Supporting Information

Combination-Decomposition Method to Synthesize Two-Dimensional Metal sulfide-amine Hybrid Nanosheets: A Highly Efficient Fe-Based Water Oxidation Electrocatalyst Guofeng Zhang^a, Qing Qin^a, Wenhao Luo^a, Yanxia Liu^a, Cen Jin^a, Jing Hao^a, Jing Zhang^a, Wenjun Zheng^{*ab}

Experimental section

Synthesis of 2D $FeS_{1.4}(Dmim)_{0.5}$ (Dmim = 1-n-butyl-2,3-dimethylimidazolium cation) hybrid nanosheets

In a typical procedure, 0.1 mmol FeCl₃.6H₂O and 0.3 g polyvinylpyrrolidone (PVP) were dissolved into 16 mL distilled water under stirring to form a transparent light yellow solution. Subsequently 2g 1-n-butyl-2, 3-dimethylimidazolium rhodanide ([Dmim]SCN) was added into the above homogeneous solution under continuous stirring, quickly obtaining a bright red precipitate. After stirring for 20 min, the total solution was transferred into a stainless-steel autoclave with a capacity of 20 mL, sealed and heated at 160 °C for 16 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant product was collected and washed with deionized water and anhydrous ethanol for several times. The final product was dried in a vacuum at 60 °C for 2 h. As for the time-dependent experiments, the resultant products were collected and washed only with water. The hybrid nanosheets based various ionic liquids were prepared just through replacing [Dmim]SCN with 1-n-butyl-3-methylimidazolium rhodanide ([Bmim]SCN) and 1-octyl-3-methylimidazolium rhodanide ([Omim]SCN) with other conditions unchanged. The temperature-dependent experiments were conducted with the same conditions as mentioned above except the hydrothermal treatment temperature change to 140 and 180°C.

Synthesis of FeS₂ nanosheets

The FeS₂ nanosheets were prepared by the further sulfidation of FeS_{1.4}(Dmim)_{0.5} nanosheets. In a typical procedure, when the last time washing of FeS_{1.4}(Dmim)_{0.5} nanosheets finished, the supernate was poured out and 5 mL anhydrous ethanol was added to the centrifuge tube, then the solution was transferred to a 20 mL crucible. After that, 64 mg elemental sulfur was added into the crucible followed by stirring for 2 min. At last, the crucible was transferred to tube furnace and heated at 600 °C for 2 h with heating rate of 2 °C min⁻¹ under Ar atmosphere. After cooling down to room temperature, the FeS₂ nanosheets were obtained.

Synthesis of Fe₇S₈ nanosheets

 Fe_7S_8 nanosheets were prepared through the aforementioned experiment procedure except without adding elemental sulfur.

Synthesis of Fe₂O₃ nanosheets

 Fe_2O_3 nanosheets were obtained by calcining $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets at 600 $^\circ C$ for 2 h in air.

Characterization

Powder X–ray diffraction (XRD) measurements were recorded on a Rigaku–Dmax 2500 diffractometer with Cu Ka radiation (λ =0.1518 nm). Scanning electron microscopy (SEM) images were performed with a JEOL JSM–6700F field emission scanning electron microscope (15 kV)

coupled with energy dispersive X–ray spectroscopy (EDS). Transmission electron microscpy (TEM) images were carried out on a Tecnai G2 F20 TEM. Atomic force microscopy (AFM) study was performed by means of Veeco DI Nano-scope IV system. X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Escalab 250Xi system. The thermogravimetric analysis (TGA) was performed on a NETZSCH produced TG/DTA thermal analyzer (STA 449F3) with a heating rate of 10 °C/min in nitrogen. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was conducted on Varian (720). Element analysis was characterized by Elementar Vario EL cube. Fourier transform infrared spectra (FTIR) were recorded on a Bruker produced TENSOR II spectrometer within the range of 400-4000 cm⁻¹ by ATR measurement.

Electrochemical Measurements

A typical catalytic run was carried out in a standard three electrode configuration using a rotating disk electrode (RDE) (PINE Research Instrumentation) at a rotation speed of 1600 rpm with a CHI 660D electrochemical workstation. The FeS_{1.4}(Dmim)_{0.5} nanosheets (other samples) coated 3 mm glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode with porous Teflon tip as the reference electrode. Unless otherwise specified, all potentials are reported versus RHE by converting the potentials measured versus Ag/AgCl according to the following formula $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$. The overpotentials (η) for OER are calculated based on the formula $\eta = E_{RHE} - 1.23$ V. Linear sweep voltammetry (LSVs) were measured in O₂ saturated 1.0 M KOH at a scan rate of 2 mV s⁻¹ to obtain the polarization curves. The stability tests were performed by chronoamperometry recorded at j = 10 mA cm⁻². Electrochemical impedance spectroscopy (EIS) measurements were performed at an overpotential of 350 mV with frequency from 0.1 to 100,000 Hz.

The fabrication of the working electrode was as follow: 3 mg of catalyst was dispersed in 0.96 mL of a mixture of deionized water and ethanol in a volume ratio of Vol _{water}: Vol _{ethanol} = 1: 3. Then, 40 μ L of Nafion solution (5 wt%, Sigma-Aldrich) was added followed by an ultrasonic process for about 20 min, obtaining a homogenous ink. 5 μ L of the dispersion was pipetted onto the GC electrode, which was dried at room temperature to obtain the catalyst film, with the catalyst loading of ~0.2 mg cm⁻².

The electrochemically active surface area (ECSA) was determined by measuring the capacitive current associated with double-layer charging from the scan rate dependence of the CVs. The CV measurements were performed in a non-Faradaic region of 0.2-0.3 V vs. Ag/AgCl at different scan rates (20, 40, 60, 80, 100 and 120 mV s⁻¹). The double layer capacitance (C_{dl}) was estimated by plotting the Δj = (ja - jc) at 0.25 V vs. Ag/AgCl against the scan rates, respectively, in which the liner slope is twice of the double layer capacitance C_{dl}.

Elements	N (% w)	С (% w)	H (% w)	S (% w)	Formulas
Before hydrothermal	19.42	45.99	5.7873	21.79	$C_{5.59}H_{8.5}N_{2.03}S_1$
After hydrothermal	7.88	30.11	4.78	25.45	$C_{4.48}H_{8.53}N_1S_{1.4}$

Tab. S1 Element analysis data of the product prepared before and after hydrothermal

Tab. S2 ICP-OES analysis results of elements Fe and S in the product prepared before and after hydrothermal

Elements	Fe (mg/kg)	S (mg/kg)
Before hydrothermal	63565.6	218180
After hydrothermal	320851	260116



Fig. S1 XRD pattern of the nanosheets obtained after 16 h hydrothermal process



Fig. S2 EDX spectrum of $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets, obtained by dropping the ethanol solution of freshly prepared $FeS_{1.4}(Dmim)_{0.5}$ nanosheets onto a piece aluminum foil. The sample was tested as soon as possible when just taken out from the vacuum drying chamber



Fig. S3 ATR measurement obtained FT-IR spectra of a) $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets, b) Fe_7S_8 and c) FeS_2 nanosheets, d) $[Fe(SCN)_6](Dmim)_3$ complex, e) [Dmim]SCN. Before measurements, the samples were washed with water and anhydrous ethanol for several times to completely remove possible organic group, and then dried in vacuum for 12 h.



Fig. S4 TG curve of $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets



Fig. S5 XPS survey spectrums of a) FeS_{1.4}(Dmim)_{0.5}



Forming mechanism study of FeS_{1.4}(Dmim)_{0.5} hybrid nanosheets

Fig. S6 SEM images of the intermediate products during the formation of the $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets at different reaction time of a) 1, b) 3, c) 5, d) 8, e) 12, f) 16 h. g) XRD patterns of the intermediate products of different reaction time, indicating a simultaneous process of decomposition of association and exfoliation of hybrid nanosheets. h) Schematic illustration of the proposed structure of the $FeS_{1.4}(Dmim)_{0.5}$ with $Dmim^+$ inserted into the $FeS_{1.4}$ layers. The yellow, green, blue, gray, white balls represent S, Fe, N, C and H atoms, and the red balls specially represent the hydrogen atom at the C2 position of the imidazole, which presents Lewis acidity.

In order to study the reaction mechanism, we have conducted a series of time-dependent morphology and phase evolution experiments (Fig. S6). Before loaded into the stainless-steel autoclave, a red precipitation was obtained immediately after adding [Dmim]SCN into the FeCl₃ aqueous solution, which was determined to be $[Fe(SCN)_6](Dmim)_3$ association complex (Tab. S1 and 2, Figure S3, 7-9). During the hydrothermal process, in the first hour, the solution was red with a red solid product similar to that before hydrothermal, which can't be dissolved into water but ethanol in ambient temperature (Fig. S10), indicating the partial dissolution and decomposition of the precursor through the hydrothermal process, in which the Fe³⁺ was reduced to Fe^{2+} by SCN⁻ as reported by Xu et al,¹ releasing Fe^{2+} , Dmim⁺ and S²⁻ for the formation of FeS1.4(Dmim)0.5. The product was ~300 nm nanoparticles (Fig. S6a), and the XRD pattern exhibited a broad peak at around $2\theta = 30^{\circ}$ (Fig. S6g), indicating the presence of amount of amorphous association complex, which further demonstrates the partial decomposition of [Fe(SCN)₆](Dmim)₃. As come to the third hour, a great deal of black product was obtained in thick plate morphology with numerous tiny and ultrathin nanosheets fluffily aggregated on the surface (Fig. S6b), and two new outstanding peaks appeared in the XRD pattern at around $2\theta = 9^{\circ}$ and 18° (Fig. S6g), indicating the formation of a type of new specie with lamellar structure.^{2,3} As for the XRD pattern of the product at 5 hour, the intensity of the peaks at around $2\theta = 9^{\circ}$ and 18° became stronger (Fig. S6g), indicating the stacking height perpendicular to the nanosheets enhanced, which may resulted from the huge surface energy of the tiny and thin nanosheets.⁴ As we can see from the SEM image (Fig. S6c), the surface of the thick bulk became denser and the tiny nanosheets became larger moreover began to exfoliate off from the parent plate, demonstrating the oriented attachment and coalescence of tiny nanosheets in the plane parallel to the nanosheets, which should resulted from the dense π - π stacking of imidazolium cations inserted into the layers of FeS_{1.4} (Fig. S6h).⁵⁻⁷ Based on the above result, we also can speculate that the occur of the exfoliation should be due to the irregular and lose lateral side of the nanosheets stacked thick plate and generated gas by the decomposition and reduction of SCN⁻, as well as the electrostatic repulsion between adjacent π conjugate layers (Fig. S6h). When the reaction processed to 8 h, numerous irregular interconnected nanosheets with sharp edge were obtained (Fig. S6d), indicating extended exfoliation and continuous growth of the nanosheets, besides, the dispersed small nanoparticles on the surface of the nanosheets manifested that there are still some association complex remain undecomposed, guaranteeing sufficient Fe²⁺ and S^{2-} for the further growth of the exfoliated nanosheets into regular shape. The XRD pattern (Fig. S6g) also demonstrated this point. With the reaction continued to process, the product obtained at 12 hour has exhibited perfect nanosheet morphology with relatively uniformed thickness and shape (Fig. S6e), the residual trace small nanoparticles and tiny nanosheets on the surface of the large nanosheet showed that the decomposition last a long time. The XRD pattern (Fig. S6g) indicated the continuous decrease of the stacking height perpendicular to the nanosheets and the nearly exhaust of the association complex. At last, through a 16 hours' process, the ultra-uniformed square-like FeS_{1.4}(Dmim)_{0.5} hybrid nanosheets were obtained (Fig. S6f), furthermore, the straight baseline of the XRD pattern (Fig. S6g) suggested the completely decomposition of the association complex. The whole process can be schematically illustrated as Fig. 1 in the main body. Interestingly, if continued increase the reaction time to 24 h, some huge irregular spheres in size for 5 μ m appeared (Fig. S12b), which demonstrated to be FeS₂ as shown in the XRD pattern (Fig. S12a). Then, we studied the influence of hydrothermal treatment

temperature on the phase and morphology of the final product (Fig. S13). In addition, PVP have restrained the anisotropic growth of $FeS_{1.4}(Dmim)_{0.5}$, rather than hindered the aggregation of nanosheets (Fig. S14). Besides, the amount of Ionic liquids 1-n-butyl-2, 3-dimethylimidazolium rhodanide have also significantly affected the synthesis of $FeS_{1.4}(mim)_{0.5}$ nanosheets (Fig. S15 and S16). Note that the lateral size and thickness of the nanosheets precursors can be easily modulated by changing the side chain lengths of cation of ionic liquids (Fig. S17-21).



Fig. S7 Optical photographs of A) the red precipitation produced by reacting [Dmim]SCN with $FeCl_3$, B) the dark red aqueous solution obtained by reacting KSCN with $FeCl_3$ in water

Interestingly, unlike to the reaction of KSCN with $FeCl_3$ in water obtaining a dark red solution, the reaction of [Dmim]SCN with $FeCl_3$ in water produced a bright red precipitation immediately, which slowly decomposition in the consequence hydrothermal process controlled the release of Fe^{2+} and S^{2-} , therefore determined the formation of well-defined hybrid nanosheets. For the most crucial reagent [Dmim]SCN, its cation part act as the organic part of hybrid nanosheets and anion part provided the sulfur source of the metal sulfide part. Furthermore, changing the length of side chain of imidazolium cation can easily modulate the lateral size and thickness of nanosheets.



Fig. S8 a) PXRD pattern and b-d) FESEM images of $[Fe(SCN)_6](Dmim)_3$ complex before hydrothermal process



Fig. S9 TG curve of [Fe(SCN)₆] (Dmim)₃ complex



Fig. S10 Optical photographs of the solution of [Fe(SCN)₆] (Dmim)₃ dissolved into Ethanol



Fig. S11 FESEM image of the particles observed in the other place of the prepared samples for the product of 3 h



Fig. S12 a) XRD pattern and b) SEM image of the sample obtained as the reaction time prolonged to 24 h



Fig. 13 Influence of hydrothermal treatment temperature on the phase and morphology of the final product: (a) XRD patterns; SEM images for the product obtained at (b) 140 $^{\circ}$ C, (c) 180 $^{\circ}$ C.

As we can see, if the hydrothermal treatment temperature was risen to 180 °C, the product contains plenty of FeS₂ (Fig. 13a), which is in the morphology of particle-aggregation (Fig. 13c). This phenomenon is in agreement with the usually reported results for the preparation of FeS₂. When lower the hydrothermal treatment temperature to 140 °C, the product showed similar XRD pattern to that of FeS_{1.4}(Dmim)_{0.5} (Fig. 13a), but with obvious steamed bread peak for amorphous product, indicating the difficult for the process of the reaction, which may be due to the high viscosity of the solution. The densely aggregated state of the product (Fig. 13b) also illustrates this point. So, an appropriate temperature is needed to guarantee the target phase and morphology, namely 160 °C.



Fig. S14 SEM images of $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanomaterials synthesized with various mass of PVP at 180 °C for 16 h: a) 0 g, b) 0.1 g, c) 0.3 g and d) 0.5 g



Fig. S15 SEM images of the samples obtained with various amount of ionic liquids addition for a) KSCN, b) 0.2 g, c) 0.6 g, d) 1.2 g. e) The corresponding XRD patterns



Fig. S16 Optical photographs of the reaction solutions of the (Dmim)SCN amount-dependent experiments before hydrothermal, a) KSCN, b) 1.2, c) 0.6, d) 0.2 g



Fig. S17 a, b) FESEM, c) TEM images and d) SAED pattern of as-synthesized hybrid nanosheets utilizing [Omim]SCN replace [Dmim]SCN as reaction reagent



Fig. S18 a, b) FESEM, c) TEM images and d) SAED pattern of as-synthesized hybrid nanosheets utilizing [Bmim]SCN replace [Dmim]SCN as reaction reagent



Fig. S19 XRD patterns of as-synthesized different hybrid nanosheets utilizing a) [Dmim]SCN, b) [Omim]SCN and c) [Bmim]SCN



Fig. S20 AFM image of the hybrid nanosheets obtained by replacing [Dmim]SCN with [Omim]SCN as reaction reagent



Fig. S21 AFM image of the hybrid nanosheets obtained by replacing [Dmim]SCN with [Bmim]SCN as reaction reagent



Fig. S22 a) PXRD pattern, b, c) FESEM and d, e) TEM images of Fe_7S_8 nanosheets synthesized by calcining $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets at 600 °C for 2 h under argon atmosphere. f) HRTEM image of the as-synthesized Fe_7S_8 nanosheets. The inserts located at up and bottom right corners showed the lattice spacing of (200) planes and SAED pattern of polycrystalline Fe_7S_8 nanosheets, respectively.



Fig. S23 a) PXRD pattern, b, c) FESEM and d, e) TEM images of FeS_2 nanosheets synthesized by the sulfuration of $FeS_{1.4}$ (Dmim)_{0.5} hybrid nanosheets using powdered sulfur at 600 °C for 2 h under argon atmosphere. f) HRTEM image of the as-synthesized FeS_2 nanosheets. The inserts located at bottom and up right corners showed the lattice spacing of (200) planes and SAED pattern of polycrystalline FeS_2 nanosheets, respectively.



Fig. S24 a) PXRD pattern, b, c) FESEM and d) TEM images of Fe_2O_3 nanosheets obtained by calcining $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets at 600 °C for 2 h in air.



Fig. 25 N₂ adsorption/desorption isotherms for a) $FeS_{1.4}(Dmim)_{0.5}$, b) FeS_2 , c) Fe_7S_8 and d) Fe_2O_3 . e) The corresponding pore size distributions calculated by the BHJ method from the adsorption branches. f) Summary of the specific surface areas and pore volumes for these four samples.

The BET experiment was conducted to observe their specific surface areas and Pore-size distributions, which result was shown in Fig. x. As we can see, these four samples showed similar

isotherms types, with some difference in the intermediate pressure section, which may be induced by different heat treatment process. The corresponding pore size distributions indicate the dominated mesopores formation in the samples. In addition, the specific surface areas for these four samples also differed a little.



Fig. 26 CV curves of these four samples obtained at a scan rate of 10 mV s⁻¹.



Fig. S27 Nyquist plots of FeS_{1.4}(Dmim)_{0.5} recorded at various overpotentials



Fig. S28 CVs performed at various scan rates (20, 40, 60, 80, 100, and 120 mV s⁻¹) from 1.223 to 1.323 V vs. RHE for a) $FeS_{1.4}(Dmim)_{0.5}$, b) FeS_2 , c) Fe_7S_8 , and d) Fe_2O_3



Fig. S29 CV (sweep rate 50 mV s⁻¹) of FeS_{1.4}(Dmim)_{0.5} measured in 1 M KOH



Fig. S30 TOF values calculated from the current at an overpotential of 350 mV for different catalysts



Fig. S31 High-resolution a) Fe 2p and b) S 2p of the $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets before (top) and after (bottom) electrolysis, c) O 1s XPS spectra after electrolysis.



Fig. S32 a) XRD patterns of the $FeS_{1.4}(Dmim)_{0.5}$ hybrid nanosheets before (top) and after (bottom) electrolysis, b, c) SEM images after electrolysis.

To improve our understanding of the nature of the catalyst, XPS analyses were performed on the samples after a 12 h chronopotentiometric responses experiment (Fig. S31). As we can see, after the chronopotentiometric responses experiment, the intensity of the low-energy peaks of Fe and S significantly decreased and the peaks corresponding to oxidized Fe species shifted to higher binding energies, indicating that further surface oxidation occurred resulting in the formation of Fe³⁺ species such as FeOOH and Fe(OH)₃ during catalysis, which was also illustrated in the O 1s

XPS spectra. In addition, the SEM images indicate the surface of the nanosheets became rough, which may also be induced by the further surface oxidation. Note that, after catalysis, the main phase was unchanged and the morphology maintained well, indicating the excellent stability of the material.



Fig. S33 Performance comparison for the three hybrid nanosheets obtained with different ionic liquids: (a) Polarization curves and (b) corresponding Tafel plots. The polarization curves were obtained at a scan rate of 2 mV s⁻¹. (c) Nyquist plots obtained at overpotential of 350 mV. (d) Chronopotentiometric curves recorded with a constant current density of 10 mA cm⁻² for about 12 h.



Fig. S34 Performance comparison for the three hybrid nanosheets obtained with different ionic liquids: (a) Polarization curves and (b) corresponding Tafel plots. The polarization curves were obtained at a scan rate of 2 mV s⁻¹. (c) Nyquist plots obtained at overpotential of 350 mV. (d) Chronopotentiometric curves recorded with a constant current density of 10 mA cm⁻² for about 12 h.



Fig. S35 CVs performed at various scan rates (20, 40, 60, 80, 100, and 120 mV s⁻¹) from 1.223 to 1.323 V vs. RHE for a) $FeS_{1.4}(Dmim)_{0.5}$, b) $FeS_{1.4}(Bmim)_{0.5}$ and c) $FeS_{1.4}(Omim)_{0.5}$; d) The plots of current densities against scan rates. Δj is the difference between anodic and cathodic current densities at a potential of 1.273 V vs. RHE.

Electrocatalyst	Electrolyte	J at η=348 mV (mA cm ⁻²)	Ref
$FeS_{1.4}(Dmim)_{0.5}$	1 M KOH	10	This work
$Fe_{0.5}V_{0.5}$	1 M KOH	~7	[8]
Nafion/hydrous iron oxide	1 M NaOH	<1	[9]
Amorphous Fe_2O_3	0.1 M KOH	<0.8	[10]
α -Fe ₂ O ₃	0.1 M KOH	0	[10]
FeS _x	0.1 M KOH	<0.5	[11]
FeOx	0.1 M KOH	0	[11]
Fe	0.1 М КОН	0	[11]
Amorphous FeOOH	1 M Na ₂ CO ₃	<1	[12]
Fe-based film	0.1 M phosphate buffer pH 7	0	[13]
MnOx	0.1 M phosphate buffer pH 7	0	[14]
MnO	1 M NaOH	<1	[15]
MnO ₂	1 M NaOH	<1	[15]
Mn ₃ O ₄	1 M NaOH	<4	[15]
LiMnP ₂ O ₇	0.5 M phosphate buffer pH 7	0	[16]

 Tab.S3 Electrocatalytic activity comparison with various iron-based compounds from some literatures

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