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.

Keywords: zeolitic imidazolate frameworks, carbon nanotubes, ZnO nanoparticles,

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 Li_2S , 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 ($5 \times 10^{-30} \text{ Scm}^{-1}$ 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 Li_2S_x ($2 \leq x \leq 8$) 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 1nm, 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 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 ($\text{Zn}(\text{MIM})_2$, $\text{MIM} = 2\text{-methylimidazolate}$), with good monodispersity have been prepared from nanosized 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. $\times$ L 6–9 nm $\times$ 5 μ m), 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 (2g, 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 hours 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 hours. The composite was then heated at 250 °C under argon for 1 hour 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 hrs 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 K α radiation ($\lambda = 1.5406 \text{ \AA}$).

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 hours (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 Figure 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 Figure 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 (Figure 1b). The MWNTs are embedded in well-dispersed and uniform ZIF crystal particles. No signs of residual ZnO nanoparticles were found by TEM (Figure 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 possibly limited by the dispersion of the initial ZnO and the voids in between the entangled nanotubes. When the molar ratio of the

HMIM and ZnO reactants is below 5:2 and the reaction time is kept constant, unreacted ZnO nanoparticles coating the MWNTs and trapped in the large ZIF-8 crystals are left. These are seen in the SEM and TEM in Figure 1d and e, respectively. These platelets also contain MWNTs. The latter observations are supported by the proposed mechanism that ZnO are initially dispersed on the surfaces of the MWNT and serve as nucleation sites for the ZIF growth. Larger empty voids between the entangled MWNTs are also seen, as a result of lower amounts of ZIF precursors available. To understand the importance of the precursors used in forming these nanocomposites, a sample was prepared from zinc nitrate as Zn source instead of ZnO. In contrast to the ZnO-derived materials, small numbers of crystals segregated from the MWNTs were obtained (Figure 2). These results clearly indicated that the formation of MWNT@ZIF from a nanoscopic precursor which is quite different from the homogeneous nucleation process of soluble Zn(II) salts, and the interactions with the MWNTs surfaces.

Comparison of the powder X-ray diffraction (XRD) patterns of the MWNT@ZIF nanocrystals with that of a previously published material, confirmed that the platelets have the ZIF-8 crystal structure (Figure 3a). Furthermore, XRD confirm the absence of unreacted ZnO in the nanocomposites shown in STEM images in Figure 1b and c. The adsorption properties of the ZIF-8 and MWNT@ZIF composite were determined by N₂ sorption measurements (Figure 3b). Both exhibit type I isotherm, typical of microporous materials. The increase in the gas uptake at high relative pressures results from adsorption in large textural mesopores and small macropores. The

specific surface area of ZIF-8 and MWNT@ZIF were comparable, being 1066 m²/g for the latter and 1309 m²/g for the former. The total pore volume decreased from 0.64 cm³/g for the ZIF-8 down to 0.51 cm³/g for the MWNT@ZIF. The calculate pore width (inset in Figure 3b) was of approximately 1.3 nm for both materials, which is in good agreement with crystallographic data for the largest cavities found ZIF-8 of 1.16 nm [46,47]. Further adsorption studies at low pressure ranges are required to probe pores smaller than 1.2 nm. The thermal stability of MWNT@ZIF composite was investigated by thermal gravimetric analysis (TG), see Figure 3c. Approximately 41 wt.% of the weight loss occurred in the temperature range of 200 to 450 °C, similar to ZIF-8 material, indicating a weight ratio of ZIF-8: MWNT of roughly 78: 22 (wt./wt.).

In order to verify the efficacy of this method to prepare conductive nanocomposites of ZIF-8 material for energy storage, the MWNT@ZIF-8-S was tested as active electrode material for Li-S battery. The MWNT@ZIF-8-S cathode was prepared by mechanically grinding MWNT@ZIF and sulfur, followed by heating at 155 °C for 6 hours and finally at 250 °C for 1 hour in flowing argon in order to eliminate the surface sulfur. The much lower N₂ uptake in the adsorption isotherm for the MWNT@ZIF-S composite, see Figure 2, indicates that most of the micropores were successfully filled with sulfur. Electrochemical experiments were conducted using coin cells and galvanostatic charge-discharge experiments to evaluate the lithium storage properties of the MWNT@ZIF-S. Figure 3d shows cyclic performance and galvanostatic discharge/charge curves (Inset) of the Li||PAF-S cell using 1 M

LiPF₆/MiPS at 25 °C. The MWNT@ZIF-S electrode exhibits a reversible capacity of 1013 mAh g⁻¹ (second cycle) at a current rate of C/20 (84 mA/g). After 5 cycles, the current rate was increased to C/10 (168 mA/g) and a capacity of 706 mAh/g still can be obtained. Hence, the MWNT@ZIF-S composite displays good cyclic stability. A capacity of 380 mAh/g can be achieved at C/10 even after 25 cycles. The latter results indicate that loading sulfur within the porous MWNT@ZIF material effectively improved the cycle stability of the sulfur electrode by trapping the polysulfide species formed. For comparison, a mixture of ZIF and MWNT was used as host substrate for Li-S battery. After loading sulfur into the mixture (ZIF-S), the Li-storage properties of the sample were also evaluated under identical conditions. As shown in Figure 3d, the ZIF-S sample shows much poorer electrochemical properties than MWNT@ZIF composite. It seems that the well-dispersed MWNTs play a key role in improving the Li-storage properties of the sulfur cathode.

4. Conclusions

In summary, nanocomposite of multi-walled carbon nanotube@zeolite imidazolate frameworks was prepared by simple template-free method and at room temperature. ZIF-8 nanocrystals were homogeneously dispersed within entangled MWNTs, whereas the latter were trapped within the interior of the platelet ZIF-8 particles. The dispersion of the ZIF-8 crystals resulted from the heterogeneous crystallization of this material from ZnO precursor previously adsorbed on the surfaces of MWNTs. The latter materials differed from those obtained from the wet-impregnation method using Zn(NO₃)₂ precursor, typically used for preparation of ZIFs. Finally, MWNT@ZIF-S

composite displays good cyclic stability with a Li-capacity of 380 mAh/g achieved at C/10 even after 25 cycles, indicating that loading sulfur within the porous MWNT@ZIF material effectively improved the cycle stability of the sulfur electrode and the MWNT was confirmed as useful composite fillers in the Li-S research. Hence, this synthesis method is promising for the preparation of various other conductive MOF nanocomposites with MWNTs and other conductive carbon nanomaterials of interest for electrochemical energy storage devices.

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Nanocomposites of multi-walled carbon nanotube@zeolite imidazolate frameworks display good cycle stability and high Li-storage capacity as cathode materials for lithium-sulfur battery.

Figure 1. (a) Proposed illustration of the formation of MWNT@ZIF composite (I – V, with the ZnO particles gradually consumed by HMIM); (b) SEM image of MWNT@ZIF composite, inset showing SEM image with higher magnification; (c) TEM image of MWNT@ZIF composite; (d) SEM image and (e) TEM image of MWNT@ZIF composite with ZnO residues in the ZIF particles, respectively (inset with higher magnification image).

Figure 2. (a) SEM image and (b) TEM image for the material obtained from the reaction as zinc nitrate instead nanosized ZnO precursor.

Figure 3. (a) XRD patterns of as made MWNT@ZIF-8; (b) N₂ adsorption-desorption isotherms of ZIF-8 nanocrystals, MWNT@ZIF composite, and MWNT@ZIF-S; (c) TGA measurement of the as-made nanocomposite of MWNT@ZIF-8 under air; (d) cyclic performance (discharge) and galvanostatic discharge/charge curves (Inset) of the MWNT@ZIF-S and ZIF-S cells in 1 M LiPF₆/MiPS at 25 °C.