

还原氧化石墨烯包覆 MOF 衍生 In_2Se_3 用于钠离子电池负极

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RGO-Coated MOF-Derived In_2Se_3 as High-Performance Anode for Sodium-Ion Batteries

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1 Experimental section

1.1 Reagents

Indium nitrate hydrate ($\text{InN}_3\text{O}_9 \cdot x\text{H}_2\text{O}$, 99.9%, Aladdin), selenium (Se, 99.9%, Macklin), benzimidazole ($\text{C}_7\text{H}_6\text{N}_2$, 98.5%, Macklin), graphite (C, 99.95%, Macklin), 1H-Imidazole-4,5-dicarboxylic ($\text{C}_5\text{H}_4\text{N}_2\text{O}_4$, 97.0%, Aladdin), hexadecyl trimethyl ammonium bromide (CTAB, 99%, Aladdin) and *N,N*-dimethylformamide (DMF, 99.9%, keshi). All the chemicals were of analytical grade and used without further purification.

1.2 Synthesis

Reduced graphene oxide (rGO) flakes with uniform size and thickness of about 2–5 nm were prepared by the modified Hummers method (rGO). Firstly, $\text{InN}_3\text{O}_9 \cdot x\text{H}_2\text{O}$ (0.15 g), benzimidazole (1 g) and 1H-imidazole-4,5 dicarboxylic acid (0.21 g) were added to 60 mL *N,N*-dimethylformamide (DMF) respectively, fully stirred and sonicated for 10 min. Then, the mixed solution was put into an oil bath at 120 °C and stirred continuously for 4 h. The product was centrifuged at 5000 rpm, washed with ethanol for 5 times, and dried in a vacuum oven at 60 °C for 12 h. Ultimately, In-MOF was acquired. Subsequently, In-MOF precursor and Se powder were placed into a tubular furnace at a mass ratio of 1 : 3, and heated to 500 °C at 2 °C·min⁻¹ in an Ar atmosphere for 6 h. $\text{In}_2\text{Se}_3@\text{C}$ was then prepared. Further, $\text{In}_2\text{Se}_3@\text{C}$ (100 mg) was ultrasonically dispersed in 40 mL water. CTAB (100 mg) was added and stirred for 10 min, centrifugal washing for re-dispersion and then 4 mL of GO was added and dispersed evenly through ultrasonication. Then the mixture was stirred at 80 °C for 4 h in oil bath. After centrifugal washing and annealing at 300 °C in Ar atmosphere, $\text{In}_2\text{Se}_3@\text{C}/\text{rGO}$ was obtained.

1.3 Material characterizations

The surface morphology of samples was observed by field-emission scanning electron microscopy (FE-SEM; JSM-7500). X-ray diffraction (XRD; D/Max-Rb, Rigaku, Japan) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) were used for phase analysis. The carbon content in samples was analyzed by TGA (STA-6000). Under the laser of $\lambda_{\text{EXC}} = 633 \text{ nm}$, the degree of carbon graphitization was analyzed by Raman shift. The size and thickness of GO were analyzed by AFM. Zeta potential (Malvern) was used to analyze the surface potential of samples. The composition and valence of the elements were verified by X-ray photoelectron spectroscopy (XPS; Perkin-Elmer, PHIX-tool).

1.4 Electrochemical characterizations

To perform electrochemical tests on the composites prepared, 70% (*w*, mass fraction) samples, 20% (*w*) super carbon and 10% (*w*) polyvinylidene fluoride (PVDF) binder were mixed in *N*-Methylpyrrolidone (NMP) to form a uniform slurry, which was then coated on copper foil. After drying for 12 h in a vacuum oven at 60 °C, then the electrode sheet with a diameter of 8 mm was cut by a Slicing machiner. Finally, with sodium foil as a reference electrode, NaPF_6 in Dimethoxyethane as an electrolyte, 2032 coin cell was assembled in an Ar filled glove box. At 0.01–3 V, galvanostatic discharging/charging test was carried out with the battery test system. To analyze the reaction mechanism in the electrochemical process, cyclic voltammetry (CV) curves was tested by the electrochemical workstation (AMETEK) in the voltage range of 0.01–3 V. To understand the impedance change during the reaction process, electrochemical impedance spectroscopy (EIS) analysis was carried out at 100000 kHz–0.01 Hz.

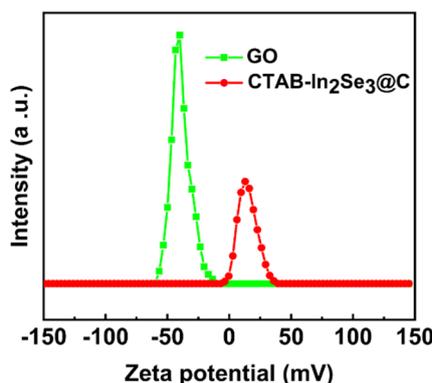


Fig. S1 Zeta potential of $\text{CTAB-In}_2\text{Se}_3@\text{C}$ and GO.

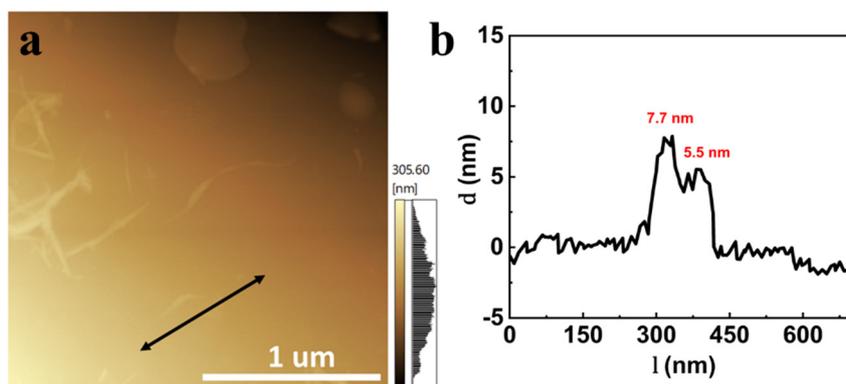


Fig. S2 (a) AFM image and (b) thickness distribution of GO.

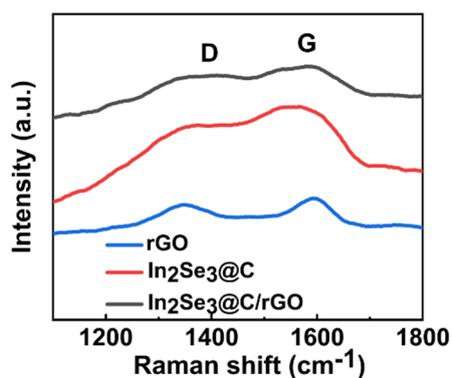


Fig. S3 Raman shift of samples.

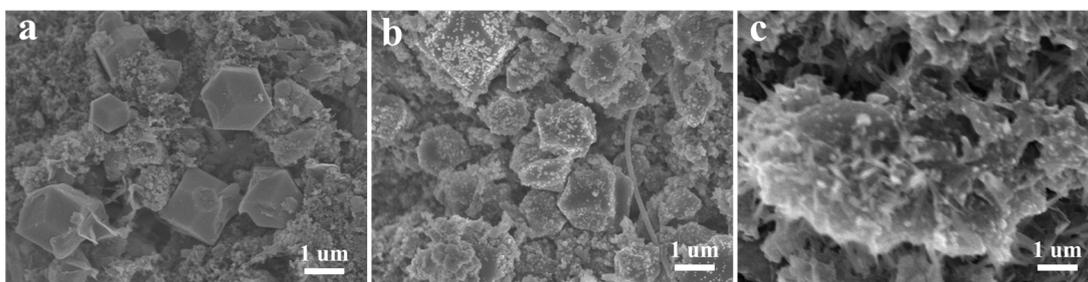


Fig. S4 (a) FE-SEM images of $\text{In}_2\text{Se}_3/\text{C}/\text{rGO}$ anode and (b) after 200 cycles at $1 \text{ A}\cdot\text{g}^{-1}$. (c) FE-SEM images of $\text{In}_2\text{Se}_3/\text{C}$ after 200 cycles at $1 \text{ A}\cdot\text{g}^{-1}$.

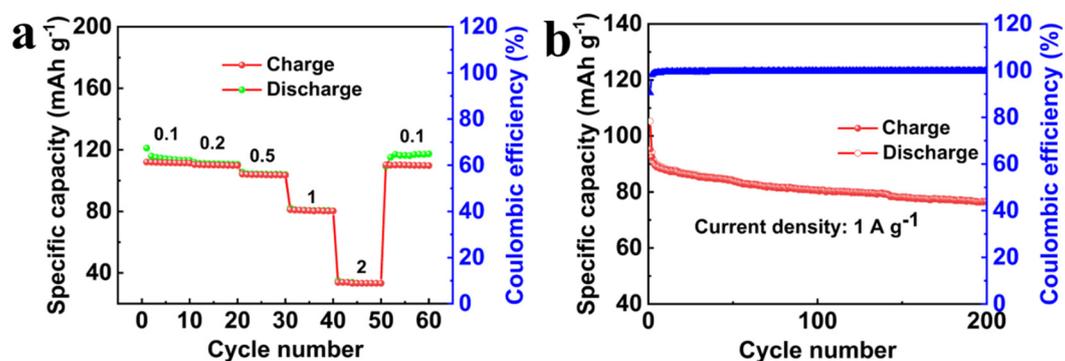


Fig. S5 The electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.

(a) Rate capability and (b) Cycling performance at $1 \text{ A}\cdot\text{g}^{-1}$.