

Facile, mild and fast thermal-decomposition reduction of graphene oxide in air and its application in high-performance lithium batteries

**Zhong-li Wang, Dan Xu, Yun Huang, Zhong Wu, Li-min Wang and Xin-bo
Zhang^{*}**

*State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of
Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China*

1. Chemicals and Materials

Graphite powders (325 mesh, Alfa Aesar, 99.8%, AR), Potassium permanganate (KMnO₄, Aldrich Reagent, AR), Sulfuric acid (H₂SO₄, ≥98%, Beijing Chemical Work, AR), Phosphoric acid (H₃PO₄, ≥85%, Beijing Chemical Work, AR), Hydrogen peroxide (H₂O₂, 30%, Aladdin Reagent, AR), Hydrochloric acid (HCl, 36%-38%, Beijing Chemical Work, AR), Vanadium pentoxide (V₂O₅, >99%, Beijing Chemical Work, AR), Ammonium persulfate ((NH₄)₂S₂O₆, ≥98%, Xilong Chemical Work, AR), Acetylene black (Hong-xin Chemical Works), Polyvinylidene fluoride (PVDF, DuPont Company, 99.9%), N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR), Separator (polypropylene film, Celgard 2400), Electrolyte (1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with the weight ratio of 1:1, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd).

2. Experimental details

2.1 Preparation of GO

Graphite oxide was synthesized by an improved Hummers method. Briefly, a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (45:5 mL) was added to a mixture of graphite flakes (0.375 g) and KMnO₄ (2.25 g). The reaction was then heated to 50 °C and stirred for 24 h. The reaction was cooled to room temperature and poured onto ice (200 mL) with 30% H₂O₂ (3 mL). Then, the

mixture was centrifuged (8000 rpm for 5 min). The remaining solid material was then washed in succession with 200 mL of 30% HCl for two times, and 200 mL of water for three times. For each wash, the mixture was centrifuged (13000 rpm for 20 min) and obtains the remaining material. The final resulting material was freeze-dried for 24 hours to obtain graphite oxide. Graphite oxide was further diluted in deionized water, ultrasonication for 60 min to obtain graphene oxide.

2.2 Thermal-decomposition reduction of GO in air

Solid GO sheets were obtained by frozen-dry of exfoliated GO sheets in water. After heating at 300 °C for 1h with 2 °C/min. GO sheets were decomposed into graphene. In order to optimize the reduction conditions, different heating temperatures (200, 250, 300, 350, and 400 °C) were investigated.

For comparison, three other methods were used to reduce graphene oxide. The first method was thermal reduction in N₂: GO was calcined in N₂ at 300 °C for 1h with 2 °C/min. The second one was thermal reduction in 5% H₂/Ar: GO was calcined in H₂/Ar at 550 °C for 1h with 2 °C/min. The third one was chemical reduction by using hydrazine as reductant: 35 µL of hydrazine solution (50% w/w) and 400 µL of ammonia solution (25% w/w) were added into 50 ml GO solution (0.5 mg/ml) and then stirred for 1h at 95 °C.

2.3 Preparation of V₂O₅ nanosheets/graphene composite

In a typical synthesis of (NH₄)₂V₆O₁₆ nanosheets, 0.36 mg V₂O₅ commercial power and 4.4 g ammonium persulfate (APS, 20 mmol) were added into 36 mL H₂O. After stirring for 48 h at 50 °C, the golden-yellow precipitate was collected by centrifugation, washed thoroughly with water, and frozen-dried. The (NH₄)₂V₆O₁₆ nanosheets/graphene oxide composite was prepared by directly mixed them in water with ultrasonication for 1h and then was frozen-dried. After treatment of the composite at 350 °C in air for 1 h, the V₂O₅/graphene composite was obtained. The content of graphene in the composite was 20 wt% by the TG analysis. As a comparison, the sample was prepared in N₂ atmosphere at the same conditions.

3. Materials Characterizations

Thermogravimetric analysis (TG) was carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 25 to 700 °C in a air flow of 80 ml/min at a heating rate of 5 °C /min. Wide-angle X-ray diffraction (XRD) patterns were collected on Bruker D8 Focus Powder X-ray diffractometer using Cu K α radiation (40 kV, 40 mA). The scanning electron microscopy (SEM)

was performed by using a field emission scanning electron microscopy (FE-SEM, HITACHI S-4800). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on a FEI Tacnai G2 electron microscope operated at 200 kV. Atomic Force Microscopy (AFM) experiments were carried out with Veeco Instruments Nanoscope in tapping mode. The electrical conductivity of the GO and graphene was measured by four-point probe method (Keithely 2400). The solid samples were pressed into disk under 20 MPa before measurement.

4. Electrochemical measurement

The positive electrodes were fabricated by mixing 80 wt% active materials, 10 wt% acetylene black and 10 wt% PVDF binder in appropriate amount of NMP as solvent. Then the resulting paste was spread on an aluminum foil by Automatic Film Coater with Vacuum Pump & Micrometer Doctor Blade (MTI). After the NMP solvent evaporation in a vacuum oven at 120 °C for 12 h, the electrodes were pressed and cut into disks. A CR2032 coin-type cell was assembled with lithium metal as the counter and reference electrode and polypropylene film as a separator. The cells were constructed and handled in an argon-filled glovebox. The charge-discharge measurements were carried out using the Land battery system (CT2001A) at a constant current density in a voltage range of 2-4 V versus Li/Li⁺.

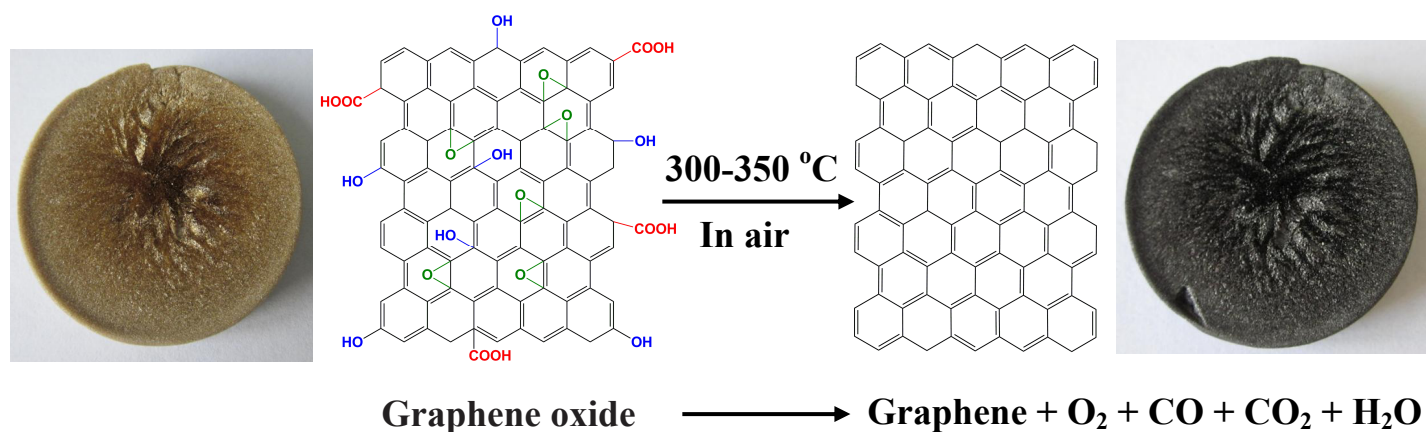


Fig. S1 Illustration of the reduction process of graphene oxide by thermal decomposition in air.

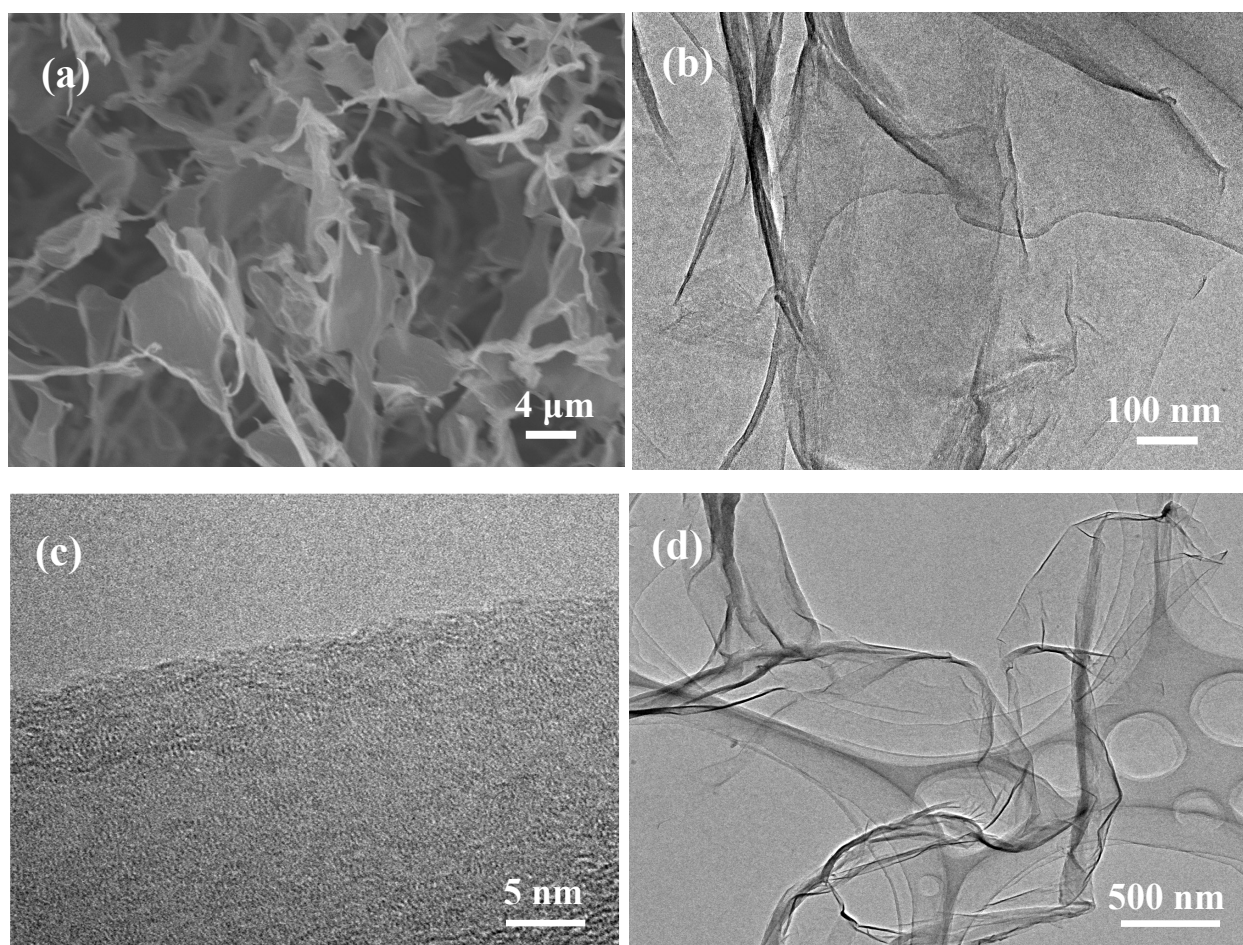


Fig. S2 SEM (a), TEM (b), and **HRTEM (c) images** of GO; (d) TEM image of GO reduced at 300 °C for 1 h in air.

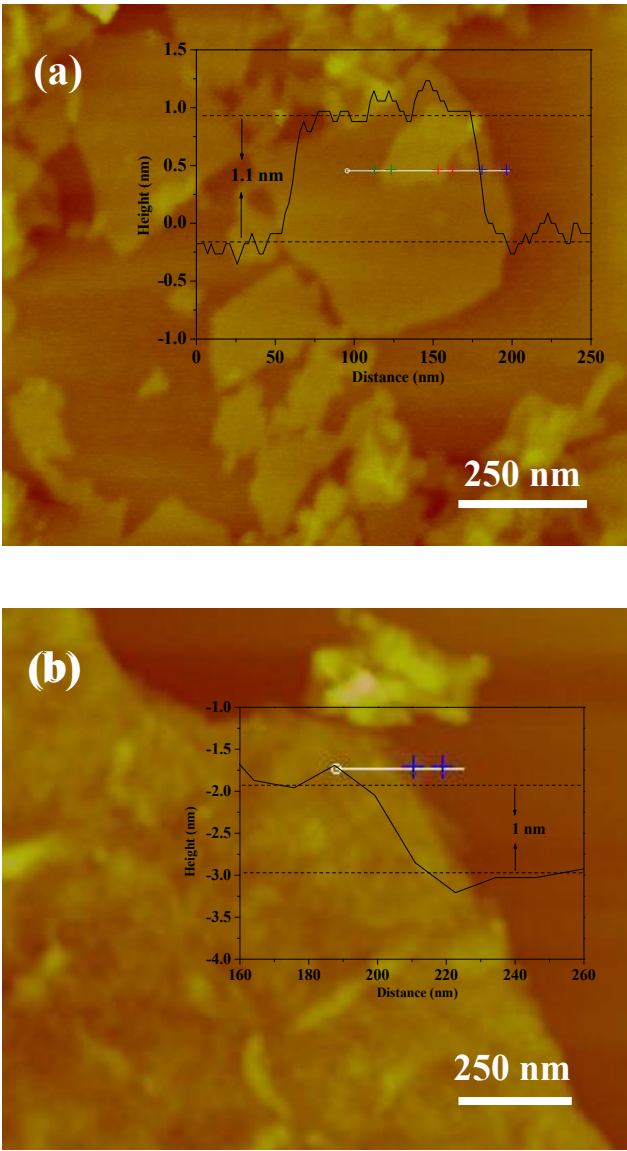


Fig. S3 AFM images of GO before (a) and after (b) reduction at 300 °C for 1 h in air.

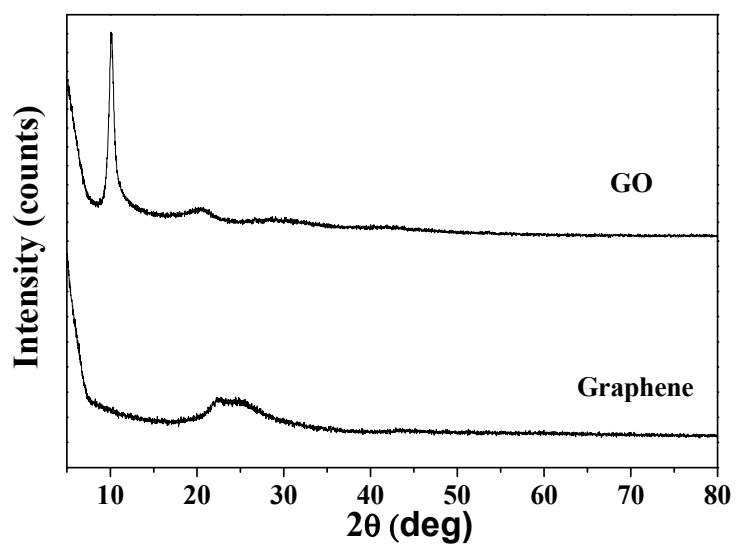


Fig. S4 X-ray diffraction (XRD) patterns of GO and reduced GO at 300 °C for 1 h in air.

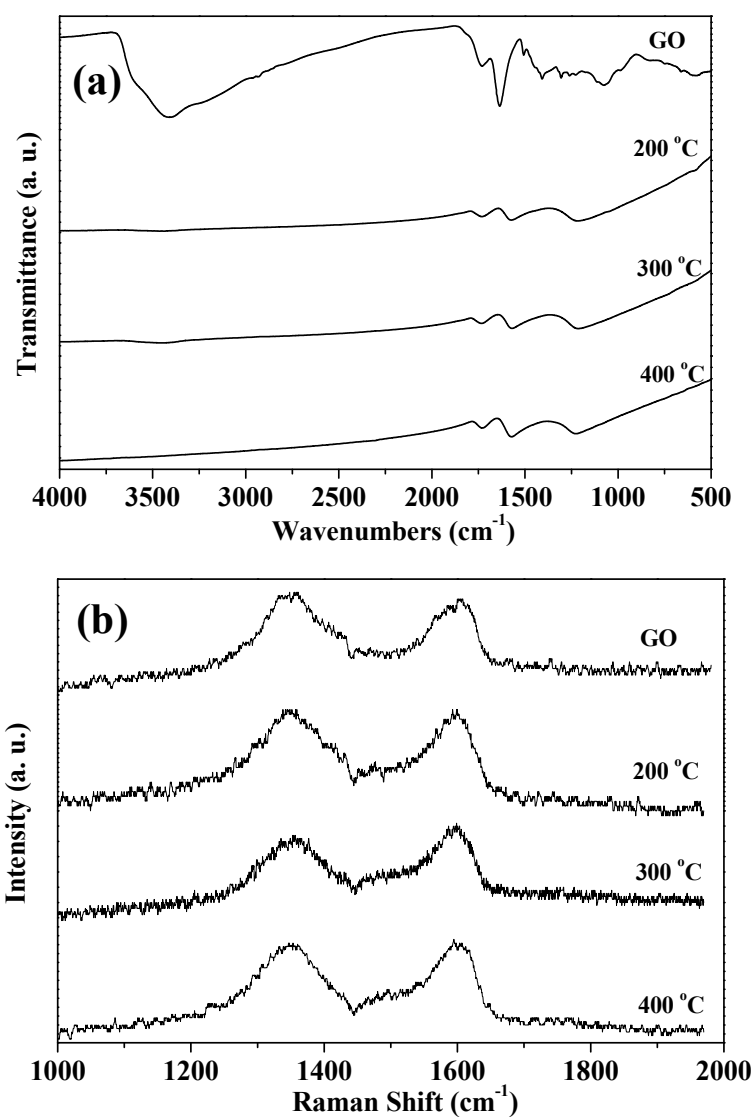


Fig. S5 FT-IR (a) and Raman (b) spectra of GO before and after decomposition at 200, 300, and 400 °C for 1h in air.

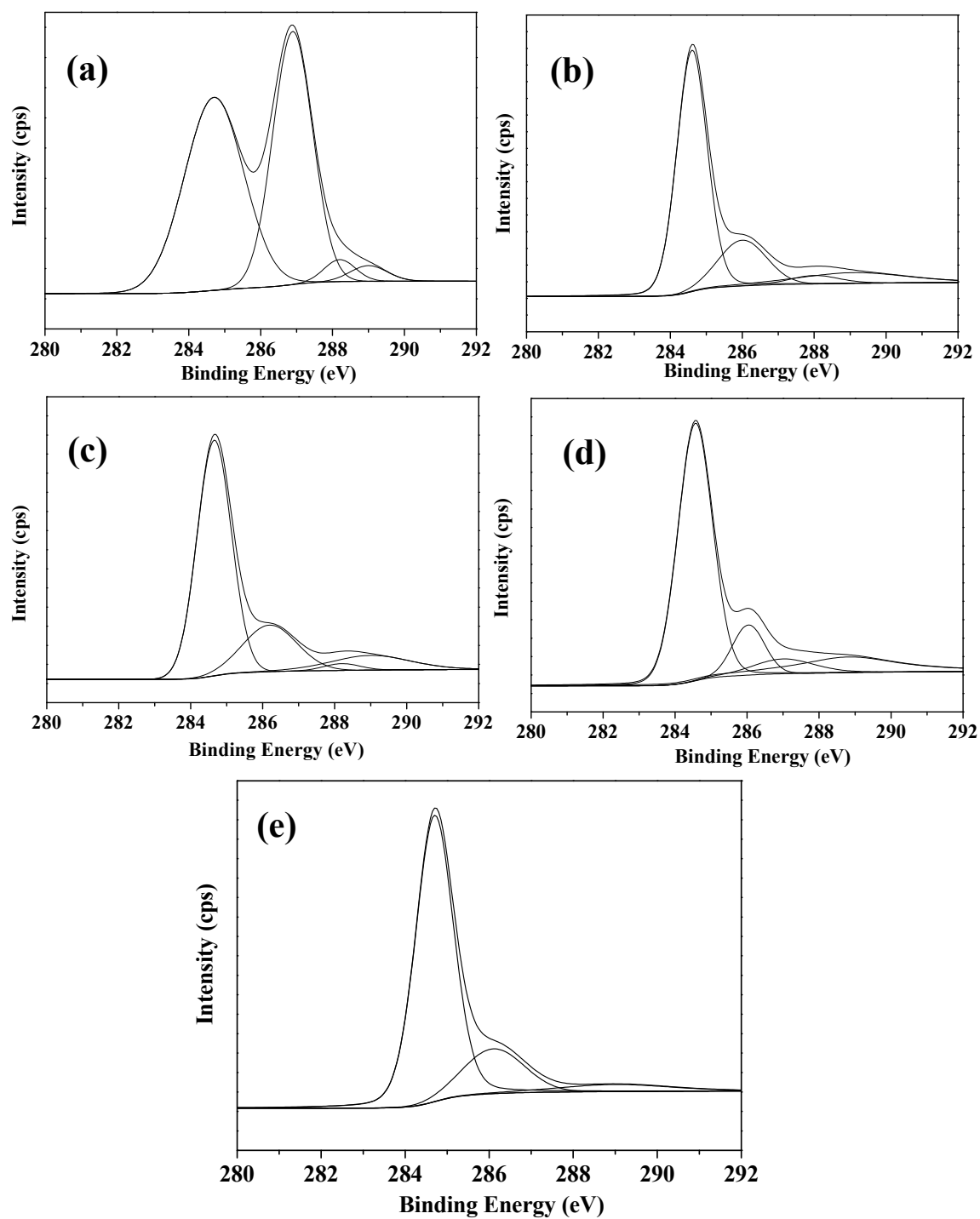


Fig. S6 XPS spectra of C1s of GO before (a) and after (b-d) decomposition at 200, 300, and 400 °C for 1h in air, respectively. (e) XPS spectra of C1s of GO reduced at 550 °C for 1h in 5% H₂/Ar.

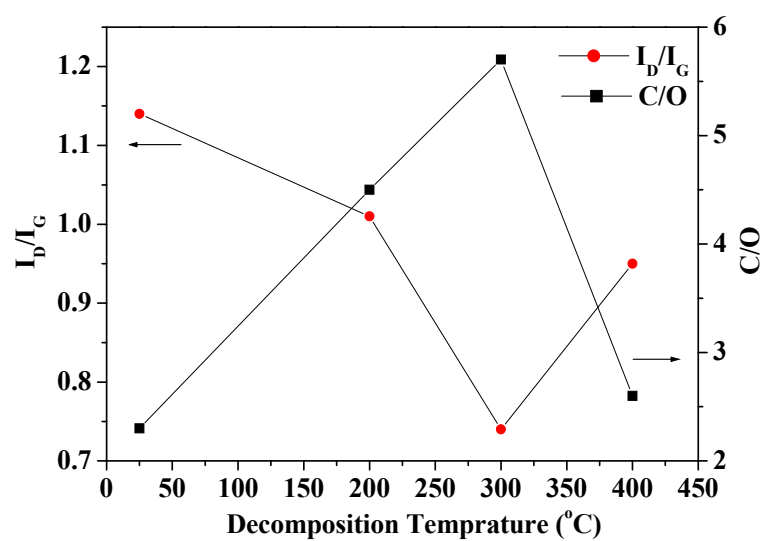


Fig. S7 The change of I_D/I_G and C/O ratios with temperatures during the thermal-decomposition reduction of GO.

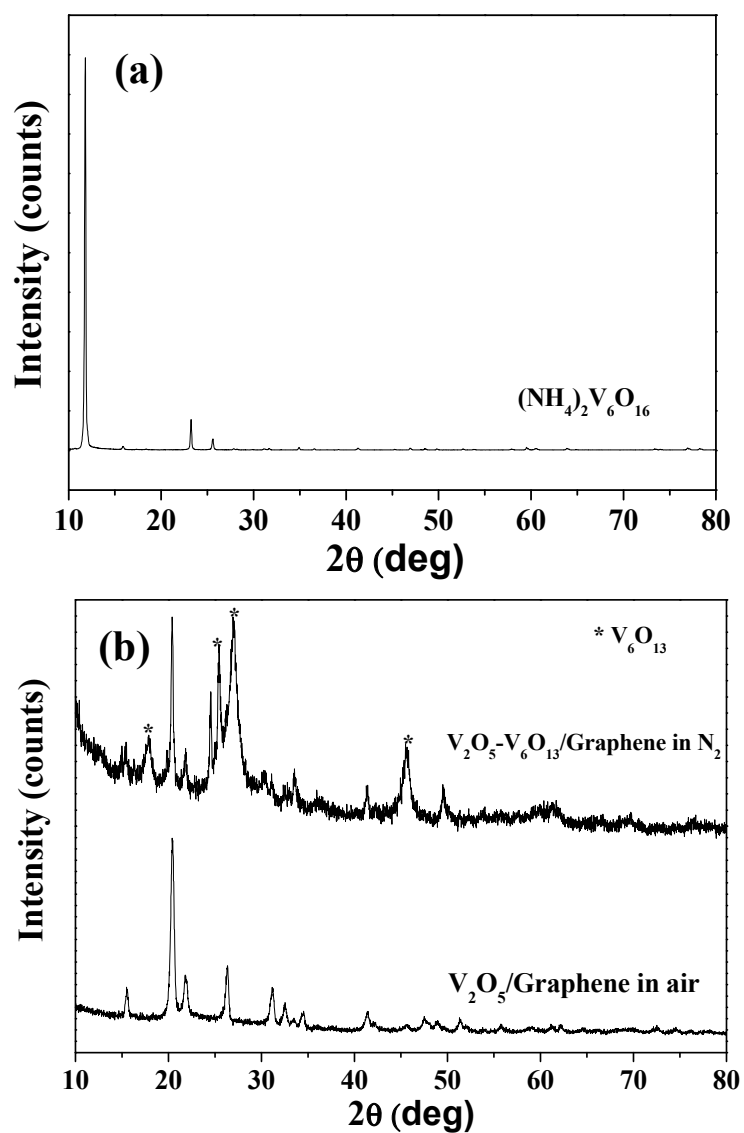


Fig. S8 (a) XRD pattern of $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ nanosheets; (b) Comparison of XRD patterns of V_2O_5 /graphene composite prepared using different reduction method of GO.

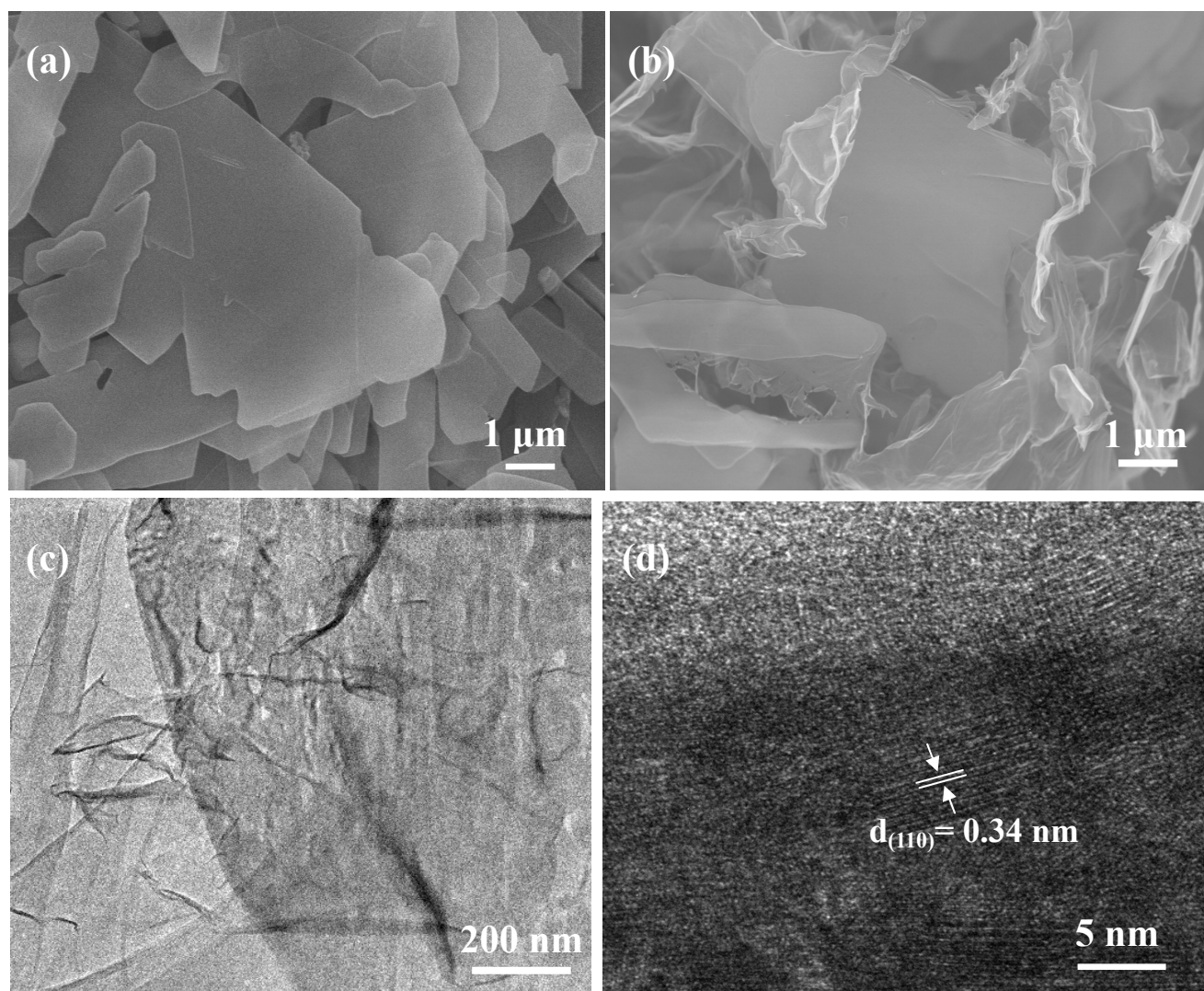


Fig. S9 SEM images of $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ nanosheets (a) and V_2O_5 nanosheets/graphene (b); (c) TEM and (d) HRTEM images of V_2O_5 nanosheets/graphene prepared at 350 °C in air.

The obtained $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ is very thin nanosheets with size of 10-20 nm in thickness and several micrometers in width (Fig. S9a). After mixing with GO uniformly and heating treatment in air, $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ nanosheets/GO is converted into V_2O_5 nanosheets/graphene composite and forms sandwich-like structure (Fig. S9b and c). The lattice fringes can be observed along (110) plane of V_2O_5 from the edge of an individual V_2O_5 nanosheets/graphene assemble (Fig. S9d).

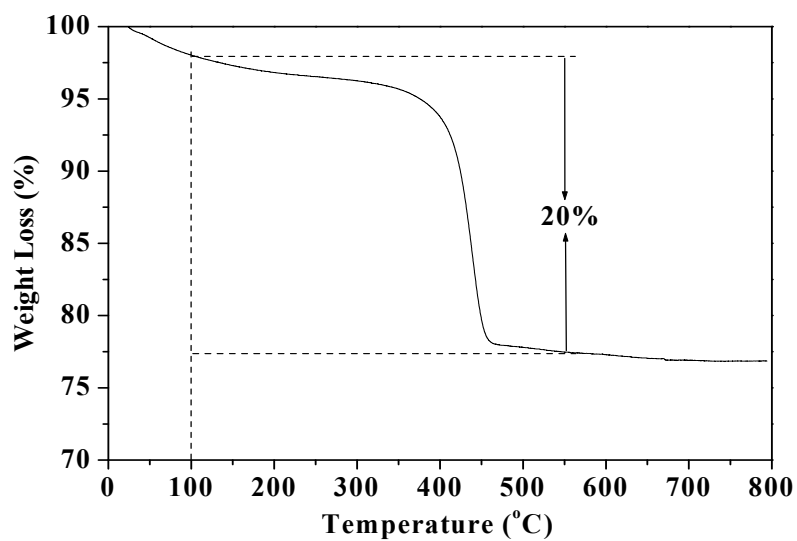


Fig. S10 Thermogravimetric analysis of the V_2O_5 /graphene composite in air atmosphere.

The weight loss of ~3% below 100 $^{\circ}C$ is probably due to the evaporation of the absorbed moisture contents. From the TG curve, the content of graphene is ~20 wt%.

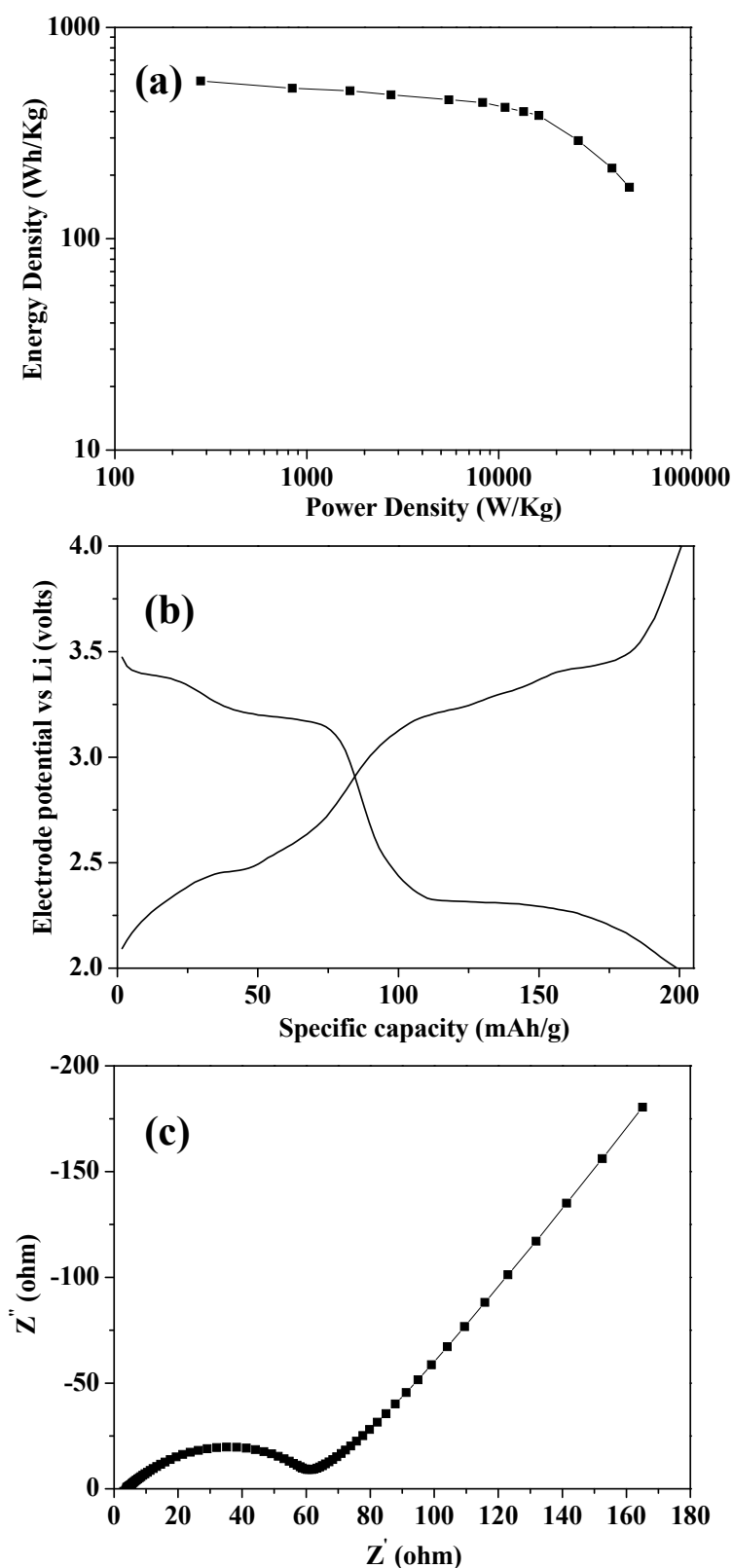


Fig. S11 (a) The Ragone plots of V_2O_5 nanosheets/graphene composite, (b) The discharge-charge curve of the composite at the current density of 300 mA/g, (c) Electrochemical impedance spectra of coin cell using V_2O_5 nanosheets/graphene composite electrode after 100 discharge-charge cycles.