



Multi-wall carbon nanotube@zeolite imidazolate framework composite from a nanoscale zinc oxide precursor



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ABSTRACT

Nanocomposite of multi-walled carbon nanotube@zeolite imidazolate frameworks (MWNT@ZIF) was prepared through a nanotube-facilitated growth based on a nanosized ZnO precursor. The electrically conductive nanocomposite displays a capacity of 380 mAh/g at 0.1 °C in Li–sulfur battery, transforming electrically inactive ZIF into the active one for battery applications.

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1. Introduction

Significant efforts have focused on the preparation of rechargeable batteries with high energy density, long cycling life, low cost, and low environmental impact. Among all known rechargeable battery systems, lithium–sulfur (Li–S) batteries are one of the most promising candidates [1–6]. The reason is in that elemental sulfur has one of the highest theoretical capacities for Li-storage (1672 mAh g⁻¹), resulting in a higher specific energy compared to conventional Li-ion batteries [7–9]. Such high capacity and energy originate from the reaction of sulfur with Li⁺ to form Li₂S, thus involving two electrons per sulfur atom. Nevertheless, the practical applications of Li–S batteries are limited because of two fatal hurdles. The first is the electrical insulating nature of elemental sulfur (5 × 10⁻³⁰ Scm⁻¹ at 25 °C) that causes poor electrochemical contact of the sulfur and leads to low utilization of active materials in the cathode [10]. The second is associated to the dissolution of lithium polysulfides Li₂S_x (2 ≤ x ≤ 8) formed in electrolyte, thus lowering the battery capacity, and resulting in a short life cycle [11].

In order to improve the electronic conductivity, sulfur has been dispersed in a conductive matrix, i.e. conductive polymers and

carbon nanomaterials [12–14]. Whereas, the use of microporous electrode materials has been demonstrated to effectively contain the soluble polysulfides in the framework, thus preventing the Li-storage loss and increasing the life cycle of the active material [15,16]. However, precise control over the micropore sizes in carbons is difficult, especially for widths approaching 1 nm, desirable for containing lithium polysulfide compounds. Hence, alternatives to templated and activated microporous carbons are of great importance for the development of more efficient Li–sulfur batteries.

Among the various types of microporous materials, a subclass of metal–organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) are promising microporous materials due to the well-defined and tailorable structure of micropores resembling those found in zeolites [17–28]. ZIFs display large surface areas and high thermal stability [29–31]. Despite the many desirable pore structure and topology of ZIFs, the large crystal sizes of these materials, typically ranging from tens of microns to a few millimetres, and their poor electronic conductivity limit their applications in the fields of energy storage. In order to broaden the use of MOFs and ZIFs, the development of recipes to prepare nanometer size MOF crystals and MOF composites is necessary for the design of lithium diffusion and of battery devices [32–34].

To date, MOF with graphene oxide [35,36], Fe₃O₄ [37], ZnO [38], metal particles [39,40], alumina or silica [41] composites have been fabricated, all displaying improved properties compared to pure

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MOFs. For instance, graphite oxide/[Cu₃(btc)₂] (HKUST-1; btc = 1,3,5-benzenetricarboxylate) nanocomposites exhibit improved hydrogen uptake compared to the pristine HKUST-1 [42]. Also graphite oxide/MOF-5 has higher ammonia adsorption capacity than the individual components [43]. Although gas separation properties and hydrothermal stability properties have been addressed, electronic properties of MOF nanocomposites have not been previously investigated. Furthermore, the fabrication of homogeneous multi-component nanocomposites displaying optimal synergistic effects of each component and controlled morphology poses great challenges. For instance, for most of the aforementioned composites, templates or several synthesis steps are required. Hence, facile methods for the in situ growth of MOF nanocrystals, homogeneously dispersed in a nanocomposite matrix are in high demand, especially for future upscale preparation of materials of interest for energy storage.

In this direction, ZIF nanoparticles can be easily prepared in large scale with diverse precursors. Recently, nanometric crystals having the ZIF-8 structure (Zn(MIM)₂, MIM = 2-methylimidazole), with good monodispersity have been prepared from nano-sized ZnO precursor [44]. Encouraged by the results, the synthesis of multi-walled carbon nanotube/zeolitic ZIF-8 composite (MWNT@ZIF) was prepared by a template-free “brick and mortar” method. Because of the combination of high surface areas, accessible microporous channels for fast ion diffusion and electronic conductivity provided by the MWNT, such nanocomposites are promising for high power and high energy density storage devices. In the present work, these were successfully tested as active cathode materials for Li–Sulfur battery, with a reversible capacity of 1013 mAh/g, comparable to other nanostructured porous carbon–sulfur composites [45].

2. Experimental

2.1. Materials

The nanoscale ZnO particles (dispersed in ethanol, 40%) with average particle size being 35 nm and largest less than 130 nm, multi-wall carbon nanotube (O.D. × L 6–9 nm × 5 μm), 2-methylimidazole, and the solvent were obtained from Aldrich Chemical Co. Inc. and used as received.

2.2. Synthesis

In 50 mL vial, 2 g 2-methylimidazole (HMIM) was added into a methanol solution containing ZnO nanoparticles (2 g, ethanol dispersion with the concentration being 40%) and 0.3 g multi-wall carbon nanotube, with the HMIM/ZnO molar ratio being 5:2. The mixture was stirred for 48 h at room temperature, washed with methanol for three times, and separated by centrifugation. The resulting grey solid was dried under vacuum at ambient temperature. The sample was characterized by powder XRD, SEM, TEM, TGA, and BET measurements. MWNT@ZIF-8-S composite was prepared by grounding MWNT@ZIF-8 powder (0.1 g) and sulfur (0.5 g) together in a mortar, followed by heating at 155 °C for 6 h. The composite was then heated at 250 °C under argon for 1 h to evaporate the surface sulfur.

2.3. Characterizations

2.3.1. Electrochemical experiments

Electrochemical experiments were carried out using coin cells. The sulfur composite electrode was prepared by casting a well-homogenized slurry of MWNT@ZIF-S composite (70 wt%), carbon black (15 wt%), and PVdF (15 wt%) in NMP on aluminum foil using

a doctor blade. The dried electrodes were pressed under a hydraulic load of 1 ton for 1 min before cutting into discs of 1.3 cm diameter. The discs were further dried at 60 °C under vacuum for 24 h before transferring into the glovebox for battery assembly. The sulfur loading within the ZIF-CNT-S cathode is in the range of 0.6 mg. The batteries were assembled as 2032-type coin cells inside an argon-filled glovebox by using the ZIF-CNT-S composite as the cathode electrode, lithium metal as the anode electrode, Celgard 3401 as the separator, and 1.0 M LiPF₆/Methyl isopropyl sulfone (MiPS) as the electrolyte. Galvanostatic discharge–charge experiments were tested in the voltage range of 1.0–3.0 V on an Arbin battery test system.

2.3.2. TGA analysis

Thermogravimetric analysis (TGA) was carried out by using a TA Instrument 2950 from room temperature to 900 °C at a heating rate of 5 °C min⁻¹ under an air atmosphere.

2.3.3. Powder X-ray diffraction (PXRD)

Powder XRD analysis of the composite sample was analyzed to confirm the crystallinity. Powder XRD patterns were recorded on a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å).

2.3.4. Gas adsorption analysis

Gas adsorption studies were done to confirm the permanent porosity of the as-synthesized composite sample as well as to determine the surface area. Low pressure gas adsorption experiments were performed on a Micromeritics Tristar 3000 analyzer at 77 K. Around 100 mg sample was evacuated for 6 h at 150 °C and subsequently loaded for adsorption analysis.

2.3.5. Scanning transmission electron microscopy (STEM)

Scanning transmission electron microscope (STEM) images were recorded using a Hitachi HD2000 STEM microscope operating at 200 kV. Samples for STEM analysis were prepared by drop casting: one drop of the sample dispersion was dropped onto a copper grid and allowed to dry at ambient temperature before subsection to STEM analysis.

3. Results and discussion

For the large scale preparation of MWNT@ZIF composite, ZnO nanoparticles and 2-methylimidazole were reacted in a methanol suspension of MWNTs for 48 h (see detailed synthesis in the SI). The proposed mechanism for the preparation of homogeneous MWNT@ZIF proceeds by an in situ ZIF nanocrystal growth around the entangled MWNTs, as shown in Fig. 1(a). In the first stage, ZnO nanoparticles adsorb on the surface of MWNTs. The protonated MIM ligand (HMIM), then reacts with the adsorbed ZnO. Because of the strong interactions between the HMIM with the carbon surfaces, the nucleation and growth of the ZIF-8 crystals proceed on the surfaces of the MWNTs.

The morphology and the structure of the samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), see Fig. 1. The ZIF nanosized crystals in both carbon-free and MWNT composites have platelet morphology with sharp facets. Platelets with four to six facets are seen, with the particle sizes ranging from 120 to 200 nm (Fig. 1b). The MWNTs are embedded in well-dispersed and uniform ZIF crystal particles. No signs of residual ZnO nanoparticles were found by TEM (Fig. 1c), indicating that the precursor ZnO nanoparticles were completely consumed during the synthesis.

While the amount of ZIF crystals can be controlled by the amount of reactants mixed with the MWNTs, the crystal sizes are

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