

Supporting information for:

**SnS₂/polypyrrole for high-efficiency photocatalytic oxidation of
benzylamine**

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1. Experimental Section

Materials. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (A. R. grade) was supplied by China National Medicines Co., Ltd. Thioacetamide (TAA, 99% purity), pyrrole (99% purity), methyl orange (MO), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (98.5% purity), 3,3',5,5'-tetramethylbenzidine (TMB), 2,2,6,6-tetramethylpiperidine (TEMP), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), sodium acetate trihydrate ($\text{NaAc} \cdot 3\text{H}_2\text{O}$, 99% purity) and amines were purchased from Beijing InnoChem Science & Technology Co., Ltd. Ethanol (A. R. grade), acetic acid (HAc, A. R. grade) and *N,N*-dimethylformamide (DMF, A.R. grade) were purchased from Beijing Chemical Works. Deionized water was provided by Beijing Analysis Instrument Factory. Nafion D-521 dispersion (5% w/w in water and 1-propanol, ≥ 0.92 meq/g exchange capacity) was purchased from Alfa Aesar China Co., Ltd. N_2 (purity 99.9%) was supplied by Beijing Analysis Instrument Factory.

Synthesis of SnS_2 . The SnS_2 nanoplates were prepared in a hydrothermal kettle by hydrothermal method.¹ In a typical experiment, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (131 mg) and TAA (22.5 mg) were dispersed in deionized water (60 mL). After stirring for 1 h at 25 °C, the mixture was transferred to a hydrothermal kettle, and then reacted at 160 °C for 12 h. After the reaction was completed, the obtained suspension was cleaned three times with deionized water and ethanol, respectively. Afterward, the SnS_2 was prepared by drying in under vacuum at 80 °C for 16 h.

Synthesis of PPy nanotubes. PPy nanotubes were prepared by a chemical polymerization.² Briefly, MO (82 mg) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (675 mg) were dissolved into 40 mL and 10 mL of water, respectively. Then 10 mL of FeCl_3 solution and 175 μL of pyrrole were slowly dropped to 40 mL of MO solution. After stirring vigorously at 25 °C for a day and night of reaction, the as-prepared product was filtered and washed with water and dried under vacuum at 80 °C for 24 h.

Synthesis of SnS_2 /PPy. Firstly, PPy (60 mg) and water (30 mL) were put into a beaker, and then sonicate for 1 h and stir for 12 h. Then, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (131.0 mg), TAA (22.5 mg) and a certain amount of PPy-dispersed aqueous solution were dispersed in water

(60 mL). After stirring for 1 h at 25 °C, the mixture was transferred to a hydrothermal kettle, and then reacted at 160 °C for 12 h. After the reaction was completed, the obtained suspension was cleaned three times with deionized water and ethanol, respectively. Afterward, the product was prepared by drying in under vacuum at 80 °C for 16 h.

Material characterizations. The morphologies were performed by SEM (HITACHI S-4800), TEM (JEM-1011) and HRTEM (JEM-2100F). XRD patterns were detected on a Rigaku D/max-2500 diffractometer (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$, 40 kV, 200 mA and 5° min^{-1}). AFM was characterized on Nanoscope V Multimode 8. The N₂ adsorption-desorption isotherms were gained from a Micromeritics ASAP 2020M system. The elemental content of Sn in SnS₂/PPy was confirmed by ICP-AES. XPS was recorded with a multipurpose X-ray photoemission spectroscope (Thermo Scientific ESCALAB 250Xi). The UV-Vis DRS spectra were characterized by spectrophotometer (V-2600, SHIMADZU). The transient state PL spectroscopy and steady-state PL spectra were obtained by a FLS980 fluorescence spectrophotometer (the excitation wavelength of 305 nm) and a FluoroMax+ fluorescence spectrophotometer (the excitation wavelength of 334 nm), respectively. ESR spectra were collected on Bruker ELEXSYS II E500.

Photocatalytic oxidation of benzyl amine. Typically, a mixture of amine (0.1 mmol), photocatalyst (10 mg) and DMF (5 mL) was dispersed in a 50 mL flask. Before irradiation, the suspension was stirred in air and dark for 1 h to ensure the complete adsorption-desorption equilibrium. Finally, the reaction was carried out at 25 °C with a 300 W Xe lamp as the simulated light source (500 mW cm^{-2}). After irradiation, the heterogeneous mixture was centrifuged at 12000 rpm for 5 min. The liquid phase was detected by ¹H NMR method (Bruker Avance III 400 HD).

Molecular oxygen activation ability measurement. The mixture of 2 mg catalyst and 10 mL TMB solution (0.5 mM, HAc/NaAc buffer solution) was illuminated by a 300 W Xe lamp ($380 < \lambda < 780 \text{ nm}$). The oxidation of TMB was determined by a UV-Vis absorption spectrum at different time.

In-situ ESR experiment. 5 mg of catalyst and 5 mL of DMF were added to a flask,

and the mixture was stirred in air for 1 h. The suspension was mixed with 60 μL trapping agent of TEMP or DMPO in a flask. Then the mixture was light-illuminated (300 W Xe lamp, $380 < \lambda < 780$ nm) for different time at room temperature and analyzed by Bruker ELEXSYS II E500.

EIS measurement. The EIS test was performed on a three-electrode system (photocatalyst-coated indium-tin oxide as the working electrode, an Ag/AgCl with 3.5 M KCl as a reference electrode and 1 cm^2 Pt net as the counter electrode) at a CHI660E electrochemical workstation (Chenhua Instrument, Shanghai, China). A 0.5 M Na_2SO_4 solution was used as electrolyte ($\text{pH} = 6.8$). To prepare the catalyst ink, the photocatalyst (5 mg) and 5 % Nafion 117 solution as conducting binder (15 μL) were added into ethanol (250 μL) and sonicated for 2 h. Then the catalyst ink was dropped on the surface of an indium-tin oxide (ITO) plate (1 cm^2) to prepare the working electrodes.

2. Results and Discussion

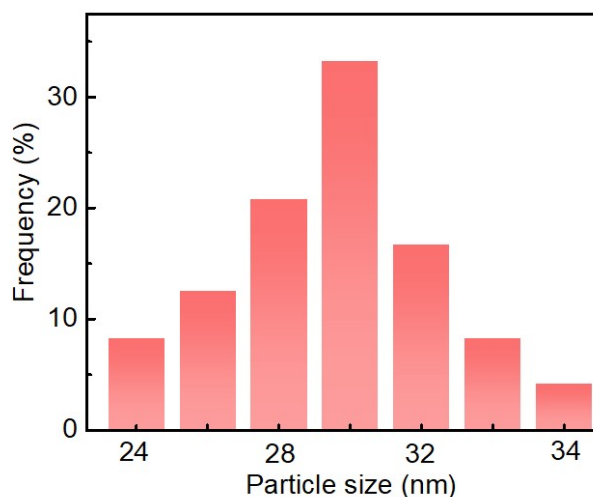


Fig. S1. Particle size distribution of SnS₂ nanoplates.

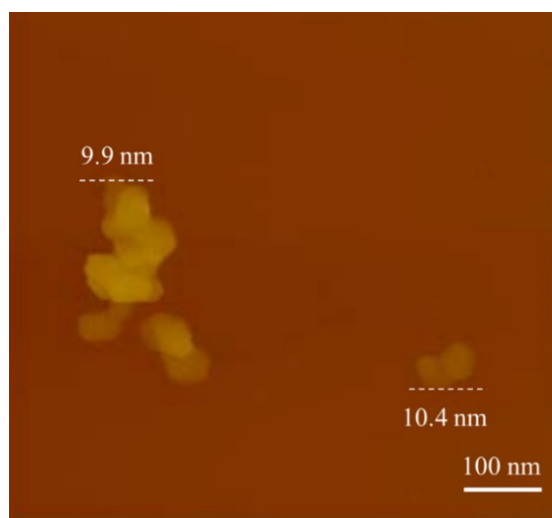


Fig. S2. AFM image of SnS₂ nanoplates.

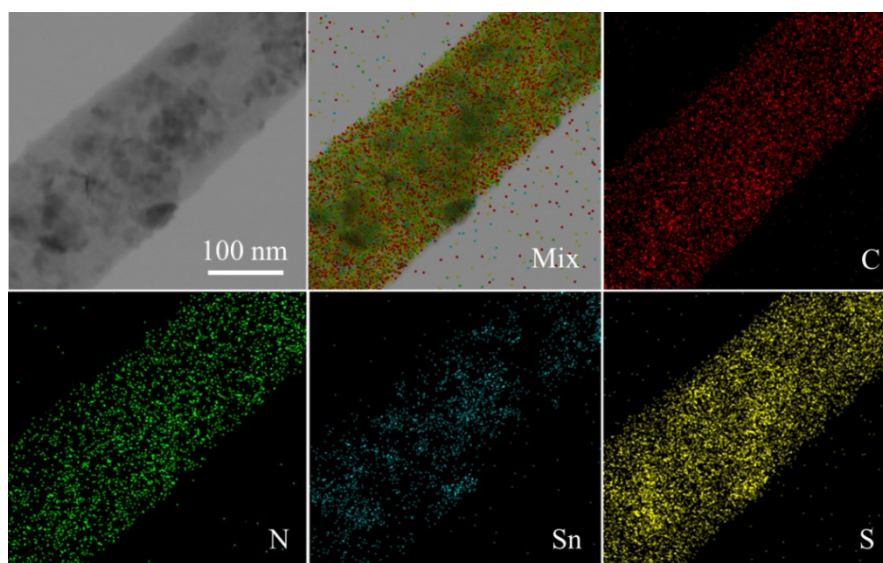


Fig. S3. EDS elemental mappings of SnS₂/PPy.

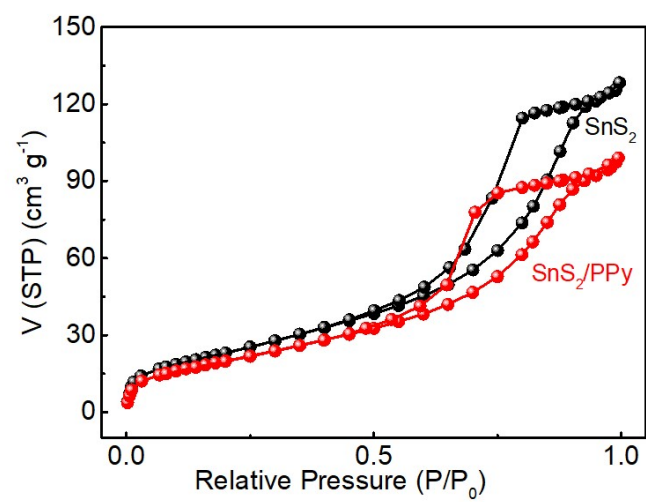


Fig. S4. N₂ adsorption-desorption isotherms of SnS₂/PPy and SnS₂.

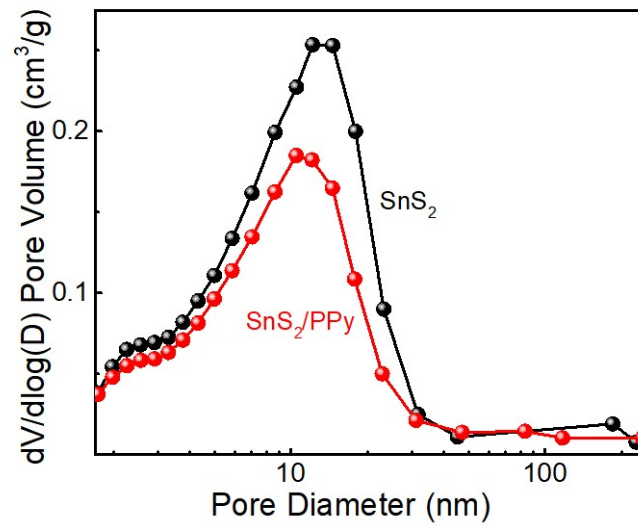


Fig. S5. Pore size distributions based on the Barrett-Joyner-Halenda (BJH) method of SnS₂/PPy and SnS₂.

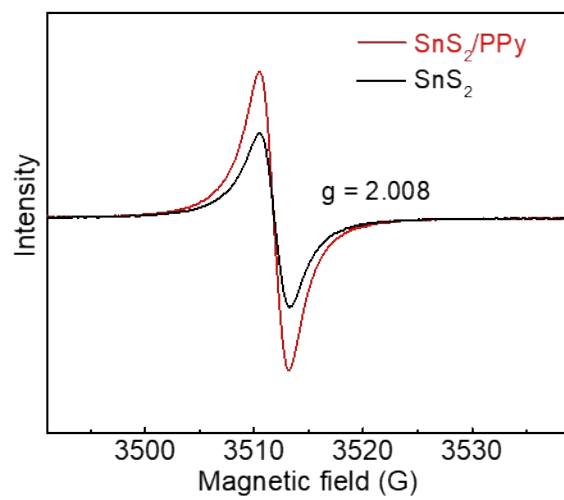


Fig. S6. ESR spectra of SnS₂/PPy and SnS₂.

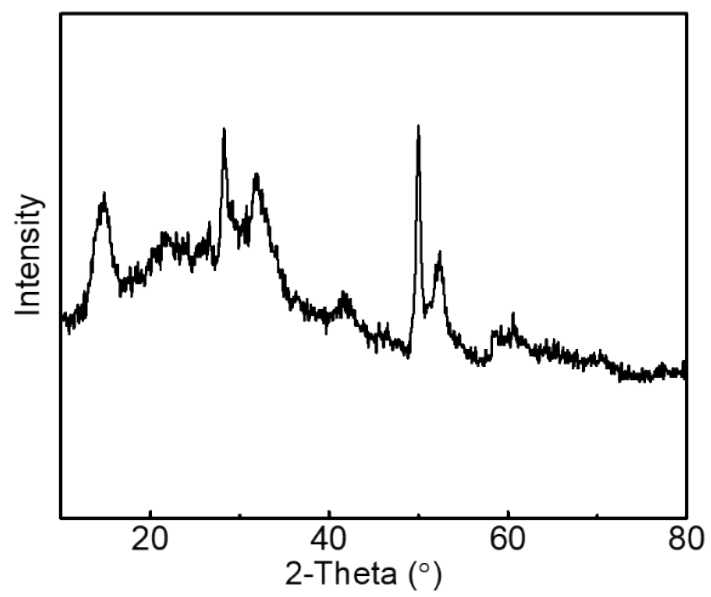


Fig. S7. XRD pattern of the SnS₂/PPy after used for five cycles.

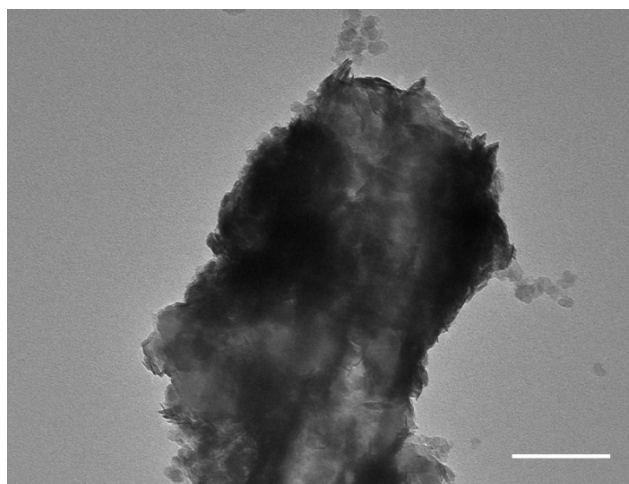


Fig. S8. TEM image of the SnS₂/PPy after used for five cycles. Scale bar: 200 nm

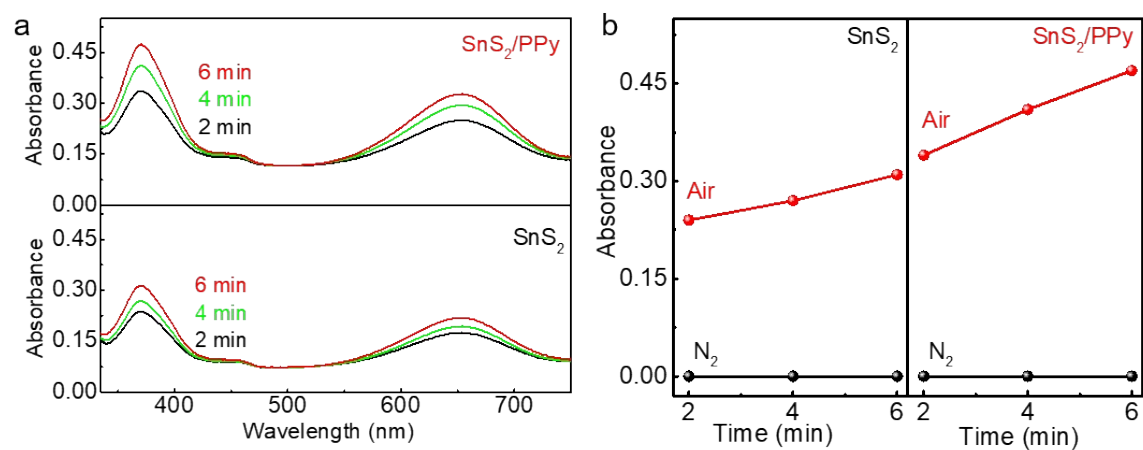


Fig. S9. (a) Time-dependent UV-Vis absorption spectra of TMB oxidation with SnS₂/PPy and SnS₂ in air. (b) The absorbance peak monitored for the product with a prolonged illumination time of SnS₂/PPy and SnS₂ in N₂ and air.

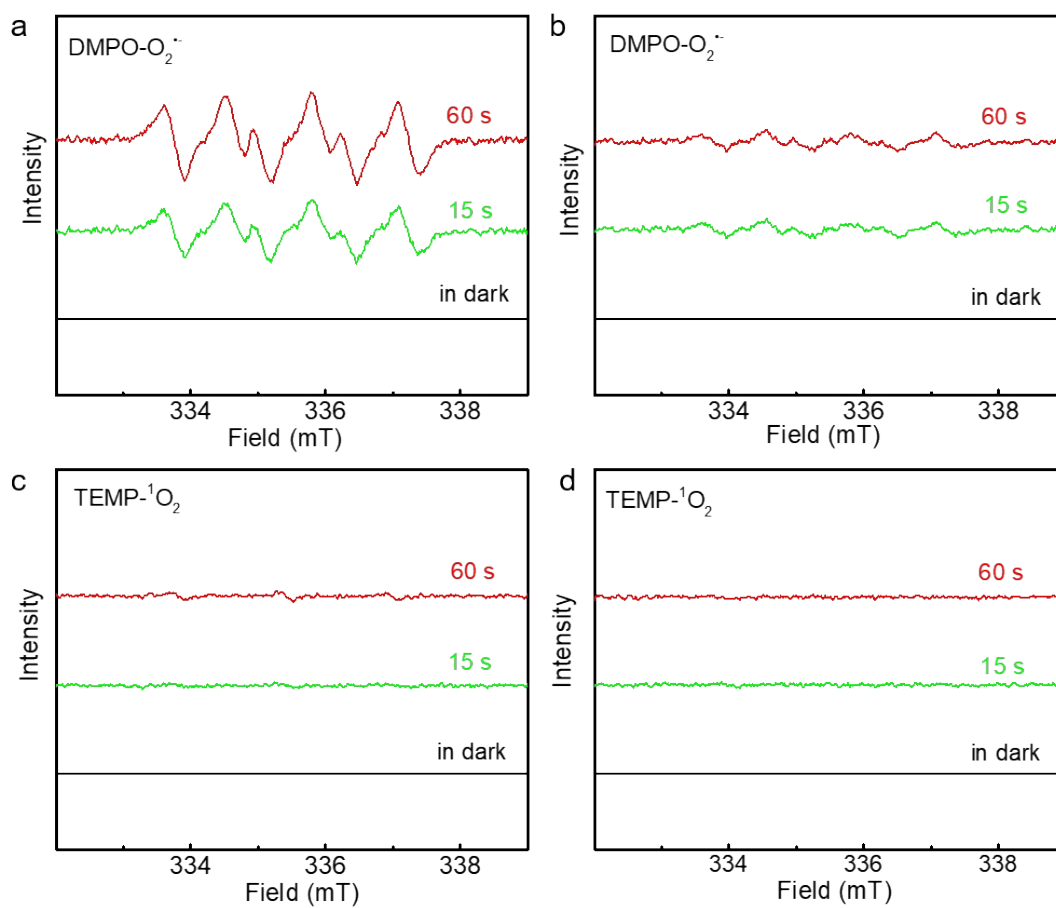


Fig. S10. *In-situ* ESR spectra of SnS₂/PPy (a) and SnS₂ (b) in the presence of DMPO. *In-situ* ESR spectra of SnS₂/PPy (c) and SnS₂ (d) in the presence of TEMP.

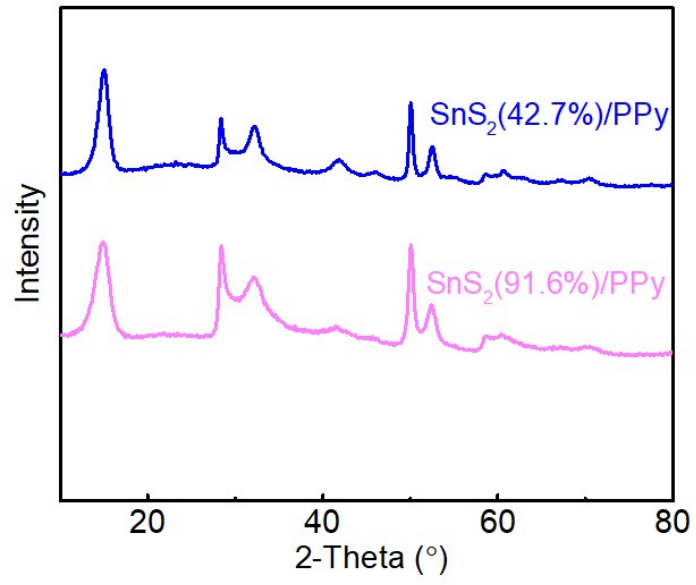


Fig. S11. XRD patterns of SnS₂/PPy with different SnS₂ contents.

Table S1. Sn and SnS₂ contents in different SnS₂/PPy samples determined by ICP-AES method.

Sample	Sn content	SnS ₂ content
1	50.85%	78.2%
2	27.74%	42.7%
3	59.57%	91.6%

Table S2. Catalytic activities of various photocatalysts in the photocatalytic oxidation of benzylamine.

Photocatalyst	Conditions	Conversion (%)	Selectivity (%)	TOF ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Reference
SnS ₂ /PPy	benzylamine (0.1 mmol), catalyst (10 mg), air, 300 W Xe lamp	99.7	>99	823	This work
BiOBr-S-110	benzylamine (0.1 mmol), catalyst (100 mg), O ₂ , 5 W fluorescent lamp	100	100	35.7	11
TiO ₂	benzylamine (0.1 mmol), catalyst (10 mg), air, 100 W Hg lamp (cut-off below 300 nm)	99	85	468	12
Nb ₂ O ₅	benzylamine (5 mmol), catalyst (100 mg), O ₂ , 500 W Hg lamp (>300 nm)	>99	97	480	13
<i>m</i> -NH ₂ -MIL-125	amine (0.2 mmol), catalyst (10 mg), air, 25 °C, 4 mL MeCN, 300 W Xe lamp	62.8	92.6	475	34
NH ₂ -UiO-66	benzylamine (0.1 mmol), catalyst (15 mg), air, RT, 3 mL MeCN, 300 W Xe lamp	83	99	274	35
Au-Pd@ZrO ₂	benzylamine (1 mmol), catalyst (50 mg), 1 atm O ₂ , 500 W Hg lamp (400-750nm)	-	96	47	36
Ag/AgI/titanate	benzylamine (0.5 mmol), catalyst (50 mg), O ₂ , 500 W Hg lamp	95	96	190	14
Pd _{0.5} /NS-OV	amine (0.2 mmol), catalyst (10 mg), air, 1.5 mL MeCN, 300 W Xe lamp	95.1	98.2	778	37

References

- [1] Z. Z. Su, B. X. Zhang, J. B. Shi, D. X. Tan, F. Y. Zhang, L. F. Liu, X. N. Tan, D. Shao, G. Y. Yang and J. L. Zhang, *Sustainable Energy & Fuels*, 2019, **3**, 1233-1238.
- [2] C. C. Shen, Y. N. Liu, X. Wang, X. X. Fang, Z. W. Zhao, N. Jiang, L. B. Ma, X. Zhou, T. Y. Cheang and A. W. Xu, *Dalton Trans.*, 2018, **47**, 11705-11712.