

## Electronic Supplementary Information

### Diethylenetriamine-Assisted Hydrothermal Synthesis of Dodecahedral $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanocrystals with Enhanced and Stable Photoelectrochemical Activity

Rui Xu, You Xu, Yi Huang, Yanmei Shi and Bin Zhang\*

Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, P. R. China

E-mail: b Zhang@tju.edu.cn

#### Experimental instruments

The scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopic (EDS) analysis were taken with a Hitachi S-4800 scanning electron microscope (3 kV) equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. Transmission electron microscopy (TEM) and higher-resolution transmission electron microscopy (HRTEM) images were obtained with JEOL-2100F system equipped with EDAX Genesis XM2. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Focus Diffraction System using a Cu K $\alpha$  source ( $\lambda = 0.15406$  nm). FTIR spectra were recorded on a MAGNA-IR 750 (Nicolet Instrument Co) FTIR spectrometer. Thermogravimetric analysis was made with a Mettler Toledo TGA/DSC STA409PC system equipped with a gas controller (GC 200) and a recirculating stage cooling bath set at 22 °C (Julabo). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded on a Lambda 750S UV-Vis-NIR spectrometer (Perkin-Elmer) equipped with an integrating sphere. The UV-Vis DRS of solid samples were collected in 200-800 nm against BaSO<sub>4</sub> reflectance standard.

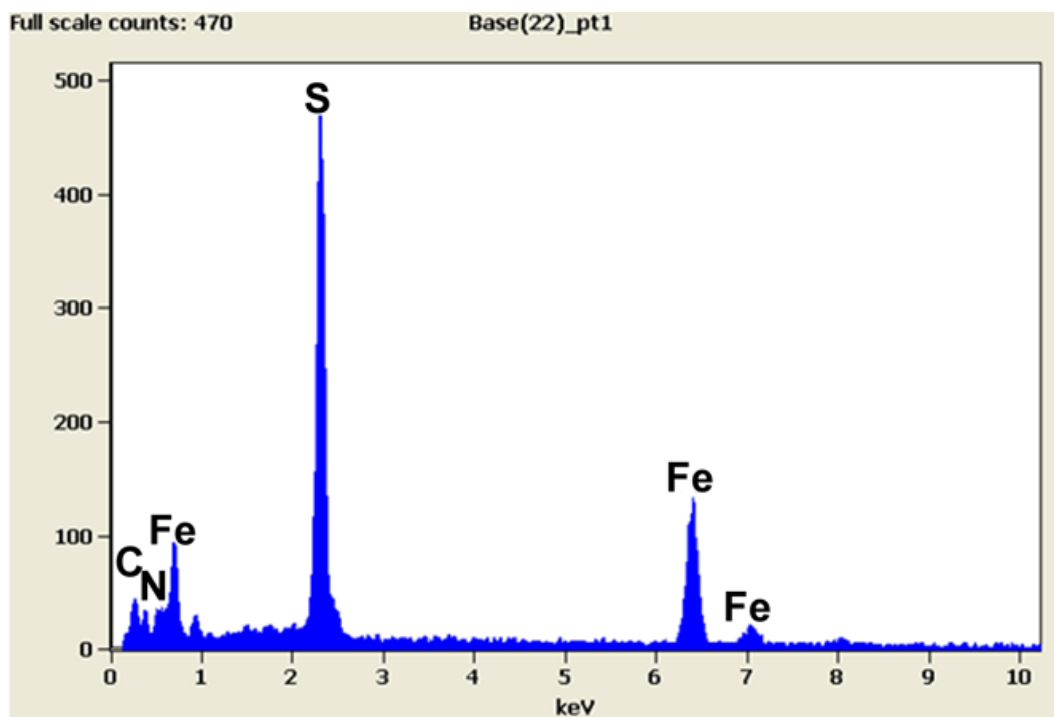
**Table S1** The photoelectrochemical activity of the reported undoped hematite without any cocatalysts in other system.

| Journal / Year             | Technique / Temperature   | Photocurrent                                 | Ref.No. |
|----------------------------|---|--|---------|
| J. Am. Chem.Soc.,<br>2011  | atomic layer deposition (ALD) technique, 500°C                        | 2.7 mA/cm <sup>2</sup><br>at 1.53 V vs RHE   | 1       |
| Nano Lett., 2011           | deposition-□annealing(DA) method, 550°C                               | 1.78 mA/cm <sup>2</sup><br>at 1.47 V vs RHE. | 2       |
| J. Am. Chem.Soc.,<br>2011  | Colloidal dispersion deposition, 820°C                                | ~1.8 mA/cm <sup>2</sup><br>at 1.60 V vs RHE  | 3       |
| Angew. Chem. Int. Ed.,2012 | Thermal decomposition in an oxygen-deficient atmosphere, 550°C        | 3.37 mA cm <sup>2</sup> at<br>1.50 V vs RHE  | 4       |
| Chemical Science,<br>2013  | Hydrothermally- annealing, 750°C                                      | ~2.75 mA/cm <sup>2</sup><br>at 1.60 V vs RHE | 5       |
| J. Am. Chem.Soc.,<br>2014  | Atmospheric pressure CVD (in fact, 1.5% silicon concentration), 545°C | ~4.0 mA/cm <sup>2</sup><br>at 1.60 V vs RHE  | 6       |

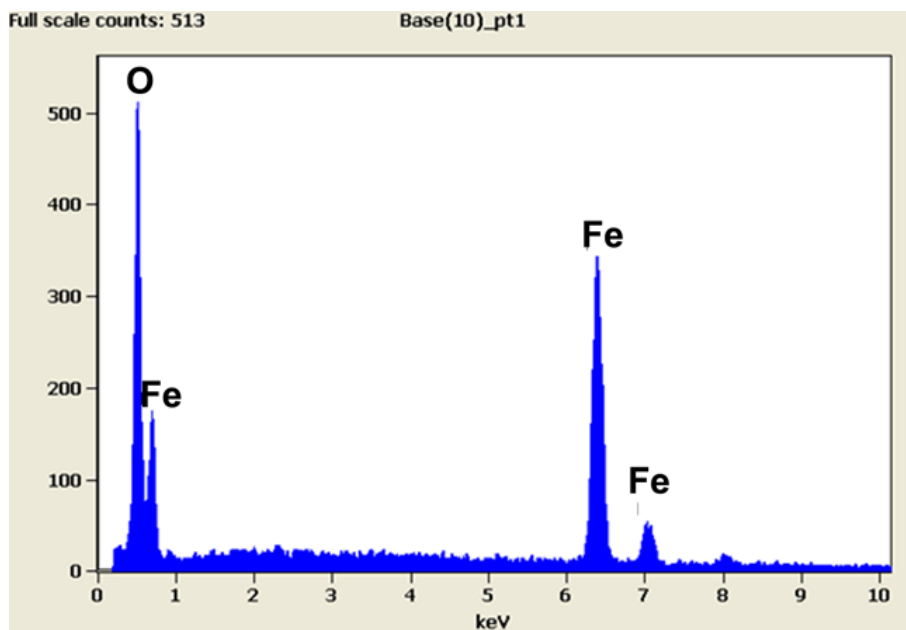
### Reference

- 1 Y. Lin, S. Zhou, S. W. Sheehan and D. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 2398.
- 2 G. Wang, Y. Ling, D. A. Wheeler, K. E. N. George, K. Horsley, C. Heske, J. Z. Zhang and Y. Li, *Nano Lett.*, 2011, **11**, 3503.
- 3 R. H. Goncalves, B. H. R. Lima and E. R. Leite, *J. Am. Chem. Soc.*, 2011, **133**, 6012.
- 4 Y. Ling, G. Wang, J. Reddy, C. Wang, J. Z. Zhang and Y. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 4074.
- 5 L. Xi, S. Y. Chiam, W. F. Mak, P. D. Tran, J. Barber, S. C. J. Loo and L. H. Wong, *Chem. Sci.*, 2013, **4**, 164.
- 6 F. L. Formal, S. R. Pendlebury, M. Cornuz, S. D. Tilley, M. Gratzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2014, **136**, 2564.

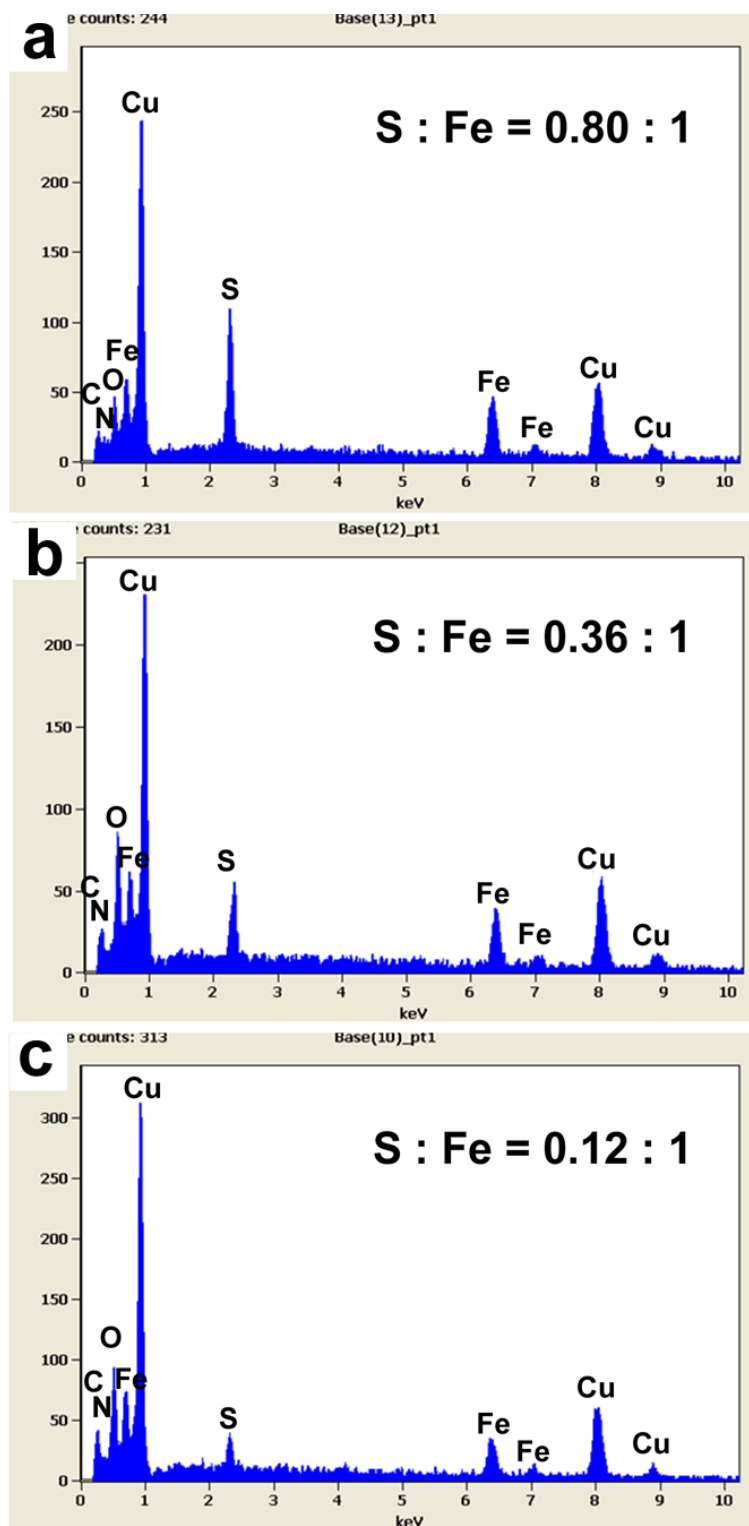
## Additional characterization results



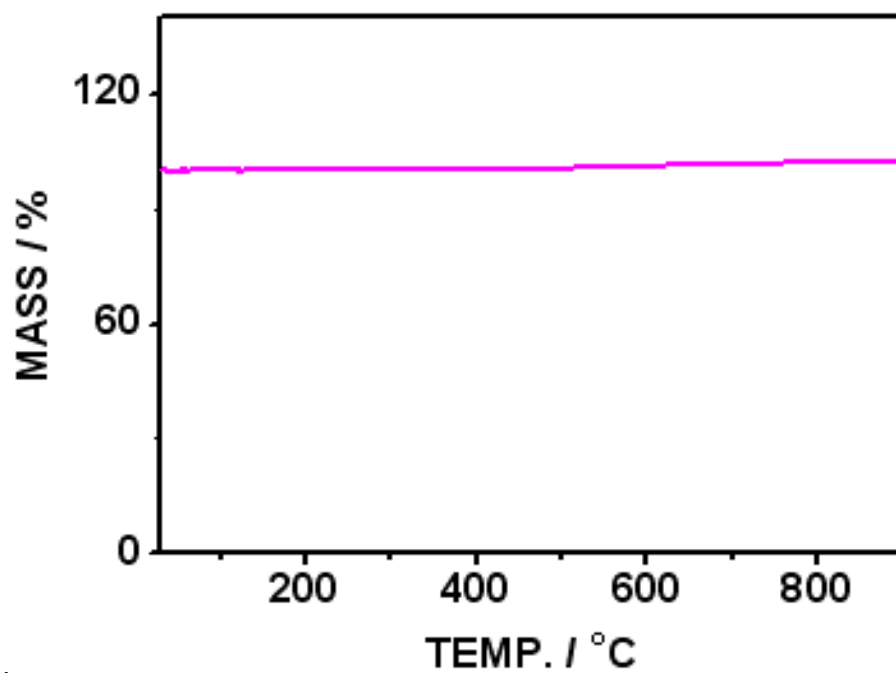
**Fig. S1** EDS spectrum of the inorganic-organic hybrid FeS-DETA nanosheets. EDS analysis showed that Fe, S, C and N were the major elements included in the precursor and the element molar ratio Fe:S:N:C=1:1.02:4.39:6.07. The result further suggested that inorganic-organic hybrid FeS-DETA nanosheets were produced.



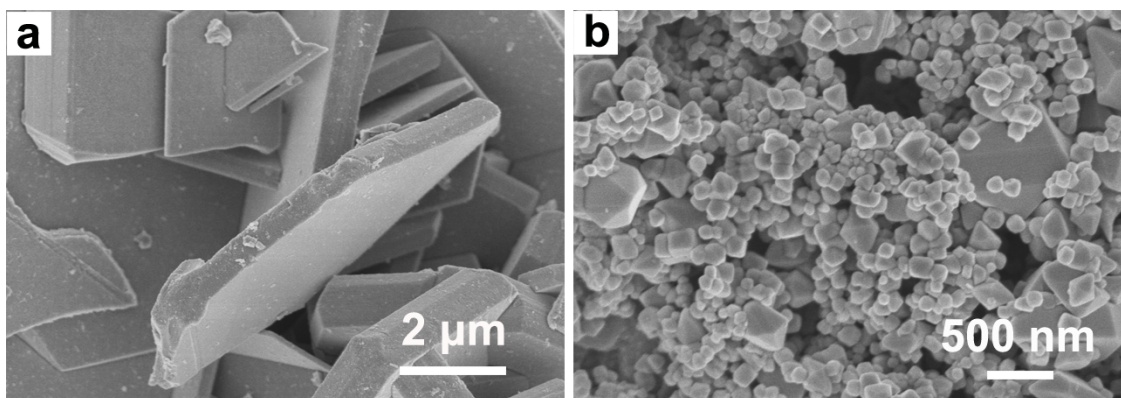
**Fig. S2** EDS spectrum of the dodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> obtained after the reaction of 6 h at 200 °C. EDS analysis showed that Fe and O were the major elements included in the resulting products after the hydrothermal reaction. The peak of element S was disappeared which indicated the totally transformation from the precursor to the product.



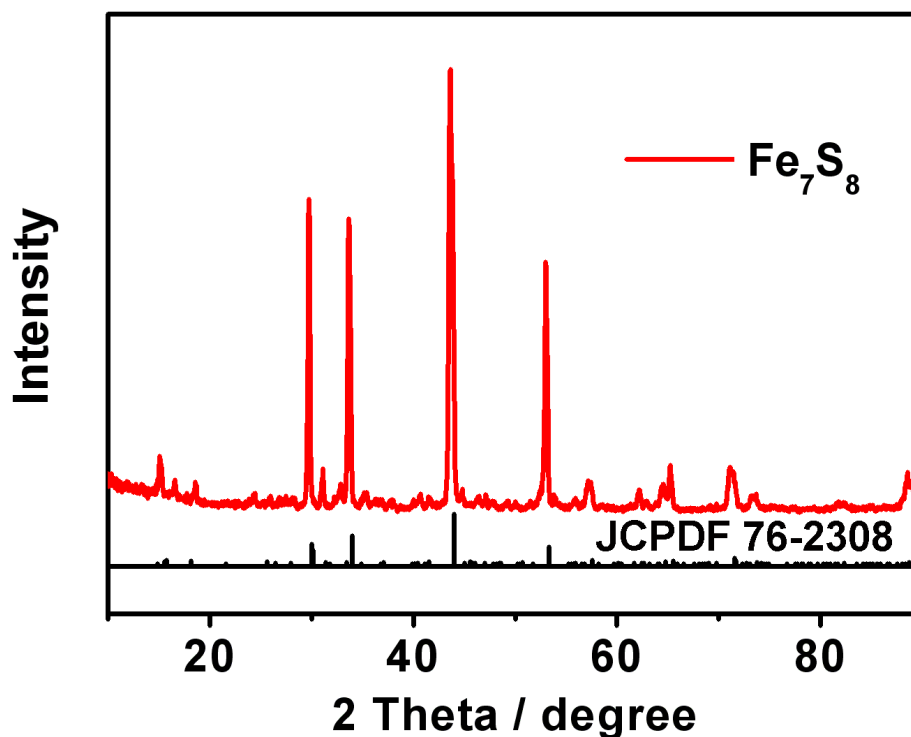
**Fig. S3** EDS spectrum of the intermediates collected after the reaction proceeded for different times:(a) 1 h, (b) 2 h, (c) 4 h. EDS analysis showed that Fe, S, C, O and N were the major elements included in the intermediates. And EDS analysis disclosed that the ratio of S:Fe experienced a decreasing and disappearing process.



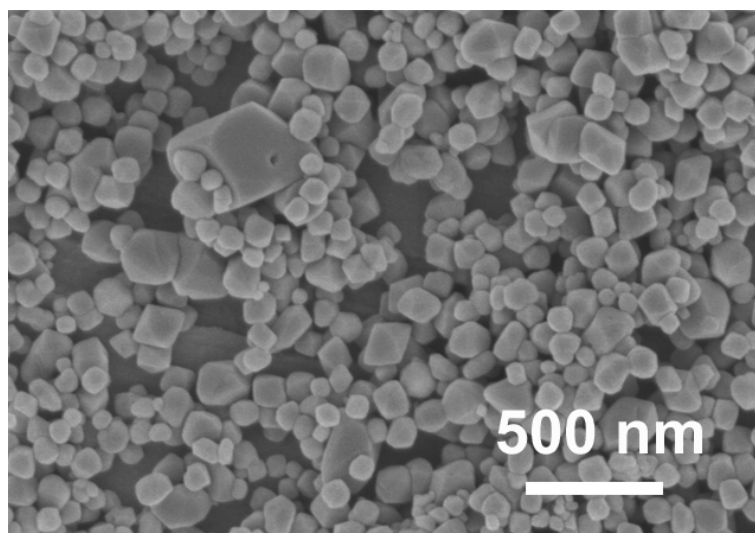
**Fig. S4** In the TG profile, there was no weight loss until 900 °C. The result further indicated the pure inorganic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> products were obtained in our method.



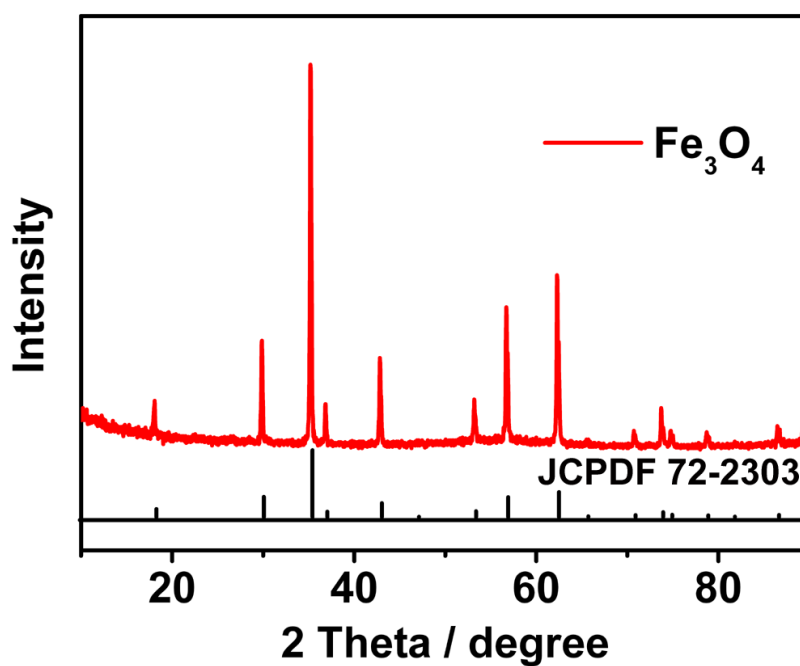
**Fig. S5** SEM images of FeS precursors (a) and as-converted products(b). The pure inorganic FeS precursors which were obtained replacing the addition of DETA with H<sub>2</sub>O according to the modified method of **Experimental section 2.2**. It could clearly be seen that pure inorganic FeS nanosheets had larger size and the proportion of the dodecahedral products in the final products was very low.



**Fig. S6** XRD pattern of as-converted products from FeS precursors. It could clearly be seen that the main products from pure inorganic FeS nanosheets are Fe<sub>7</sub>S<sub>8</sub>.

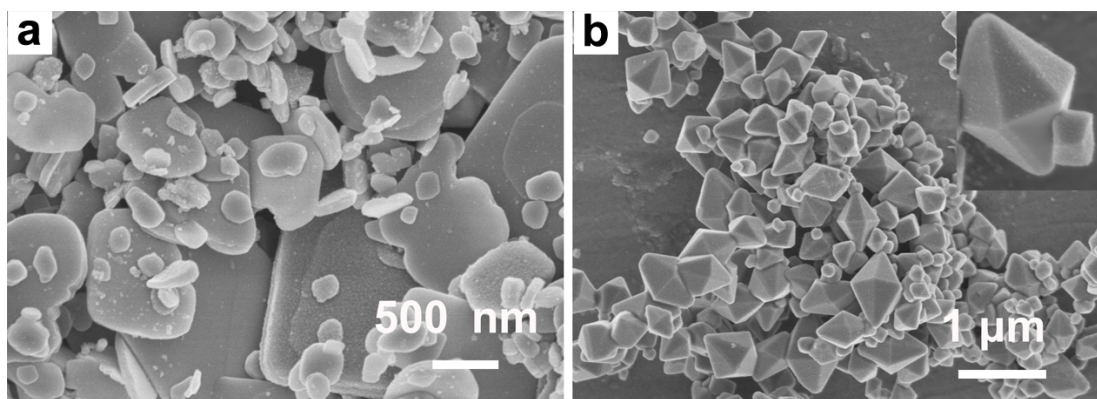


**Fig. S7** SEM images of as-converted products in the case of pure inorganic  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as precursor. It could clearly be seen that the proportion of the dodecahedral products in the final products was very low.

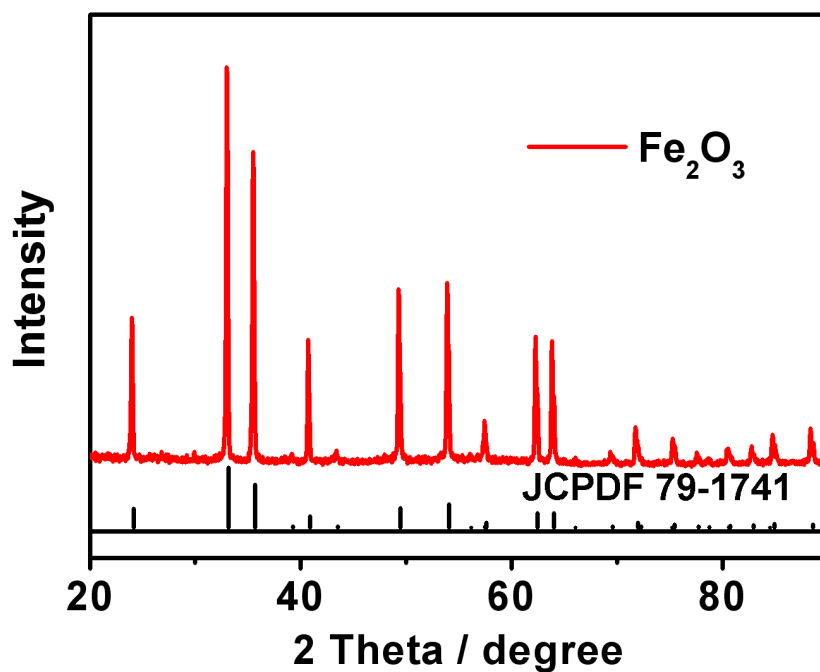


**Fig. S8** XRD pattern of as-converted products in the case of pure inorganic  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as precursor. It could clearly be seen that the main products from pure inorganic  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  are  $\text{Fe}_3\text{O}_4$ .

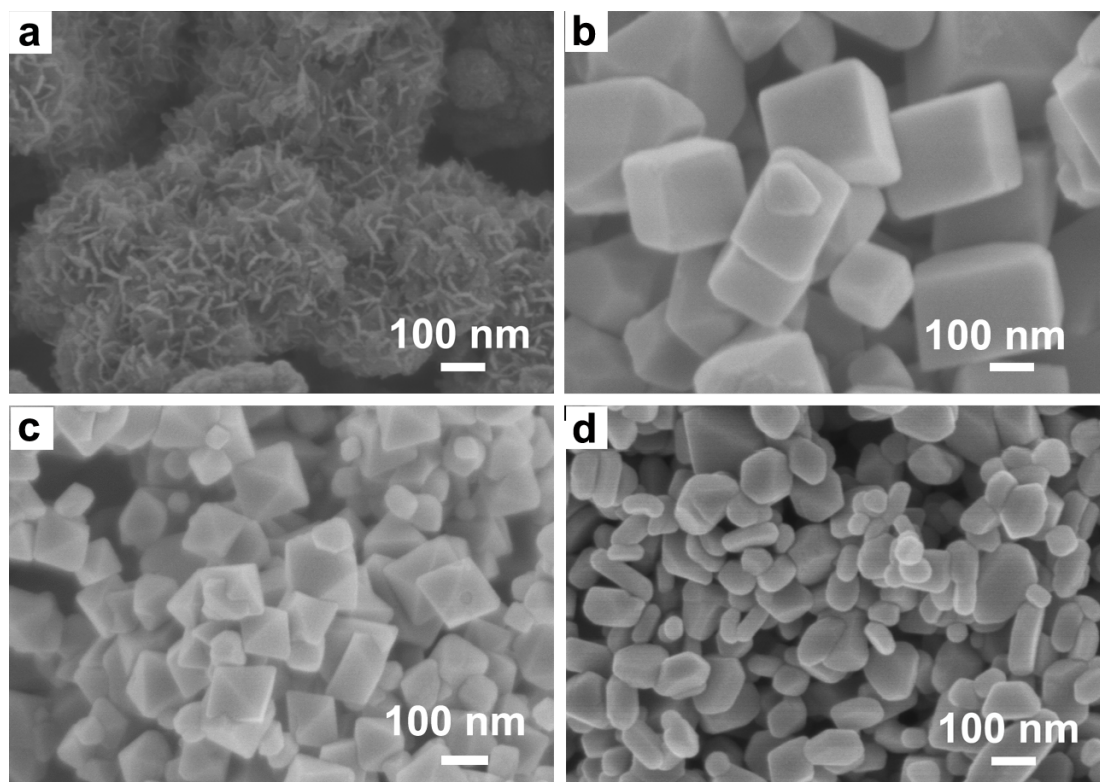




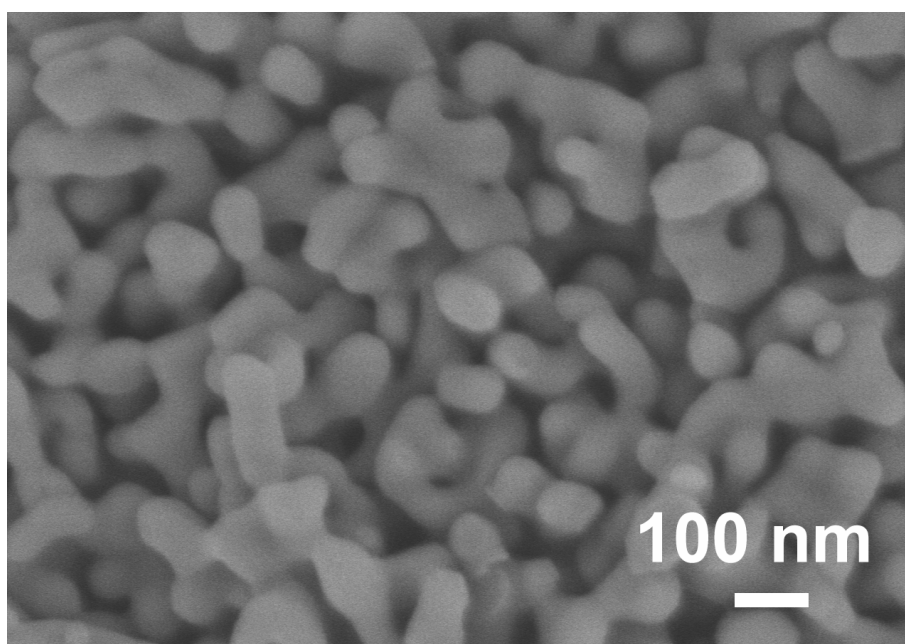
**Fig. S9** SEM images of FeS-TETA precursors (a) and as-converted  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> products (b). The FeS-TETA precursors were obtained replacing the addition of DETA with TETA the modified method of **Experimental section 2.2 and 2.3**. The products had larger size and the company of smaller nanoparticles in the case of FeS-TETA as precursor.



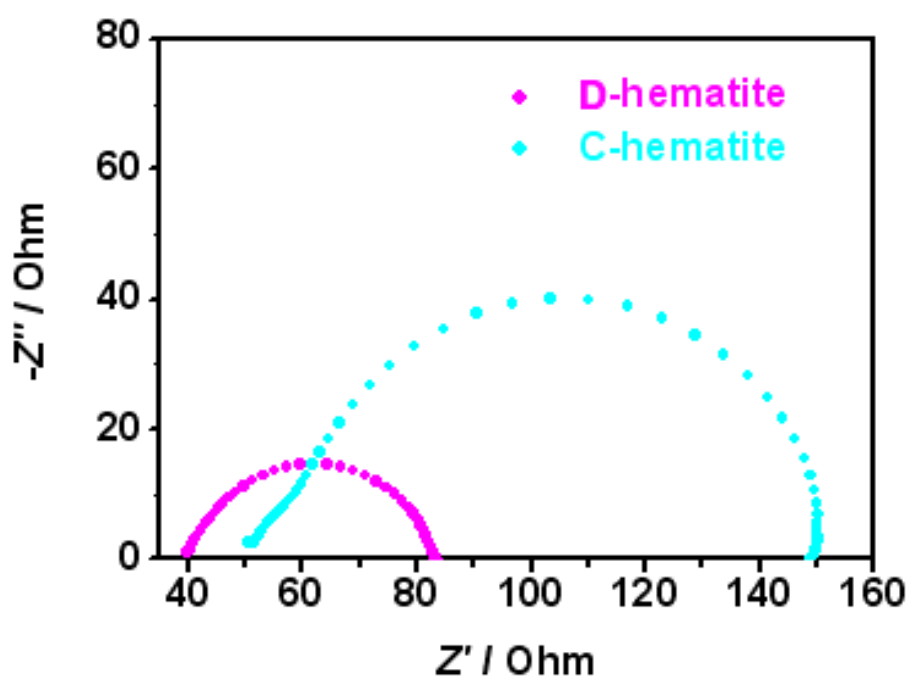
**Fig. S10** XRD pattern of as-converted products in the case of FeS-TETA as precursor. It could clearly be seen that the main products from FeS-TETA are  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



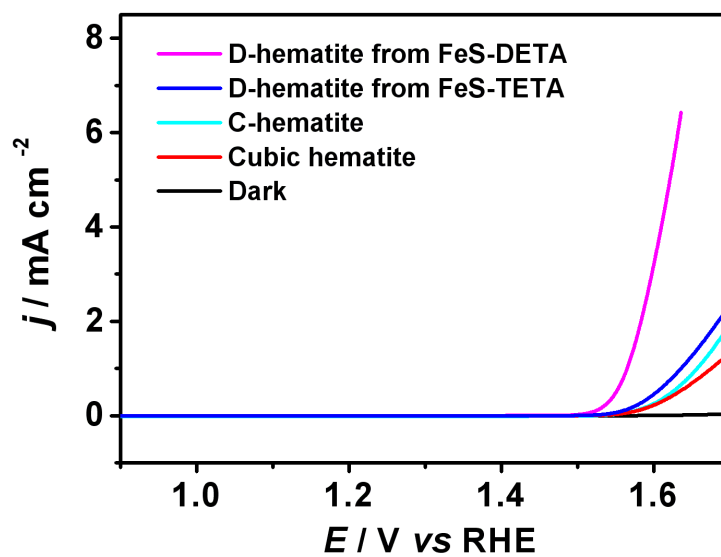
**Fig. S11** SEM images of as-converted products according to the modified method of **Experimental section 2.3** without the change of total volume in the autoclave: (a) pH=7 with the addition of 0.5M H<sub>2</sub>SO<sub>4</sub>, verifying the importance of the adjustment of suitable pH value. (b) Without the addition of DETA, resulting the nanocube morphology which is the typical morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (X. Liang, X. Wang, J. Zhuang, Y. Chen, D. Wang, and Y. Li, *Adv. Funct. Mater.*, 2006, 16, 1805.) (c) replacing the addition of DETA with 2.0 M NaOH, resulting the octahedral morphology which is the typical morphology of Fe<sub>3</sub>O<sub>4</sub>. (C. Hu, Z. Gao and X. Yang, *Chem. Phys. Lett.*, 2006, 429, 513.) (d) DETA/H<sub>2</sub>O > 1:1, proving that the release of DETA is also a vital factor in the synthesis of the dodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



**Fig. S12** SEM image of commercial  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles. The commercial  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles (C-hematite) also showed small size and uniform morphology.



**Fig. S13** Electrochemical impedance spectroscopy of D-hematite and C-hematite measured in the dark at 1.6V vs RHE from 0.1 Hz to 100 kHz in 1.0 M KOH aqueous solution from 0.1 Hz to 1000 kHz with the three-electrode system. The result showed that D-hematite exhibited smaller impedance (Faradic impedance, or charge-transfer impedance, of about 40  $\Omega$ ).



**Fig. S14** Polarization curves for oxygen evolution reaction (OER) under visible light illumination ( $\lambda > 420$  nm) for different samples (D-hematite from FeS-DETA precursors, magenta line; D-hematite from FeS-TETA precursors, blue line; C-hematite, cyan line; cubic hematite, red line) and in the dark (black line, because the dark I-V curves are negligible, so just one curve is shown) with scan speed at  $10\text{mV s}^{-1}$  in  $1.0$  M KOH.