsequently rinsed by water and sonicated in distilled water and ethyl alcohol. The NiCo<sub>2</sub>S<sub>4</sub> NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> modified GC electrodes were obtained in the same procedure.

#### **Electrochemical measurements**

The electrocatalytic activity of samples for OER was studied in 1 M KOH solution and recorded on a CHI 660E electrochemical station at ambient temperature. All tests were performed in a three-electrode electrochemical cell with an Ag/AgCl electrode (3M KCl) and a Pt wire as the reference electrode and counter electrode, respectively. The prepared NiCo<sub>2</sub>S<sub>4</sub>, NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> modified GC electrodes were used as the working electrodes to investigate their electrocatalytic activities toward OER. To enhance mass transport and remove generated gas bubbles on surface of the electrode, the electrolyte was stirred at a constant/fate of 300 rpm. The potential was calibrated against the reversible hydrogen electrode (RHE) in oxygen saturated electrolyte with a platinum wire as the working electrode. The related polarization curves shown in the article were calibrated after *iR* correction. The onset potential is defined as the potential at the current density of 1.0 mA·cm<sup>-2</sup> for OER.

The linear sweep voltammograms (LSV) curves of NiCo<sub>2</sub>S<sub>4</sub> were performed with a scan rate of 5 mV·s<sup>-1</sup> for OER in 1 M KOH. Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode from 0.1 kHz to 1000 kHz. The Faradic efficiency was obtained during the chronoamperometry test. The experimental evolved O<sub>2</sub> gas amount was measured by gas chromatography analysis (Ar carrier, molecule sieve 5A column, TCD detector).

## Conclusions

In summary, a novel PEGylated DES composed of PEG 200 and thiourea in mole ratio of 2:1 was developed and it was used for solvothermal synthesis of metal sulfides with uniform and hierarchical structure and tunable composition. The PEGylated DES plays multiple roles as solvent, shape-control agent, and reactant (sulfur source) in the synthesis of the metal sulfides. The XRD pattern of the sample confirmed the crystal structure and high purity of the as-synthesized metal sulfides. This proposed one-step route for the synthesis of metal sulfides is cost-effective and energy-efficient by combing solvothermal synthesis and sulfuration process together compared with traditional two-step (solvothermal synthesis and sulfuration) routes. Furthermore, the prepared nickel cobalt sulfides were used as catalysts for electrochemical water splitting and they exhibited excellent oxygen evolution reaction (OER) performance. The relatively high BET area and multi porous structure of sulfides increased the catalytic surface area and improved the transport property of electrons throughout the entire electrode. We also found that sulfides have an improved OER performance compared with the corresponding oxides. Among them, hierarchically structured ternary metal sulfide NiCo<sub>2</sub>S<sub>4</sub> exhibited best OER performance. Notably, the asprepared  $NiCo_2S_4$  catalyst exhibited low overpotential of 337 mV with the current density reaching 10 mA·cm<sup>-2</sup> and low Tafel slope of 64 mV·dec<sup>-1</sup> performing on the GC electrode. Moreover, the NiCo<sub>2</sub>S<sub>4</sub> catalyst also has excellent durability and high FE of 95.8%. The proposed PEGylated DES could be an excellent media to synthesis efficient electrocatalysts for OER and opens a new area in the synthesis of metal sulfides not only for water oxidation but also for other energy conversion and storage applications.

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PEGylated deep eutectic solvent was developed and used for one step solvothermal synthesis  $NiCo_2S_4$  for efficient oxygen evolution reaction.