Construction of spongy antimony-doped tin oxide/graphene nanocomposites using commercially available products and its excellent electrochemical performance

Xiaowei Zhao [a, b, d], Jingwei Zhang [a, b, c, *], Jiwei Zhang [a, b], Chunhong Gong [a, d], Xiufang Gu [a, b], Zhihua Ma [a, b], Jingfang Zhou [c], Laigui Yu [a, b], Zhijun Zhang [a, b, *]

[a] Key Laboratory of Ministry of Education for Special Functional Materials, Henan University, Kaifeng, 475004, PR China
[b] Collaborative Innovation Center of Nano Functional Materials and Applications, Henan Province, China
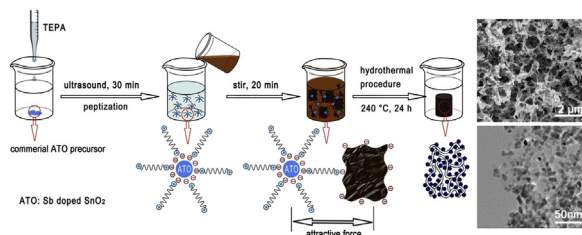[c] Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA, 5095, Australia
[d] College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, PR China

HIGHLIGHTS

- The spongy ATO/NG/TEPA hybrid was constructed by a one-pot hydrothermal process.
- TEPA, as a multifunctional agent, plays a crucial role.
- The commercial ATO precursor was used as raw material.
- The hybrid exhibits high electrochemical performance for lithium ion battery.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

We construct successfully a porous antimony-doped tin oxide (ATO)/nitrogen-doped graphene 3-dimensional (3D) frameworks (denoted as ATO/NG/TEPA; TEPA refers to tetraethylenepentamine) by a one-pot hydrothermal process, with which TEPA aqueous solution is adopted to easily re-disperse commercial ATO precursor forming a transparent hydrosol. The results show that TEPA plays a key role in the construction of ATO/NG/TEPA, not only acting as a peptization reagent to re-disperse ATO precursor nanoparticles, and as a linker to combine ATO with graphene sheets. The as-fabricated ATO/NG/TEPA hybrid as the negative electrode of lithium ion batteries exhibits excellent lithium storage capacity and cycling stability. With the advantage of easily re-dispersing commercial ATO, the present synthetic route may be put into use for the large-scale production of the titled nanocomposites as the anode material of lithium ion batteries.

1. Introduction

Rechargeable lithium ion batteries (LIBs) are viewed as the most promising candidates for applications in portable electronics, electric vehicles (EVs) and hybrid electric vehicles [1,2] because they exhibit relatively high energy density and power density [3–5]. However, in terms of the limited capacity of commercial carbon-based anode, it is urgent to seek upgrade substitute active

* Corresponding authors. Key Laboratory of Ministry of Education for Special Functional Materials, Henan University, Kaifeng, 475004, PR China.
E-mail addresses: jwzhang@henu.edu.cn (J. Zhang), zhangzhijun@henu.edu.cn (Z. Zhang).

materials for next-generation LIBs applicable to EVs requiring higher specific capacity.

Tin-based electrode materials such as Sn, SnO_x and Sb-doped SnO_2 (ATO) have attracted numerous attention owing to their high theoretical Li storage capacity (991 mAh g^{-1} for Sn [6] and 1491 mAh g^{-1} for SnO_2 [6]). However, the practical application of tin-based material is hampered by the drastic capacity fading resulted from huge volume change [6,7] and aggregation accompanied with repeated alloying/dealloying process [8]. Fortunately, constructing graphene-based hybrid materials, especially 3-dimensional (3D) graphene/SnO_2 hybrid, is an effective strategy to buffer the volume expansion, avoid the aggregation and improve the conductivity of tin oxide, thereby promoting the electrochemical performance for LIBs [9–20].

Up to now, chlorinous tin salt such as $SnCl_2$ and $SnCl_4$ are mainly adopted as the tin sources for preparing SnO_2/graphene composites. This is because Sn^{2+} or Sn^{4+} cation originated from the aqueous solution of the tin salt can be easily adsorbed on graphene oxide (GO) sheets with the assistance of electrostatic attractive force and then transformed to crystalline SnO_2 upon hydrothermal treatment [12,19] or calcination treatment [10,14,16,17]. Unfortunately, chloride ion causes erosion of the containers especially at an elevated temperature in acid solution, which makes it imperative to adopt apparatus with excellent anticorrosion ability for preparing SnO_2/graphene composites [12,16,21,22]. In the meantime, chloride ion is difficult to be washed off from resultant products, due to its strong nucleophilicity and adsorbability [23]. Therefore, it is urgent to simplify the preparation process and reduce the production cost of SnO_2/graphene composites with $SnCl_2$ and $SnCl_4$ as the tin sources.

Considering that both SnO_2 and GO are commercially accessible products, it could be of significance to fabricate 3D SnO_2/graphene nanocomposites with commercial SnO_2 and GO as the starting materials, though this still remains a challenge. In this sense, the researches separately conducted by two research groups could be of special significance. Namely, Liang et al. and Gao et al., with commercial SnO_2 powder as the raw material, independently fabricated a free-standing SnO_2/graphene hybrid paper by simple filtration in combination with annealing in Ar flow [24] or with hydrothermal reduction in HBr acid [25]; and they reported that the as-obtained SnO_2/graphene hybrid electrodes exhibit enhanced energy storage stability. However, the irreversible agglomeration of commercial nanoparticles, always along with their drying or annealing treatment, leads to poor solution re-dispersibility and nanoscale inhomogeneity of the as-prepared SnO_2/graphene products.

To deal with the abovementioned issue associated with the fabrication of SnO_2/graphene nanocomposites, we draw attention to a facile and efficient one-pot wet-chemical process, hoping to get rid of the agglomeration of commercial SnO_2 nanoparticles thereby acquiring SnO_2/graphene nanocomposites with desired solution re-dispersibility and nanoscale homogeneity. Viewing that ATO as the electrode for LIBs possesses higher electrical conductivity and mechanical stability than SnO_2 [26,27], we choose ATO as the active anode material to construct graphene-based nanocomposites. The route to materialize this strategy, however, is challenging, because both GO sheets and ATO are highly negative charged in a wide range of pH value [28–30], and they can hardly be uniformly combined owing to electrostatic repulsion, not to mention that commercial ATO nanoparticles unavoidably tend to agglomerate. Pointing to those issues, we select tetraethylenepent amine (TEPA), a kind of polyamine, as a multifunctional agent to fabricate 3D architectural porous graphene/ATO nanocomposite as potential anode material of LIBs. Such a synthetic strategy is feasible, because, on the one hand, TEPA can act as a peptization reagent to re-disperse ATO precursor nanoparticles thereby avoiding their agglomeration. On the other hand, TEPA can also act as a linker to combine ATO with graphene oxide and as the nitrogen-doping agent of graphene thereby affording desired 3D ATO/N-doped graphene nanocomposite (ATO/NG/TEPA). This article reports the fabrication and electrochemical properties of the as-fabricated ATO/NG/TEPA nanocomposites in relation to their structural characterization by transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy.

2. Experimental section

2.1. Materials

Graphite powder was purchased from Qingdao Xingyuan Colloidal Graphite Co., Ltd (Qingdao, China). Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), ethylene diamine (EDA) and TEPA were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (Tianjin, China). sulfuric acid (H_2SO_4 98%), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl; mass fraction: 35%) and ammonia (AM; mass fraction: 25%–28%) were bought from Luoyang Haohua Chemical Reagent Co., Ltd (Luoyang, China). The wet ATO precursor slurry (solid content: 20%; particle size: 2–3 nm) was purchased from Henan Wangwu Nanoscience and Technology Co., Ltd (Jiyuan, China), and it was prepared through a wet-chemical route in the absence of chloride reagent.

2.2. Methods

GO was prepared from natural graphite powder by modified Hummer's method [31,32]. Briefly, natural graphite powder (60 g) was mixed with $NaNO_3$ (30 g) and concentrated H_2SO_4 (1500 mL) at 0 °C, and then $KMnO_4$ (400 g) was slowly added into the mixed solution. Resultant mixed solution was stirred below 8 °C for 1 h and then heated to 45 °C and held there for 16 h. Upon completion of the reaction, 7.5 L of water and 70 mL of 30% H_2O_2 solution were sequentially added to terminate the reaction. The reaction system was washed with 5 L of dilute HCl (volume fraction: 10%) and adjusted to pH = 7 with dilute ammonia (10%), followed by dialyzing to completely remove residual Cl$^-$ thereby affording GO sol.

The graphene/ATO hybrids were synthesized *via* a one-pot hydrothermal route. Typically, 2.0 g of wet ATO precursor was peptized in 30 mL of distilled water containing 1.0 mL of TEPA to form a transparent colloidal solution after a 30 min sonication. Then 20 mL of GO sol (5 mg mL^{-1}) was added into the colloidal solution under stirring for 20 min. Resultant mixture was transferred into a Teflon-lined stainless autoclave and kept at 240 °C for 24 h. At the end of the reaction, the target product, ATO/NG/TEPA nanocomposite was washed with distilled water and lyophilized. Nanocomposites ATO/NG/AM and ATO/NG/EDA were synthesized in the same manners while AM or EDA was used to replace TEPA. Similarly with ATO/NG/TEPA, ATO and NG were prepared without GO or ATO being added, respectively. Reduced graphene oxide (rGO) was obtained *via* the hydrothermal treatment of GO colloid. ATO/rGO was obtained in the presence of ATO precursor and GO colloid under the weak acidic condition *via* the same hydrothermal process as well.

2.3. Assembling battery

For assembling the working electrodes, a proper amount of active materials (as-prepared ATO/NG/TEPA, ATO/NG/AM and ATO/NG/EDA nanocomposites) was mixed with polyvinylidene difluoride (PVDF) and carbon black in N-methyl-2-pyrrolidone (NMP) solvent at a mass ratio of 80:10:10 to form homogeneous slurries. As-obtained slurries were uniformly coated onto Cu foil with a