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1D ultrafine SnO_2 nanorods anchored on 3D graphene aerogels with hierarchical porous structures for high-performance lithium/sodium storage

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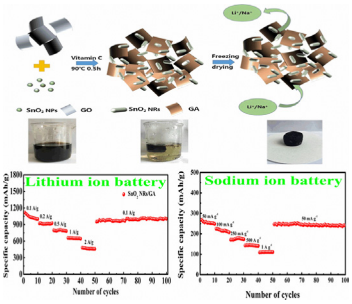
GRAPHICAL ABSTRACT

1D ultrafine SnO_2 nanorods anchored on 3D graphene aerogel (SnO_2 NRs/GA) composite is prepared through a simple reduction-induced self-assembly method. The unique 3D network structure as well as the synergistic effect between 3D graphene nanoshhet and 1D SnO_2 nanorods endows the as-prepared SnO_2 NRs/GA composite with the good electrochemical lithium/sodium storage performance.



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ABSTRACT

SnO_2 is considered as one of the most promising alternative anode materials for lithium ion batteries (LIBs) and sodium ion batteries (SIBs) due to high specific capacity, low discharge voltage plateau and environmental friendliness. In this work, 1D ultrafine SnO_2 nanorods anchored on 3D graphene aerogel (SnO_2 NRs/GA) composite is prepared through a simple reduction-induced self-assembly method in the solution of graphene oxide (GO), Vitamin C and SnO_2 nanoparticles. Vitamin C plays an important role in the reduction of GO. The structural and morphological characterizations demonstrate that 1D ultrafine SnO_2 nanorods are uniformly and tightly anchored on the surface of 3D graphene nanosheet aerogels. The unique 3D network structure as well as the synergistic effect between 3D graphene nanoshhet and 1D SnO_2 nanorods endows the as-prepared SnO_2 NRs/GA composite with the good electrochemical lithium/sodium storage performance. It delivers the high initial discharge capacity (1713 mA h g^{-1} at 0.1 A g^{-1} for LIBs and 539 mA h g^{-1} at 0.05 A g^{-1} for SIBs) and good cycle stability (869 mA h g^{-1} at 0.1 A g^{-1} after 50 cycles for LIBs and 232 mA h g^{-1} at 0.05 A g^{-1} after 100 cycles for SIBs). Moreover, the SnO_2 NRs/GA composite exhibits excellent cycle stability for SIBs with a high reversible capacity of 96 mA h g^{-1} at as high as 1 A g^{-1} for 500 cycles. This work provides a simple method to fabricate the electro-active materials-graphene aerogel composites for high-performance LIBs and SIBs.

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1. Introduction

Recently, lithium ion batteries (LIBs) have become the most attractive technologies for electric vehicles and portable electronics due to their high energy density and environmental benignity [1–4]. More importantly, sodium ion batteries (SIBs) have attracted unprecedented attention recently on account of their low cost and abundant resource compared to LIBs [5–9]. However, the energy densities and cycle life of LIBs and SIBs are insufficient to completely satisfy social needs and have become a critical issue. Therefore, to solve these problems, it is necessary to develop advanced electrode materials with high performance for both LIBs and SIBs. In the case of anode materials, SnO_2 is a promising anode material in both LIBs and SIBs because of its high capacity, low cost and environmental friendliness [9–11]. However, the use of SnO_2 has been mainly restricted by the low electrical conductivity, easy agglomeration and inferior cycling stability resulting from a large volume change during Li^+/Na^+ insertion/extraction process. To circumvent these problems, many efforts have been made to enhance the electrochemical performance of SnO_2 by designed nanostructured materials or hybridized with carbon-based material. To date, nanostructured SnO_2 anode materials with various morphologies have been developed, such as nanosheets [12,13], nanorods [14,15], nanowires [16–18], nanotubes [19,20] and 3D hollow nanostructures [21–23]. The electrochemical results demonstrate that the morphology of SnO_2 plays an important role on its lithium/sodium storage performance. In contrast, 1D structure, such as nanowires, nanotubes and nanorods, can relieve large volume strain relaxation during the charge/discharge process and display short Li^+/Na^+ transport distance [24–26]. Unfortunately, the pure 1D SnO_2 structure tends to aggregate together, which largely limits its specific capacity. To deal with this issue, an effective strategy is to distribute 1D SnO_2 into the carbon substrate. Zhao and coworkers [27] reported 1D SnO_2 nanowires coated with amorphous carbon nanotube composite with a reversible capacity of 441 mA h g^{-1} and a good cycle performance. Kim et al. [28] prepared SnO_2 nanorod-planted graphite composite via a catalyst-assisted hydrothermal method. The SnO_2 nanorod-graphite composite exhibited the high initial lithium storage capacity (1010 mA h g^{-1} at 72 mA g^{-1}) and good cycle stability along with high Coulombic efficiency. Wang and coworkers [29] designed sandwiched graphene/carbon coated SnO_2 nanorods structure by a seed assisted hydrothermal growth approach, which delivered an extremely high reversible lithium storage capacity of 1419 mA h g^{-1} and displayed a high rate capability (540 mA h g^{-1} at 3 A g^{-1}). Recently, Liu and coworkers [30] reported the SnO_2 nanorods/graphene composite prepared via a two-step hydrothermal process followed by thermal treatment. The composite exhibits a high reversible capacity of 815 mA h g^{-1} at 0.1 A g^{-1} after 150 cycles as well as good cycle performance at 1 A g^{-1}. According to the reported results, it can be concluded the preparation process of 1D SnO_2-carbon composites requires multiple and complex steps. Meanwhile, it should be noteworthy that graphene may be considered as a promising carbon substrate to load the 1D SnO_2 with good electrochemical lithium storage performance. Importantly, compared with 2D graphene, 3D graphene have recently emerged as an attractive support to fabricate novel functional materials according to the following reasons [31–33]: (1) An interconnected graphene framework facilitates the electron transport across the electrode; (2) Numerous multidimensional channels in GA could effectively accelerate the lithium/sodium diffusion within the bulk electrode; and (3) an elastic matrix of GA could accommodate the volume expansion of metal oxides during long-term cycling. Despite these improvements, it is still a great challenge to use a simple method to design and fabricate 1D SnO_2 on the 3D graphene substrate with the good distribution.

In this work, we successfully construct 1D ultrafine SnO_2 nanorods/3D graphene aerogels (SnO_2 NRs/GA) composite consisted of self-assembled graphene networks and SnO_2 nanorod (length of 3–7 nm and diameter of about 2 nm) via a novel chemical reduction-induced self-assembly process. The resultant SnO_2 NRs/GA composite possesses high surface area (124.5 m^2 g^{-1}) and hierarchical porous structure. Such unique structure can facilitate the ultrafast diffusion of ion/electron and accommodate the volume change of SnO_2 during cycling. Benefitting from 1D SnO_2 nanorods and 3D graphene frameworks, the SnO_2 NRs/GA composite exhibits the good lithium storage performance with excellent rate capability (1001, 925, 781, 643 and 458 mA h g^{-1} at a charge/discharge rate of 100 mA g^{-1}, 200 mA g^{-1}, 500 mA g^{-1}, 1 A g^{-1} and 2 A g^{-1}, respectively) and outstanding long-term cyclic stability at high current densities (869 mA h g^{-1} after 50 cycles at 100 mA g^{-1}). Importantly, when test as anode materials for SIBs, the SnO_2 NRs/GA composite still achieve a high reversible capacity of 232 mA h g^{-1} at 0.05 A g^{-1} after 100 cycles and good rate performance. This work described here can be extended to prepare various metal oxide/graphene aerogel composite for the wide range of applications in supercapacitors, sensors, solar cells and catalysts.

2. Experimental section

2.1. Preparation of SnO_2 nanoparticles (SnO_2 NPs)

SnO_2 NPs were synthesized via a facile hydrothermal method. In a typical synthesis, $SnCl_4{\cdot}5H_2O$ (0.1 mol) was firstly dissolved in 50 mL distilled water, stirring for about 30 min. The solution was transferred to a 100 mL Teflon-lined autoclave, which was heated at 180 °C for 12 h. After heated, the autoclave was cooled to room temperature naturally. The product was collected by centrifugation and washed with deionized water for several times, and then dried at 60 °C in a vacuum drying oven overnight.

2.2. Preparation of SnO_2 nanorods/graphene aerogels (SnO_2 NRs/GA)

Graphene oxide (GO) was synthesized from natural graphite flakes by a modified Hummers' method [34,35]. The obtained SnO_2 NPs (2 mmol) were dispersed in 50 mL of GO (1.5 mg mL^{-1}) aqueous solution, and then vitamin C (4.1 mmol) was added. After stirring and ultrasonic dispersion, the solution was heated at 90 °C for 0.5 h via water bath without auxiliary ultrasonication and agitation. Finally, the resultant product was washed with deionized water for several times and freeze-dried under vacuum. By comparison, bare graphene aerogel (GA) and SnO_2 nanorods (SnO_2 NRs) were prepared in the absence of SnO_2 NPs and GO using same method, respectively.

2.3. Physical characterizations

The surface morphologies of as-prepared samples were characterized via field emission scanning electron microscopy (FESEM; JSM-6701F, JEOL, Japan) with an energy dispersive spectrometer (EDS), transmission electron microscopy (TEM; JEOL-2100) and high resolution transmission electron microscope (HRTEM) accompanied with selected area electron diffraction (SAED) pattern, respectively. X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker AXS D8 with Cu Kα radiation (λ = 0.1541 nm). Fourier transformation infrared spectra (FTIR, Nicolet Nexus 670, USA) which were carried out from 400 to 3200 cm^{-1} with a resolution of 4 cm^{-1} and Raman spectra (JY HR800, France) were also recorded. The thermogravimetric analysis (TGA/DSC 1/1100 SF) was conducted under air atmosphere with the heating rate of 10 °C min^{-1} from 25