

## Experimental Section

**Synthesis of NaFeSO<sub>4</sub>F fluorosulphate.** For benzene thermal synthesis of the NaFeSO<sub>4</sub>F, corresponding metal sulfate FeSO<sub>4</sub>·7H<sub>2</sub>O (2.5 mmol) and NaF (2.5 mmol) were taken as raw materials and mixed for 5 min in agate mortar and then moved into the autoclave (20 ml) with iron cap. At last, 15 ml benzene was moved into the autoclave as the reaction medium. The autoclave with the raw materials was heated from room temperature to 200 °C in 10 min and then kept 1 min at 200 °C. After the reaction, the benzene in the autoclave was taken out and the product in the bottom was dried at 60 °C for 4 h in the vacuum oven.

**XRD.** The samples were analyzed by X-ray diffraction (XRD) employing a Philips X'pert X-ray diffractometer with Cu K<sub>α</sub> radiation ( $\lambda = 1.54178 \text{ \AA}$ ). A scan rate of  $0.05 \text{ deg}\cdot\text{s}^{-1}$  was applied to record the pattern in the  $2\theta$  range of  $10\text{-}55^\circ$ .

**Electron Microscopy.** The transmission electron microscope (TEM) images and the corresponding selected-area electron diffraction (SAED) pattern were taken on a JEOL 2010 HRTEM at an acceleration voltage of 200 kV.

**X-ray photoelectron spectra (XPS).** X-ray photoelectron spectra (XPS) were recorded on a VG ESCALABMKII X-ray photoelectron spectrometer (VG Scientific, England), using nonmonochromatized Al K<sub>α</sub> radiation (1486.5 eV) as the excitation source, and the binding energies were standardized using C1s at 284.6 eV as a reference.

**Thermal gravimetric analysis.** Around 12 mg of powder sample, kept inside an alumina crucible, was heated from room temperature to 700 °C (heating rate=  $10 \text{ }^\circ\text{C} / \text{min}$ ) in N<sub>2</sub> ( $25 \text{ ml}\cdot\text{min}^{-1}$ ) regulated atmosphere and the TGA data were collected with a TGA-50 (Sahimadzu Corporation, Japan).

**Electrochemical measurements.** The electrochemical performances of NaFeSO<sub>4</sub>F and NaFeSO<sub>4</sub>F·2H<sub>2</sub>O were performed using CR2016 coin cells in which a lithium metal foil was used as anode. The working electrodes were made of the active materials NaFeSO<sub>4</sub>F or NaFeSO<sub>4</sub>F·2H<sub>2</sub>O, acetylene black and PVDF weight ratio of 70: 15: 15 in N-methyl pyrrolidinone (NMP) solvent by milling and then coated uniformly on an aluminum foil. Finally, the electrode was dried under vacuum at 120 °C for 12 h. The electrolyte was 1M LiPF<sub>6</sub> in ethylene carbonate and dimethyl carbonate solution (EC+DMC) (1: 1) in volume, and layer of celgard 2400 as the battery separator. The cells were assembled in a glove box filled with highly pure argon gas, and charge/discharge tests were performed in the voltage range of 2.5-5.0 V at C/20 to NaFeSO<sub>4</sub>F and 1.5-4.7 V at C/20 to NaFeSO<sub>4</sub>F·2H<sub>2</sub>O on the Land CT 2001A automatic battery tester (Wuhan, China).

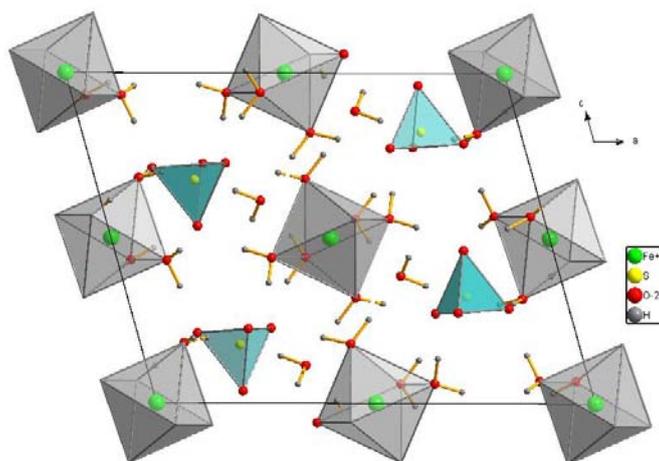


Fig. 1 The crystal structure of FeSO<sub>4</sub>·7H<sub>2</sub>O

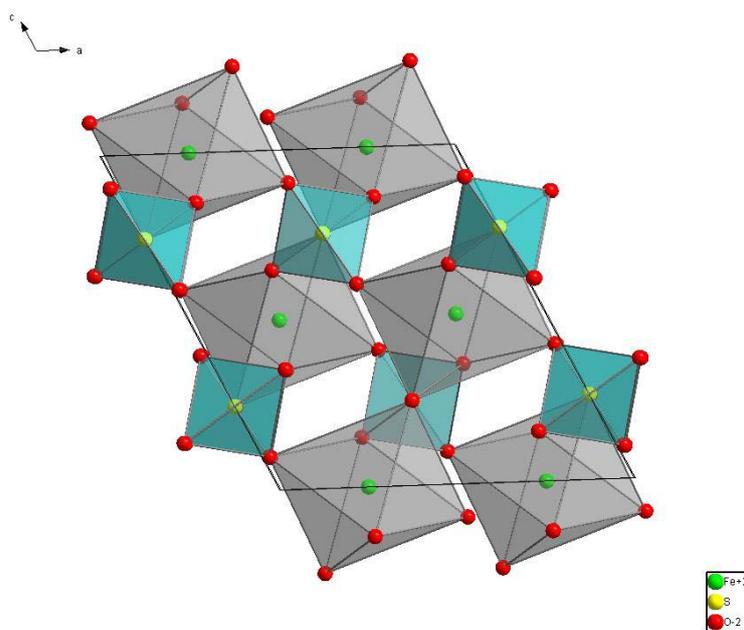


Fig. 2 The crystal structure of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$

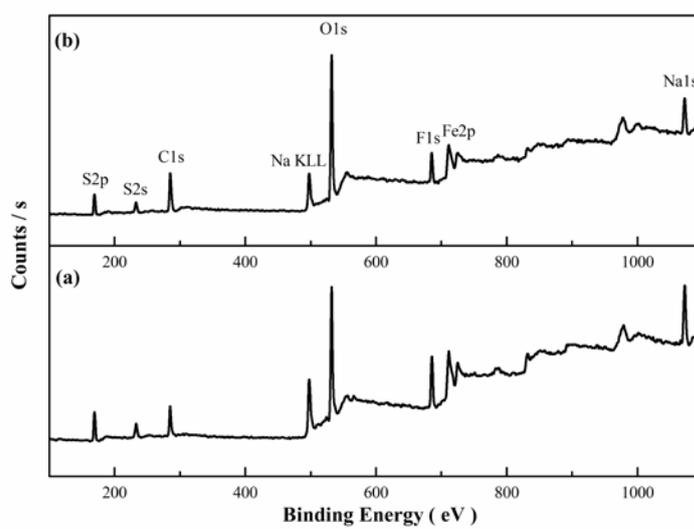


Fig. 3 XPS spectra of (a)  $\text{NaFeSO}_4\text{F}$  and (b)  $\text{NaFeSO}_4\text{F} \cdot 2\text{H}_2\text{O}$ .

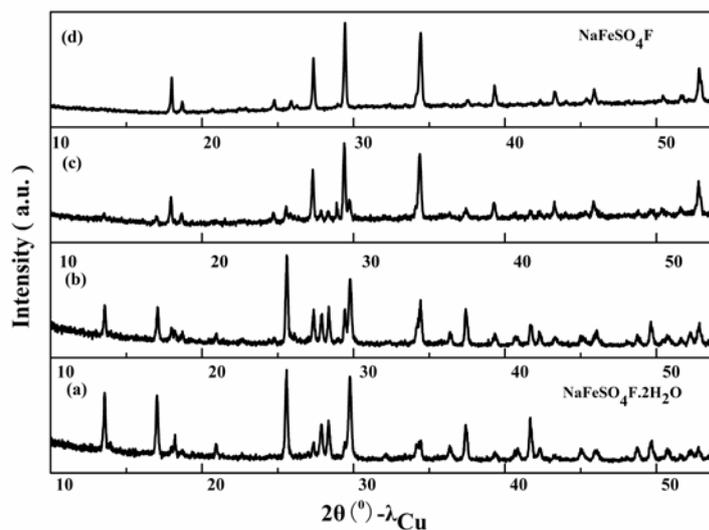


Fig. 4 XRD patterns of the products obtained in different reaction time: (a) 1 min, (b) 2 h, (c) 20 h, and (d) 40 h.

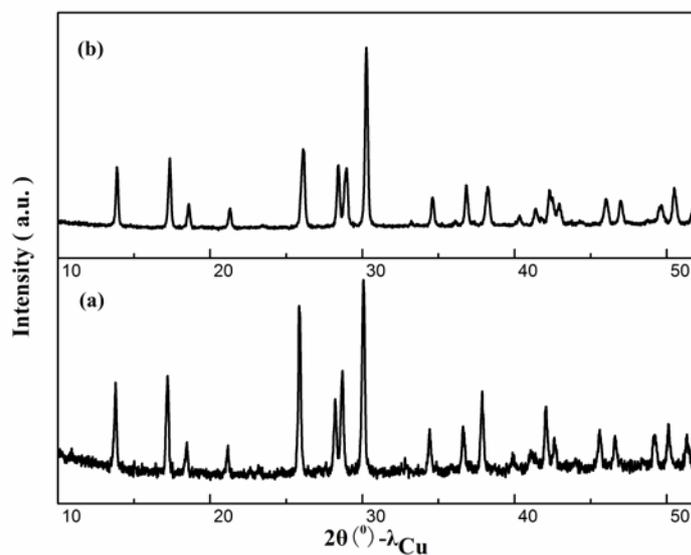


Fig. 5 X-ray powder diffraction pattern with the experimental data shown for (a)  $NaCoSO_4F \cdot 2H_2O$  ( $\lambda$  Cu): P21/m,  $a = 5.7317(1)$  Å,  $b = 7.3162(3)$  Å,  $c = 7.1918(3)$  Å,  $\beta = 113.53(0)^\circ$ ,  $V = 276.50(9)$  Å<sup>3</sup>; (b)  $NaNiSO_4F \cdot 2H_2O$  ( $\lambda$  Cu): P21/m,  $a = 5.6873(2)$  Å,  $b = 7.2583(7)$  Å,  $c = 7.1305(2)$  Å,  $\beta = 112.697(3)^\circ$ ,  $V = 269.34(8)$  Å<sup>3</sup>.

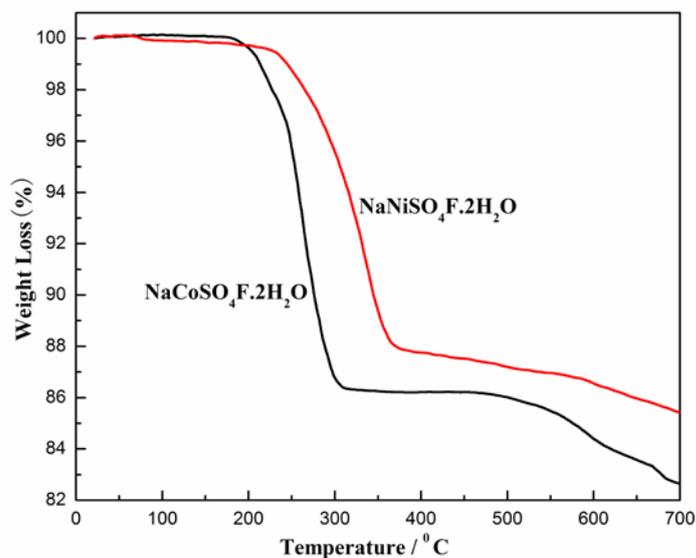


Fig. 6 Thermogravimetric analysis (TGA) of NaCoSO<sub>4</sub>F·2H<sub>2</sub>O and NaNiSO<sub>4</sub>F·2H<sub>2</sub>O conducted from RT to 700 °C at a rate of 10 °C / min under N<sub>2</sub>. For NaCoSO<sub>4</sub>F·2H<sub>2</sub>O, a 14% weight loss was noted from 180 °C to 300 °C corresponding to the departure of water<sup>12</sup>. For NaNiSO<sub>4</sub>F·2H<sub>2</sub>O, the water departure temperature started at 240 °C.

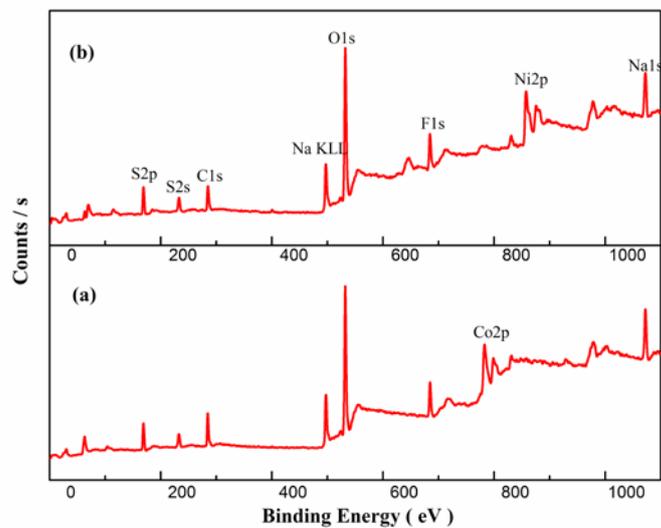


Fig. 7 XPS spectras of (a) NaCoSO<sub>4</sub>F·2H<sub>2</sub>O and (b) NaNiSO<sub>4</sub>F·2H<sub>2</sub>O. The molar ratio of Na: M: S: O: F is close to 1: 1: 1: 6: 1 in the NaMSO<sub>4</sub>F, M= Co, Ni.