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Reduced graphene oxide modified V_2O_3 with enhanced performance for lithium-ion battery

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ABSTRACT

Reduced graphene oxide (rGO) modified vanadium teroxide (V_2O_3) is synthesized by a solvothermal process followed with calcination treatment in a reducing atmosphere. The as-prepared hybrid materials were quite uniform and V_2O_3 distributed homogeneously in the hybrid composite. The influence of annealing atmospheres to the electrochemical performance of the electrode material was also studied. As an anode material for lithium ion batteries, the V_2O_3–rGO composite exhibited higher capacity and better cyclic stability.

1. Introduction

Clean and renewable power source is of great importance to alleviate the energy shortage and environmental pollution [1]. Hybrid functional materials are explored in electrical energy storage field, such as rechargeable Li-ion batteries [2–4] and supercapacitors [5,6], owing to their enhanced performance as compared to the individual components [7].

Vanadium oxides have been explored as promising electrode materials for lithium-ion batteries due to their low cost, easy synthesis method and large theoretical specific capacity. Vanadium oxides have varied oxidation states and are redox active during the electrochemical process, which enable their application in rechargeable lithium batteries [8–11]. V_2O_3 was firstly studied in the 1970s as metal–insulator transitions [12]. The low conductivity of V_2O_3 has limited its use in energy storage. Although many works have been devoted to improve the electrochemical performance of V_2O_3 in LIBs [13–18], its cyclic stability still needs further improvement.

Graphene has drawn extensive attention due to its outstanding electrical conductivity, large specific surface area and high thermal/chemical stability [19–21]. Moreover, it can prevent the direct exposure of electrode from electrolyte and preserve the structural stabilization of active materials. To date, many methods have been reported to synthesize metal oxide–graphene composites [4,22,23]. In this work, reduced graphene oxide (rGO) modified V_2O_3 was synthesized by a solvothermal method with following heat treatment in a reducing atmosphere, in which graphene is used as a conductive additive to enhance the cyclic stability and high rate capability of V_2O_3.

2. Experimental section

Materials synthesis: Vanadyl oxalate (VOC_2O_4) was firstly prepared as intermediate vanadium sources [11]. V_2O_5 and $H_2C_2O_4 \cdot 2H_2O$ (molar ratio 1:3) were dissolved in de-ionized water under vigorous stirring at 80 °C until a clear blue VOC_2O_4 solution was formed. The graphene oxide (GO) was synthesized by a modified Hummers method [24]. In the solvothermal process, 1.5 mL VOC_2O_4 and 5 mL (5 mg mL^{-1}) GO were dispersed uniformly in 25 ml ethylene glycol (EG). Then the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 200 °C for 12 h. The product was collected by centrifugation and washed with ethanol for several times. The obtained products were dried in vacuum and then annealed at 600 °C for 4 h in 8% H_2 and 92% Ar mixed atmosphere. In comparison, rGO was produced following the same procedures except no VOC_2O_4 was added in the solvothermal process. V_2O_3–rGO–Ar composite was synthesized at 100% Ar atmosphere without any reducing atmosphere in the calcinations step.

Structural characterizations: The crystalline structure of the V_2O_3–rGO composite was analyzed by X-ray diffraction (XRD, Rigaku D/max 2500 XRD). The morphology was analyzed by Scanning electron microscopy (SEM, Quanta FEG 250). The thermogravimetric analysis (TGA, NETZSCH STA 449C) was conducted under ambient atmosphere with a heating rate of 10 °C min^{-1}

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from room temperature to 650 °C. Electron Probe Microanalysis (EPMA, JXA-8230) was performed to characterize the elemental distribution in the composites.

Electrochemical measurements: V_2O_3–rGO composite was mixed with acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 in an N-methyl-2-pyrrolidone (NMP)

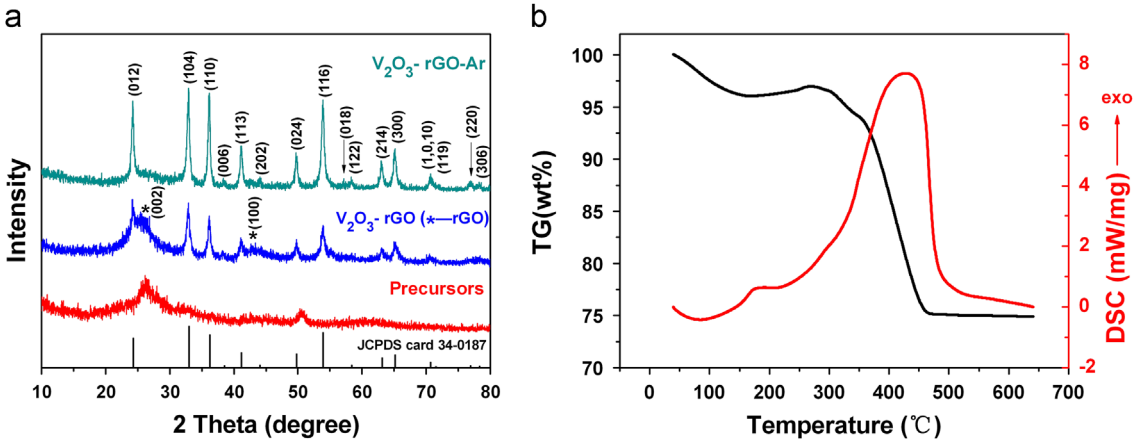

Fig. 1. (a) XRD patterns of the solvothermally prepared precursors, V_2O_3–rGO and V_2O_3–rGO–Ar; (b) TG and DSC curves of the V_2O_3–rGO composite.

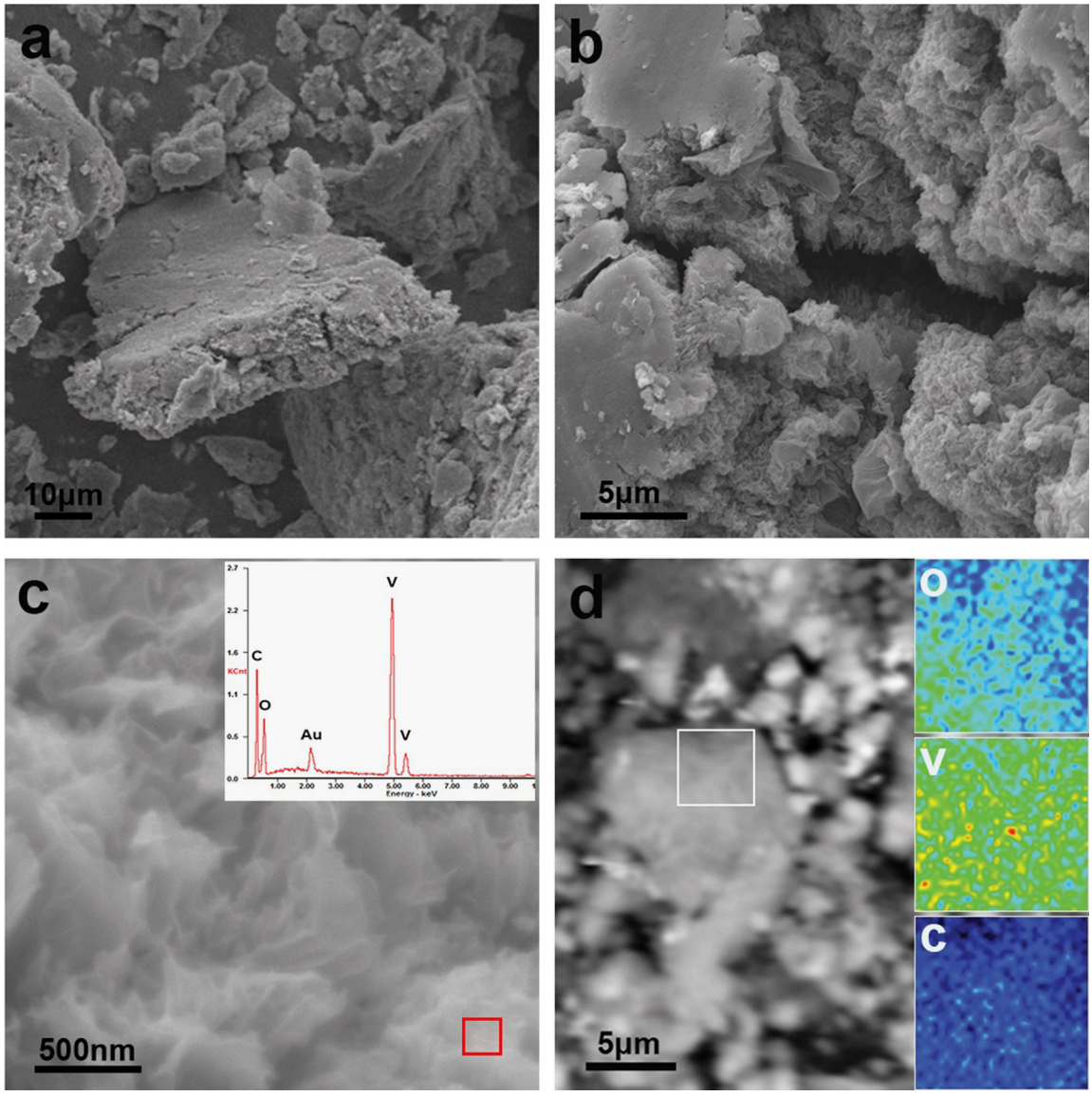

Fig. 2. (a–c) SEM images and EDS (inset in c) of V_2O_3–rGO composite; (d) EMPA images of the V_2O_3–rGO composite. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)