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A novel strategy to prepare graphene oxide-wrapped nanocrystals composite for high-performance lithium storage

Danfeng Wang, Kailong Zhang, Yongchun Zhu *, Yang Lan, Lei Hu, Ning Lin, Jianbin Zhou, Yitai Qian *

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

A novel strategy is developed to prepare graphene oxide-wrapped nanocrystals composite (GO@NCs) by the assistance of chitosan (CS). This assembly process can be accomplished at room temperature within two minutes, which is driven by both hydrogen bonding and electrostatic interaction between GO sheets and CS chains. It's also worth pointing out that this novel method can be widely applied in preparing various kinds of GO-wrapped nanocrystals composites, and the coated GO can further enhance the electrochemical performance of the GO@NCs composite. For instance, the GO-wrapped tin selenide nanorods composite (GO@SnSe) prepared by this method is evaluated as an anode for lithium ion batteries and delivers an enhanced reversible capacity of 764 mA h g^{-1} at the current density of 100 mA g^{-1} after 100 cycles, which is much higher than that of bare SnSe nanorods.

1. Introduction

Graphene, a novel carbonaceous matrix material with large surface area, good mechanical strength and high conductivity, has attracted great interest in supporting host materials in the fields of energy storage and conversion for achieving better properties [1,2]. Specifically, when these graphene-based nanocomposites are used as anode materials for lithium ion batteries (LIBs), the graphene in the composites plays an important role in alleviating volume expansion and suppressing aggregation of the host materials, and thus leading enhanced electrochemical performances [3–6]. In this regard, various strategies have been developed to fabricate the graphene-based composite. For example, Müllen et al. modified Co_3O_4 nanoparticles to be positively charged with aminopropyltrimethoxysilane by refluxing in dry toluene solution for 24 h under argon atmosphere, and then incorporated it with negatively charged GO sheets through electrostatic interaction [4]. Lu et al. modified hollow Fe_3O_4 nanoparticles to be positively charged with 3-aminopropyltriethoxysilane by stirring the mixture in toluene solution for 24 h, and then assembled it with GO in alkaline solution [5]. Son et al. synthesized graphene-$SnSe_2$ composite by heat treatment of the mixture of GO, $SnSe_2$, acetonitrile and water at 80 °C for 3 h [6]. Although great development has been made with the efforts of many researchers, a simple and time-saving strategy is still an urgent need for preparing graphene-based composites with enhanced performance.

Here, we have developed a novel strategy to fabricate GO-wrapped nanocrystals composite (GO@NCs) by the assistance of chitosan (CS). This assembly process can be accomplished at room temperature within two minutes. The driven forces are hydrogen bonding and electrostatic interaction between GO sheets and CS chains. Several GO-based composites have been prepared by this method, such as GO-wrapped tin selenide nanorods composite (GO@SnSe), GO-wrapped Fe_2O_3 nanorices composite (GO@Fe_2O_3), GO-wrapped $CoSn(OH)_6$ nanocubes composite (GO@$CoSn(OH)_6$) and GO-wrapped selenium nanospheres composite (GO@Se). All the SEM and TEM images reveal that the fabricated GO@NCs composites possess flexible GO shells with effectively enwrapped NCs. As an example, the GO@SnSe nanocomposite is evaluated as an anode for LIBs and it exhibits much better electrochemical performance compared with bare SnSe nanorods.

2. Experimental section

The detailed materials preparation and characterization are available in ESI.

3. Results and discussion

The synthetic procedure involves two steps (Scheme 1). In the first step, the synthesized nanocrystals without any other

* Corresponding authors.
E-mail addresses: ychzhu@ustc.edu.cn (Y. Zhu), ytqian@ustc.edu.cn (Y. Qian).

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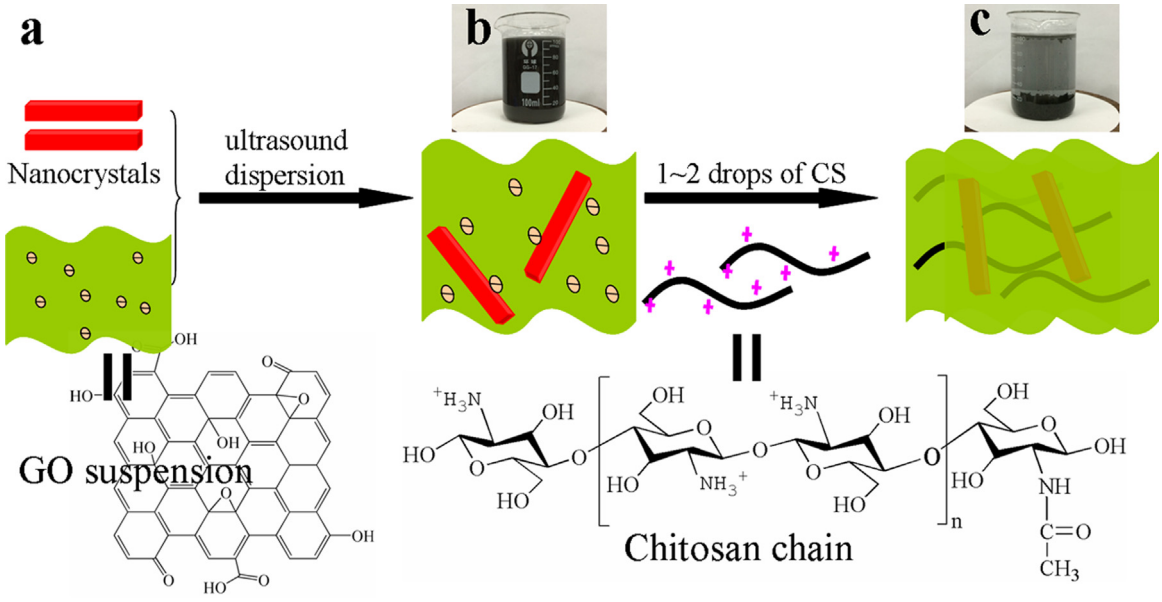

Scheme 1. Fabrication of graphene oxide-wrapped nanocrystals composite (GO@NCs).

treatments are dispersed into GO suspension. In the second step, 1–2 drops of CS solution are added into the mixed suspension. With constantly stirring for about 2 min at room temperature, a large amount of flocculent precipitates can be observed in the mixed solution (Scheme 1c). However, in the mixed solution without the addition of CS, the precipitates can not be obtained (Scheme 1b). This can be ascribed to the assistance of CS which can make GO sheets aggregate to facilitate the generation of GO network with NCs in-situ encapsulated (The reaction between pure GO and CS is shown in Fig. S1). The driven forces of the assembly process can be mainly ascribed to two: (i) hydrogen bonding between groups of amino and hydroxyl in CS chains and oxygen-containing functional groups on GO sheets, and (ii) electrostatic interaction between positively charged CS chains and negatively charged GO sheets [4,7].

We initially examined the validity of this method by fabricating GO@SnSe, in which SnSe nanorods were prepared by our modified method. Fig. 1a reveals the SEM image of the prepared SnSe nanorods. Fig. 1b and c display the typical SEM and TEM images of GO@SnSe, where the wrinkled GO sheets are effectively wrapped around the surface of SnSe nanorods. The fabricated SnSe nanorods and GO@SnSe composites were further characterized by XRD. As presented in Fig. 1d, all the diffraction peaks of bare SnSe nanorods can be indexed to orthorhombic phase SnSe (JCPDS Card

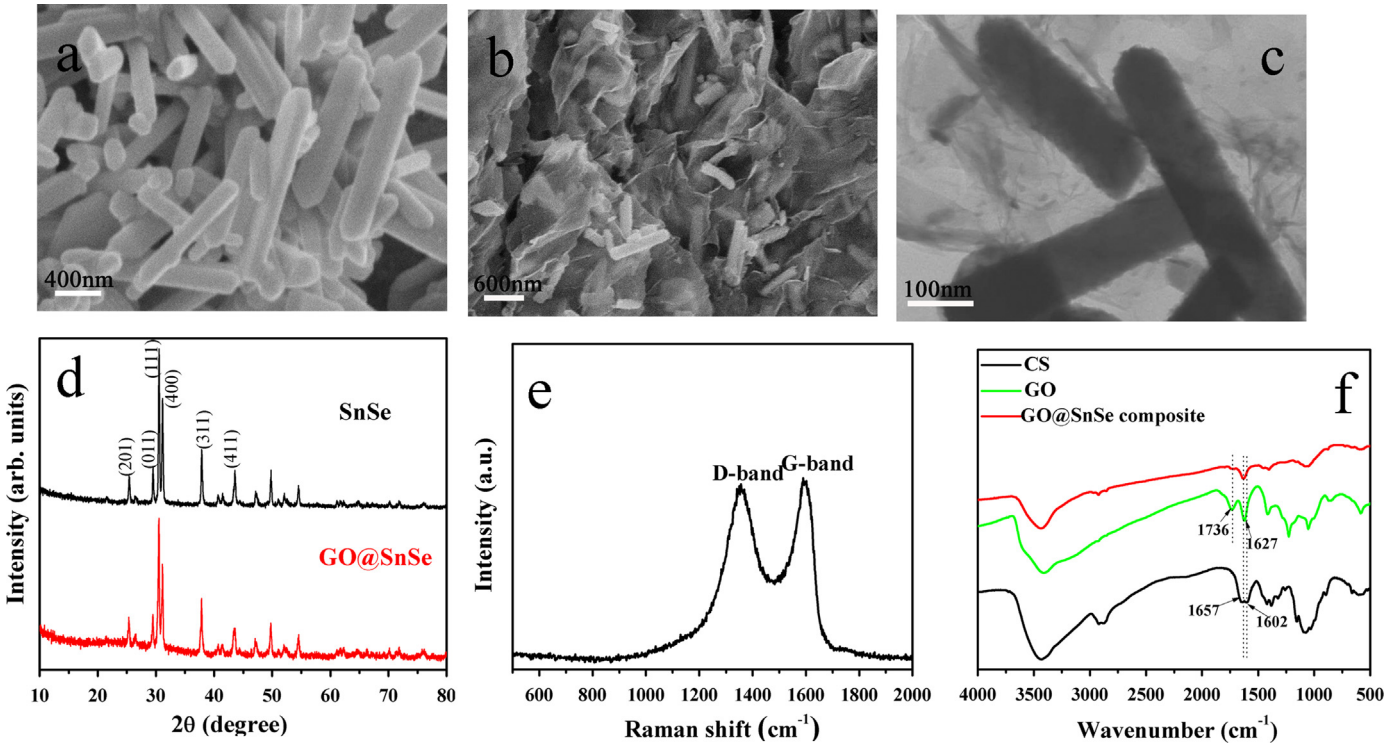

Fig. 1. SEM images of (a) SnSe nanorods and (b) GO@SnSe composite; TEM image of (c) GO@SnSe composite; (d) XRD patterns of SnSe nanorods and GO@SnSe composite; (e) Raman spectrum of GO@SnSe composite; (f) FTIR spectrum of GO, CS, and GO@SnSe composite.