Electronic Supplementary Information

Deep eutectic-solvothermal synthesis of nanostructured Fe₃S₄ for electrochemical

N₂ fixation under ambient conditions

Xinhui Zhao,^a Xue Lan,^a Dongkun Yu,^a Hui Fu,^{*b} Zhimin Liu,^c and Tiancheng Mu^{*a}

^a Department of Chemistry, Renmin University of China, Beijing 100872, China. E-mail: tcmu@ruc.edu.cn; Tel: +86-10-62514925.

^b College of Science, China University of Petroleum, Qingdao 266580, Shandong, China. E-mail: fuhui@upc.edu.cn

^c Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Table of the contents

- 1. Experiment Section
- 2. Supplementary Figures
- 3. Supplementary Tables
- 4. Supplementary References

Experiment Section

Chemicals

Polyethylene glycol 200 (PEG 200, AR), ammonium chloride (NH₄Cl, AR), ethyl alcohol (C₂H₅OH, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid (HCl, 35.0-38.0%) was obtained from Beijing Chemical Works. Salicylic acid (C₇H₆O₃, 99.5%), sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O, 99.0%), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O, 99.0%), sodium hypochlorite solution (NaClO, available chlorine 4.0%) were purchased from Macklin Ltd. Thiourea (CH₄N₂S, 99.0%), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, 99.5%), nickel(II) chloride hexahydrate (NiCl₂·6H₂O, 99.5%), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, 99.5%) and p-dimethylaminobenzaldehyde (C₃H₁₁NO, 99.0%) were bought from J&K Ltd. Carbon paper electrode (Toray, THP-H-60) was purchased from Alfa. 5 wt. % Nafion solution and 212 Nafion membrane were obtained from Dupont. Nitrogen (N₂, 99.99%) was bought from Beijing Beiwen Gas factory (Beijing, China). All chemicals were of analytical grade and used as received without further purification. Milli-Q water of 18.2 MΩ cm⁻¹ was used in all experiments.

Synthesis of Fe₃S₄ nanosheets

In a typical synthesis process, the PEG based DES was obtained by simply mixing PEG 200 and thiourea in the molar ratio of 2: 1. Unless otherwise stated, the PEG based DES was prepared in 2: 1 molar ratio of PEG 200 and thiourea. Then, 5 mmol FeCl₂·4H₂O (0.994 g) was dissolved in 40 ml PEG based DES under oxygen-free conditions. Next, the mixture was placed into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was treated at 200 °C and maintained for 16 h before cooling in the air. The resulting precipitates were washed thoroughly with deionized (DI) water and ethanol three times and then dried in air at 60 °C for 12 h.

Synthesis of NiS₂ nanosheets

 NiS_2 nanosheets were prepared using the same procedure, except with $NiCl_2 \cdot 6H_2O$ (5 mmol, 1.188 g) as metal precursor.

Synthesis of CoS₂ nanosheets

 CoS_2 nanosheets were prepared using the same procedure, except with $CoCl_2 \cdot 6H_2O$ (5 mmol, 1.190 g) as metal precursor.

Characterizations

The IR spectra were obtained by coupling of the attenuated total reflection (ATR-IR) equipment with the FTIR spectrometer (Prestige 21, Shimadzu, Japan, DTGS detector) in the range of 600 to 4500 cm⁻¹. Solution ¹H NMR experiments were performed on a Bruker DMX 300 NMR spectrometer (300 MHz) with d⁶-dimethyl sulfoxide as the standard. The chemical shift data were later processed by the MestReNova 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⁻¹. Thiourea was run in an aluminum 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. Thermal gravimetric analysis (TGA) was conducted by the instrument (Q50, TA Instrument Company, America). The viscosity (n) of the PEG based DES was measured at 298.15 K using an Anton Paar DMA 5000 M for five times and the average value was reported. The conductivity of the PEG based 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%.

The XRD patterns of the samples were recorded using an X-ray diffractometer (Rigaku D/Max-2500) using Cu K α as X-ray radiation (λ = 1.5418 Å) under 40 kV and 30 mA. Data were collected in Bragg-Brettano mode using 0.02° divergence with a scan rate of 2° min⁻¹. The SEM images, EDS spectra and elemental mapping images of the samples were acquired using a Hitachi SU 8010 field emission scanning electron microscope coupled with energy dispersive X-ray spectroscopy operated at 15.0 kV. The samples were prepared by dropping catalyst powder dispersed in isopropanol onto 300 nm silicon dioxide-coated silicon wafer (Zhejiang Lijing Technology Corp., China) using micropipettes and were dried under ambient conditions. The TEM patterns were prepared by dropping catalyst powder dispersed in isopropanol onto using a JEM-1011 transmission electron microscope at 100.0 kV. The samples were prepared by dropping catalyst powder dispersed in isopropanol onto using a JEM-1011 transmission electron microscope at 100.0 kV. The samples were prepared by dropping catalyst powder dispersed in isopropanol onto using a JEM-1011 transmission electron microscope at 100.0 kV. The samples were prepared by dropping catalyst powder dispersed in isopropanol onto carbon-coated copper TEM grids (Beijing Zhongxing Braim Technology Corp., China) using micropipettes and were dried under ambient conditions.

conducted using a FT Bruker RFS 106/S spectrometer equipped with a 532 nm laser. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al K α radiation. The 500 μ m X-ray spot was used for SAXPS analysis. The base pressure in the analysis chamber was about 3×10^{-9} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing in XPS experiments. UV-vis experiments were performed on a UV-3600 Plus UV-Vis-NIR Spectroscopy (Shimadzu Corp., Japan).

Computational details

First-principles calculations were performed using the DFT with the projector augmented wave pseudo potentials as implemented in the Vienna Ab intio Simulation Package¹. The exchange-correalition functional was the generalized gradient approximation with the Perdew-Burke-Ernzerhof². The cutoff energy the plane wave-basis expansion was set to 400 eV and the atomic relaxation was continued until the forces acting on atoms were smaller than 0.05 eVÅ⁻¹. The Brillion zone was sampled with $1 \times 1 \times 1$ Monkhorst-Pack k-point mesh, and the Gaussian smearing of σ was 0.05 eV. The van der Waals interaction was taken into account within DFT+U[3-5](U_{eff}=3.4eV for Ni and Co, U_{eff}=3.29eV for Fe). The surfaces are represented as slabs, periodically repeated in the z direction perpendicular to the surface and separated from their images by a 10 Å vacuum gap. The 4-layer slabs are used to describe the surfaces, with two bottom layers being fixed in the bulk position, and the top two layers and adsorbed N₂ are allowed to fully relax.

Electrochemical measurements

Before NRR tests, the Nafion membrane was pretreated by heating it in H_2O_2 (5%) aqueous solution at 80 °C for 1 h and ultrapure water at 80 °C for another 1 h, respectively. The electrochemical experiments were conducted on CHI 660E electrochemical workstation by using a three-electrode configuration with Fe₃S₄ working electrode, Pt gauze counter electrode and Ag/AgCI (saturated KCI electrolyte) reference electrode, respectively. All potentials were converted to reversible hydrogen electrode (RHE). Typically, 6 mg of catalyst powder was dispersed in 1 mL mixture of water and ethanol (1:1, v/v) and then 20 µL of 5 wt. % Nafion solution was added. The suspension was immersed in an ultrasonic bath for 30 min to prepare a homogeneous ink. The working electrodes were prepared by depositing 50 μ l catalyst ink onto 1x1 cm² carbon paper electrode (catalyst loading: ~0.30 mg cm⁻²).

For electrochemical NRR, potentiostatic tests were carried out in N₂ saturated diluted hydrochloric acid electrolyte (pH = 1, 50 mL), which was bubbled with N₂ for 30 min before the measurement. A two-compartment cell with three-electrode configuration was separated by Nafion membrane. Pure N₂ was continuously fed into the cathodic compartment with a properly positioned sparger so that the whole cathode was hit by the gas bubbles during the experiments. The potentiostatic NRR tests are conducted at desired conditions for 2h. Unless otherwise stated, all experiments were performed at ambient temperature (25 ± 2 °C) and electrode potentials were converted to the RHE scale using E(RHE) = E(Ag/AgCl) + 0.197 V + 0.059 * pH.

Determination of ammonia

Concentration of produced ammonia was spectrophotometrically determined by the indophenol blue method with modification.³ First, 2 mL aliquot of the solution was removed from the electrochemical reaction vessel. Then, 2 mL of a 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, followed by addition of 1 mL of 0.05 M NaClO and 0.2 mL of an aqueous solution of 1 wt % C₅FeN₆Na₂O·2H₂O (sodium nitroferricyanide dihydrate). After 2 h at room temperature, the absorption spectrum was measured using an ultraviolet-visible spectrophotometer. The formation of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentration–absorbance curves were calibrated using standard NH₄Cl solution with NH₃ concentrations of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 µg mL⁻¹ in 0.1 M HCl. The calibration curve below was used to calculate the NH₃ concentration. The fitting curve ($\gamma = 0.338x + 0.016$, R² = 0.999) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.

Determination of hydrazine

The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp.⁴ A mixture of *p*-dimethylaminobenzaldehyde (5.99 g), HCI (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Calibration curve was plotted as follow: First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydratenitrogen 0.1 M HCl solution in colorimetric tubes; Second, making up to 5 mL with 0.1 M HCl solution; Third, adding 5 mL above prepared color reagent and stirring 10 min at room temperature; Fourth, the absorbance of the resulting solution was measured at 455 nm, and the yields of hydrazine were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using standard hydrazine monohydrate solutions with N₂H₄ concentrations of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 µg mL⁻¹ in 0.1 M HCl. The calibration curve below was used to calculate the N₂H₄ concentration. The fitting curve (y = 0.515x + 0.013, R² = 0.999) shows good linear relation of absorbance value with N₂H₄ concentration by three times independent calibrations.

¹⁵N isotope labeled experiment

The ¹⁵N isotope labeled experiment was carried out using ¹⁵N₂ as the feeding gas in 0.1 M HCl electrolyte. After electrolysis at -0.4 V vs. RHE for 2 h, the obtained NH4⁺-contained electrolyte was detected by using ¹H NMR spectroscopy (Bruker Avance III 400 MHz).

Faradic efficiency

The Faradic efficiency (FE) was calculated from the total charge *Q* passed through the cell and the total amount of NH₃ produced. The total amount of NH₃ produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH₃ molecule, the Faradaic efficiency can be calculated as follows:

$$FE = \frac{3F * c(NH_3) * V}{17 * Q}$$

where *F* is the Faraday constant (96485 s A mol⁻¹), $c(NH_3)$ is the measured NH₃ concentration, *V* is the volume of electrolyte.

The rate of NH₃ formation was calculated using the following equation:

$$v(NH_3) = \frac{c(NH_3) * V}{m * t}$$

Where *t* is the reduction reaction time and *m* is the catalyst mass.



Fig. S1. DSC curves for a) PEG 200 and thiourea, b) PEG based DES, and c) phase diagram of PEG 200, thiourea and DES. The PEG based DES was prepared by mixing PEG 200 and thiourea at different molar ratio. The PEG based DES attaches eutectic point (-89 °C) at 2: 1 molar ratio of PEG 200 and thiourea.



Fig. S2. a) TGA curve, b) IR spectrum and c) H¹ NMR spectrum of PEG 200, thiourea and PEG based DES in 2: 1 molar ratio of PEG 200 and thiourea.



Fig. S3. XRD pattern of as-obtained Fe_3S_4 nanosheets.



Fig. S4. EDS spectrum of the as-obtained Fe_3S_4 nanosheets. The stoichiometric proportion of Fe and S is around 3: 4.



Fig. S5. a) N_2 adsorption/desorption isotherms, and b) corresponding pore size distribution of Fe_3S_4 nanosheets.



Fig. S6. XPS spectrum for the Fe_3S_4 nanosheets.



Fig. S7. Raman spectrum of Fe_3S_4 nanosheets.



Fig. S8. Quantitative determination of NH_3 generated by the as-prepared Fe_3S_4 nanosheets.



Fig. S9. Absolute calibration of the indophenol blue method for estimating NH₃ concentration, using NH₄Cl solutions of known concentration as standards. a) UV-Vis curves of indophenol assays with NH₃ after incubated for 2 hours at room temperature; b) calibration curve used for calculation of NH₃ concentrations. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH₃ concentration curves. The inset in b) shows the chromogenic reaction of indophenol indicator with NH₃.



Fig. S10. Absolute calibration of the Watt and Chrisp (*p*-dimethylamino-benzaldehyde) method for estimating N_2H_4 concentration, using N_2H_4 solutions of known concentration as standards. a) UV-Vis curves of various N_2H_4 concentration after incubated for 10 min at room temperature; b) calibration curve used for estimation of N_2H_4 concentration. The absorbance at 455 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N_2H_4 concentration (y = 0.515x + 0.013, R² = 0.999) of three times independent calibration curves. The inset in b) shows the chromogenic reaction of *p*-dimethylamino-benzaldehyde indicator with N_2H_4 .



Fig. S11. The linear sweep voltammetric curve using Fe_3S_4 nanosheets as the working electrode in pH=1 HCl aqueous solution.



Fig. S12. UV–Vis absorption spectra of the electrolyte stained with indophenol indicator before and after charging at -0.4 V versus RHE for 2 h in Ar atmosphere on the Fe₃S₄ catalyst.



Fig. S13. UV–Vis absorption spectra of the electrolyte stained with indophenol indicator before and after charging at -0.4 V versus RHE for 2 h in N₂ atmosphere on bare carbon paper (CP) electrode and Fe₃S₄/CP electrode, respectively.



Fig. S14. UV–Vis absorption spectra of the electrolyte stained with indophenol indicator after charging at open circuit for 2 h in N_2 atmosphere on Fe₃S₄/CP electrode.



Fig. S15. $^1\!H$ NMR analysis of the electrolyte fed by $^{14}N_2$ and $^{15}N_2$ after the electrolytic reaction.



Fig. S16. Yield rate of NH_3 and FE under different N_2 flow rate at -0.4 V vs. RHE. All experiments were carried out in 0.1 M HCl at room temperature and ambient pressure.



Fig. S17. Chronoamperometric curve of Fe_3S_4 on the carbon paper support measured in N₂-saturated 0.1M HCl electrolyte at -0.4 V vs. RHE for continuous 20 h.



Fig. S18. The SEM image of Fe_3S_4 nanosheets after stability test in 0.1 M HCl.



Fig. S19. XRD pattern for Fe_3S_4 after stability test in 0.1 M HCl.



Fig. S20. XPS spectra for Fe_3S_4 after stability test in 0.1 M HCl.



Fig. S21. Physical characterizations of CoS_2 and NiS_2 catalysts. a), b) SEM images, c), d) EDS analyses, and e), f) XRD patterns of the a), c), e) CoS_2 and b), d), f) NiS₂ catalysts prepared via the solvothermal synthesis method.



Fig. S22. HRTEM images of a) CoS_2 and b) NiS_2 catalysts. HRTEM of CoS_2 shows the atomic lattice fringes of the catalysts with lattice plane spacing determined to be 0.27 nm, corresponding to the (200) lattice spacing of CoS_2 , while 0.25 nm represents (210) lattice spacing of CoS_2 . HRTEM of NiS_2 shows the atomic lattice fringes of the catalysts with lattice plane spacing determined to be 0.28 nm, corresponding to the (200) lattice spacing of NiS_2 . The results show that (200) lattice plane are the most exposed lattice plane both for CoS_2 and NiS_2 catalysts.



Fig. S23. Comparison of the Fe_3S_4 catalyst with CoS_2 and NiS_2 catalysts for electrocatalytic NRR. NH₃ yield rates and Faradaic efficiencies of the Fe_3S_4 , CoS_2 and NiS_2 catalysts on the carbon paper support measured in N₂-saturated 0.1M HCl electrolyte at -0.4 V vs. RHE. Inset: chronoamperometric curves obtained for each catalyst.



Fig. S24. a) The side view of the NiS₂(200) (Ni atom in green, S atom in yellow); b) the side view of the $CoS_2(200)$ (Co atom in purple, S atom in yellow); c) the side view of the $Fe_3S_4(220)$ (octahedral Fe atoms in light purple, tetrahedral Fe atoms in black, S atom in yellow). All surfaces are with (2×1) cell.



Fig. S25. The most preferred N_2 adsorption configuration on Fe₃S₄(220) surface. (octahedral Fe atoms in light purple, tetrahedral Fe atoms in black, S atoms in yellow, N atoms in blue).

Process	Catalyst	Conditions	Reaction system	NH₃ yield/ Faradaic efficiency	Ref
	Fe_3S_4 nanosheets	Room Temperature	0.1 M HCl	75.5 μg h ⁻¹ mg ⁻¹ _{cat.} 6.45%(FE)	This work
	Au/TiO₂ Sub- nanocluster	Room Temperature	0.1 M HCI	21.4 μg h ⁻¹ mg ⁻¹ _{cat.} 8.11%(FE)	5
	Au nanorods	Room Temperature	0.1 M KOH	1.648 μg h ⁻¹ cm ⁻² 4.02%(FE)	4
Electrocatalysis	amorphous -Au/CeOx– RGO	Room Temperature	0.1 M HCI	8.3 μg h ⁻¹ mg ⁻¹ _{cat.} 10.10%(FE)	6
	VN nanowires	Room Temperature	0.1 M HCI	2.48 × 10 ⁻¹⁰ mol ⁻¹ s ⁻¹ cm ⁻² 3.58%(FE)	7
	N-doped carbon foam	Room Temperature	0.1 M HCI	15.7 μg h ⁻¹ mg ⁻¹ _{cat.} 1.45%(FE)	8
	Rh nanosheets	Room Temperature	0.1 M KOH	23.88 μg h ⁻¹ mg ⁻¹ _{cat.} 0.217%(FE)	9
	$Bi_4V_2O_{11}/Ce$ O_2 nanofibers	Room Temperature	0.1 M HCl	23.21 μg h ⁻¹ mg ⁻¹ _{cat.} 10.16%(FE)	10
	Fe ₂ O ₃	250 °C, 25 bar N ₂	Molten hydroxide	35% (N ₂ conversion rate)	11
	MoS ₂	Room Temperature	0.1 m Na ₂ SO ₄	8.08 × 10 ⁻¹¹ mol s ⁻¹ cm ⁻¹ 1.17%(FE)	12
Photocatalysis	Au/(BiO)₂C O₃ hybrid	Room Temperature	H ₂ O	38.23 μmol h ⁻¹ g ⁻¹ _{cət.}	13
	black silicon	Room Temperature	H ₂ O	13.3 mg m ⁻² h ⁻¹	14
	Bi₅O7Br	Room Temperature	H ₂ O	1.38 mmol h ⁻¹ g ⁻¹ _{cat.}	15
	CuCr- nanosheet	Room Temperature	H ₂ O	2.84 μmol h ⁻¹ g ⁻¹ _{cat.}	16
	5 wt% Ru@n-GaN nanowires	10 °C	H ₂ (75%) , N ₂ (25%)	514 μmol g ⁻¹ _{cat.} for 24h	17
Harsh-	LaCoSi	400 °C, 0.1 MPa	N ₂ , H ₂	1,250 μmol h ⁻¹ g ⁻¹ _{cət.}	18
	$Pr_{0.6}Ba_{0.4}Fe_0$	400 °C	Wet N_2	1.07×10 ⁻⁶ mol m ⁻² s ⁻¹	19

Table S1. Some represented reports for $N_{\rm 2}$ fixation.

	. ₈ Cu _{0.2} O _{3-δ}				
	7.8 wt% Ru	400 °C, 0.1	N ₂ , H ₂	1.9 mmol h ⁻¹ g ⁻¹ _{cat.}	20
	/Y₅Si₃	MPa			
	Fe ₂ O ₃ /activ	250 °C	Molten hydroxide	8.27 × 10 ⁻⁹ mol s ⁻¹ cm ⁻²	21
	ated				
	carbon				

Reference

- 1. G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169.
- 2. John P. Perdew, Kieron Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 3. D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, Nat. Mater., 2013, 12, 836-841.
- D. Bao, Q. Zhang, F. L. Meng, H. X. Zhong, M. M. Shi, Y. Zhang, J. M. Yan, Q. Jiang and X. B. Zhang, *Adv. Mater.*, 2017, **29**, 1604799.
- M. M. Shi, D. Bao, B. R. Wulan, Y. H. Li, Y. F. Zhang, J. M. Yan and Q. Jiang, *Adv. Mater.*, 2017, 29, 1606550.
- 6. S. J. Li, D. Bao, M. M. Shi, B. R. Wulan, J. M. Yan and Q. Jiang, *Adv. Mater.*, 2017, **29**, 1700001.
- 7. X. Zhang, R.-M. Kong, H. Du, L. Xia and F. Qu, *Chem. Commun.*, 2018, **54**, 5323-5325.
- X. Yang, K. Li, D. Cheng, W.-L. Pang, J. Lv, X. Chen, H.-Y. Zang, X.-L. Wu, H. Tan, Y.-H. Wang and Y.-G. Li, J. Mater. Chem. A, 2018, 6, 7762-7769
- H.-M. Liu, S.-H. Han, Y. Zhao, Y.-Y. Zhu, X.-L. Tian, J.-H. Zeng, J.-X. Jiang, B. Y. Xia and Y. Chen, J. Mater. Chem. A, 2018, 6, 3211-3217.
- 10. C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou and G. Yu, *Angew. Chem. Int. Ed.*, 2018, **57**, 6073-6076.
- 11. S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau and S. Liu, Science, 2014, 345, 637.
- 12. L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.*, 2018, **30**, 1800191.
- 13. C. Xiao, H. Hu, X. Zhang and D. R. MacFarlane, ACS Sustainable Chem. Eng., 2017, 5, 10858-10863.
- 14. M. Ali, F. Zhou, K. Chen, C. Kotzur, C. Xiao, L. Bourgeois, X. Zhang and D. R. MacFarlane, *Nat. Commun.*, 2016, **7**, 11335.
- S. Wang, X. Hai, X. Ding, K. Chang, Y. Xiang, X. Meng, Z. Yang, H. Chen and J. Ye, *Adv. Mater.*, 2017, 29, 1701774.
- Y. Zhao, Y. Zhao, G. I. N. Waterhouse, L. Zheng, X. Cao, F. Teng, L. Z. Wu, C. H. Tung, D. O'Hare and T. Zhang, *Adv. Mater.*, 2017, **29**, 1703828.
- 17. L. Li, Y. Wang, S. Vanka, X. Mu, Z. Mi and C. J. Li, Angew. Chem. Int. Ed., 2017, 56, 8701 –8705
- Y. Gong, J. Wu, M. Kitano, J. Wang, T.-N. Ye, J. Li, Y. Kobayashi, K. Kishida, H. Abe, Y. Niwa, H. Yang, T. Tada and H. Hosono, *Nature Catal.*, 2018, 1, 178-185.
- 19. R. Lan, K. A. Alkhazmi, I. A. Amar and S. Tao, Appl. Catal., B, 2014, 152-153, 212-217.
- 20. Y. Lu, J. Li, T. Tada, Y. Toda, S. Ueda, T. Yokoyama, M. Kitano and H. Hosono, *J. Am. Chem. Soc.*, 2016, **138**, 3970-3973.
- B. Cui, J. Zhang, S. Liu, X. Liu, W. Xiang, L. Liu, H. Xin, M. J. Lefler and S. Licht, *Green Chem.*, 2017, 19, 298-304.