



# FeOF ellipsoidal nanoparticles anchored on reduced graphene oxides as a cathode material for sodium-ion batteries

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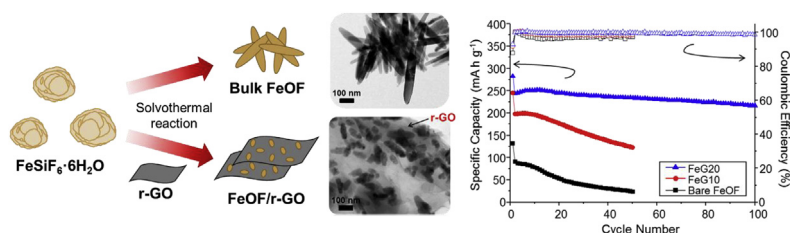
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## HIGHLIGHTS

- Ellipsoidal FeOF nanoparticles anchored on r-GO were fabricated in a mild condition.
- The particle size of FeOF was decreased with the r-GO contents in the FeOF/r-GO composites.
- The FeOF/r-GO composites show superior electrochemical performances to those of bare FeOF.

## GRAPHICAL ABSTRACT



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## ABSTRACT

FeOF/reduced graphene oxide (r-GO) nanocomposites are synthesized with approximately 8 and 13 wt% r-GO. The FeOF nanoparticles are fabricated using FeSiF<sub>6</sub>·6H<sub>2</sub>O as a precursor through solvothermal treatment with 1-propanol. This method provides a more reliable and facile wet-chemical route to synthesize phase-pure FeOF without FeF<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> impurities, as compared to the annealing process in air. The FeF<sub>2</sub> phase is formed as an intermediate during the synthetic process. The prepared FeOF/r-GO sample with 13 wt% r-GO (FeG20) exhibits improved discharge capacity, cycling stability, and rate performance as a cathode material in sodium-ion batteries, compared to the bare FeOF at 1.2–4.0 V. The enhanced electrochemical properties for sodium-ion storage are mainly attributed to the size-controlled FeOF nanoparticles and their intimate contact with the conductive r-GO matrix.

## 1. Introduction

Over the past few decades, lithium-ion batteries (LIBs) have been developed as convenient and effective power supplies for portable electronic devices, hybrid vehicles, and electric vehicles [1,2]. In recent years, their energy density and cycling performance have been significantly improved [3,4]. However, the high cost and scarcity of lithium have spurred the exploration of alternative energy storage systems to LIBs, especially for large-scale applications [5]. Sodium-ion batteries (SIBs) have been extensively investigated as next-generation energy storage devices because of their low cost, abundance,

comparable energy density, and similar redox reactions to LIBs [6,7]. However, it is challenging to develop and optimize electrode materials for SIBs due to the larger radius of sodium ion compared to the lithium ion (1.02 vs. 0.59 Å, respectively, an increase of approximately 70%), which often leads to sluggish diffusion kinetics of sodium ions and structural instability of the host materials during repeated charge/discharge cycles in SIBs [8–10]. To solve these issues, various cathode materials have been developed and their electrochemical properties have been improved in SIBs because the reversible capacities of full cells are predominantly determined by the capacities of their cathode materials. However, previously reported cathode materials such as

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layered sodium metal oxides, olivine sodium metal phosphates, NASICON sodium metal polyanions, and sodium metal fluorophosphates have limited theoretical capacities of less than approximately 180 mAh g<sup>-1</sup> through intercalation reactions [11–14]. Therefore, it may be advantageous to investigate conversion-type cathode materials with higher theoretical capacities to develop improved SIBs.

Iron oxyfluoride (FeOF) has received increasing attention as a promising cathode material for SIBs because it is low-cost and has a high theoretical capacity approximately 885 mAh g<sup>-1</sup>. This is achieved through insertion and conversion reactions, for example (1) FeOF + Na<sup>+</sup> + 1e<sup>-</sup> → NaFeOF and (2) NaFeOF + 2Na<sup>+</sup> + 2e<sup>-</sup> → Fe(O) + NaF + Na<sub>2</sub>O [15–17]. In addition, the coexistence of covalent Fe–O bonds and ionic Fe–F bonds can improve the reversible capacity and cycling stability, and increase operating voltages [18–20]. Despite these benefits, its slow ionic diffusion kinetics and low electrical conductivity must be improved to achieve sufficient electrochemical performance in SIBs. Several studies have been conducted on the synthesis of high performance FeOF based cathode materials by investigating FeOF/C nanocomposites and nanostructured FeOF particles for LIBs and SIBs [18,21–25]. However, the developed synthetic methods require a high energy ball-milling process, which often causes structural defects, corrosive HF acid, toxic F<sub>2</sub> gas, high calcination temperatures above 950 °C with expensive Pt tubes, and special experimental tools to use plasma [18,21–25]. In addition, FeSiF<sub>6</sub>·6H<sub>2</sub>O, which was prepared by reacting H<sub>2</sub>SiF<sub>6</sub> and metallic Fe(0), was used as an intermediate to form FeOF by heat treatment at a low temperature (< 250 °C) in air [18,21,23]. However, it is difficult to obtain phase-pure FeOF particles without FeF<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> impurities by this approach, which are less active as cathode electrodes for sodium-ion storage [26–28]. Furthermore, FeOF/carbon or organic polymer electrodes were usually fabricated by compositing preformed FeOF particles with activated carbon black or poly(3,4-ethylenedioxythiophene) (PEDOT) [18,21,23,25]. However, establishing closer contacts between FeOF and carbon matrices at the molecular level has not yet been fully explored, for example, by intermixing liquid-phase precursors, although the positive effects of forming the effective electrical networks to improve the electrochemical properties of insulative metal fluorides (e.g. FeF<sub>3</sub>, FeF<sub>2</sub>, and CoF<sub>2</sub>) have been reported [29–31]. This is mainly because of the poor stability of FeOF against reductive thermal treatments at high temperatures above 600 °C. Therefore, it is important to develop an easily accessible synthetic route to fabricate FeOF nanoparticles intimately composited with a conductive carbon matrix for use in high performance SIBs.

In this work, FeOF/r-GO nanocomposites were synthesized by simply anchoring FeSiF<sub>6</sub>·6H<sub>2</sub>O on r-GO in a liquid phase and performing a subsequent solvothermal reaction, as shown in Fig. 1. Utilizing the dissolved FeSiF<sub>6</sub> phase as a precursor of FeOF facilitated the establishment of intimate contacts between the FeOF particles and r-GO sheets and provided less corrosive synthetic conditions than other

previous methods, which used HF and F<sub>2</sub> gas to prepare FeF<sub>3</sub> or FeF<sub>3</sub>·3H<sub>2</sub>O powders as the precursors of FeOF. In addition, oxidative damage of r-GO was mitigated by performing the solvothermal reaction instead of the heat treatments above approximately 250 °C in air to convert FeSiF<sub>6</sub>·6H<sub>2</sub>O to FeOF [18,21,23]. The as-prepared FeOF nanoparticles wrapped by r-GO exhibited significantly improved electrochemical properties compared to bare FeOF particles in SIBs. To our knowledge, this study is the first attempt to prepare r-GO wrapped FeOF nanoparticles.

## 2. Experimental section

### 2.1. Samples preparation

#### 2.1.1. Reduced graphene oxide (r-GO)

Graphene oxide (GO) was fabricated by a modified Hummer's method [32,33]. Briefly, 0.1 g of natural graphite flakes (Asbury, USA), 0.5 g K<sub>2</sub>SO<sub>5</sub> (99%, Aldrich), and 0.5 g P<sub>2</sub>O<sub>5</sub> (98%, Aldrich) were added to 10 mL of H<sub>2</sub>SO<sub>4</sub> (95–98%, Aldrich), sonicated for 1 h, and stirred at 80 °C for 5 h. Afterwards, the solution was filtered, washed with deionized (DI) water, and dried at 80 °C in an oven for 12 h. The dried powder was then dispersed in 20 mL H<sub>2</sub>SO<sub>4</sub> (95–98%, Aldrich), and 0.5 g KMnO<sub>4</sub> (99%, Aldrich) and 18 mL H<sub>2</sub>SO<sub>4</sub> (95–98%, Aldrich) were added and stirred for 2 h in an ice bath. Subsequently, 300 mL of DI water and 4.2 mL of a H<sub>2</sub>O<sub>2</sub> solution (30 wt%, Aldrich) were slowly added to the mixture. When the color of the solution turned to yellowish-brown, the GO solution was decanted and treated with 1200 mL of 10 wt% HCl solution (Aldrich). The resulting GO solution was repeatedly centrifuged and washed with DI water until the supernatant solution reach a neutral pH. Finally, the neutralized GO solution was freeze-dried and thermally reduced to r-GO at 800 °C for 3 h under a flow of 96% Ar and 4% H<sub>2</sub> (50 mL/min).

#### 2.1.2. FeOF/r-GO composites

Fe powder (99%, Aldrich) was dissolved in H<sub>2</sub>SiF<sub>6</sub> (33.5–35%, Aldrich) with a 1:8 M ratio at 50 °C for 12 h. Unreacted Fe was removed by a filtration. Then, 5 mL of the filtered homogeneous FeSiF<sub>6</sub> solution was added dropwise to 5 mL of the r-GO solution (1 mg r-GO/mL ethanol) under stirring for 2 h at 25 °C, and subsequently heated at 110 °C to completely evaporate the solvents. The obtained FeSiF<sub>6</sub>/r-GO powder (70 mg) was solvothermally treated in 32 mL 1-propanol (99%, Aldrich) at 200 °C for 24 h using a Teflon-lined steel autoclave (50 mL), washed with ethanol, and dried at 80 °C for 12 h. The resulting sample was named FeG10. The other FeOF/r-GO sample was prepared using 10 mL of the r-GO solution and designated FeG20. For comparison, bare FeOF was also synthesized without r-GO following the same synthetic procedure.

### 2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku model Miniflex 600 X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ). The observed peaks were matched with Joint Committee on Powder Diffraction Standards (JCPDS) files. Fourier transform-infrared (FT-IR) spectra were measured between 400 and 4000 cm<sup>-1</sup> with a FT/IR-4600 spectrometer (JASCO). UV-vis spectra were obtained with JASCO V-770. Raman spectra were recorded on a WITec alpha 300 R with a He-Ne laser (532 nm in wavelength). X-ray photoelectron spectroscopy (XPS) experiments were conducted with a Theta Probe AR-XPS and the obtained spectra were analyzed using XPS Peak 4.1 software. Thermogravimetric analysis (TGA) was performed by a SETARAM SETSYS Evolution TGA between 25 and 800 °C at a heating rate of 5 °C min<sup>-1</sup> in air. The carbon contents of the samples were estimated using a Flash EA1112 elemental analyzer. The morphologies and particle sizes were characterized by field emission scanning electron microscope (FESEM, FEI Inspect F50) and a Cs-

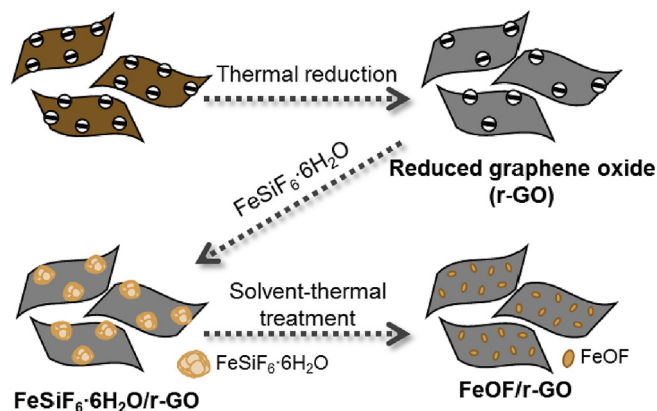


Fig. 1. Preparation of the FeOF/r-GO nanocomposites.

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