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Facile synthesis and electrochemical properties of carbon-coated ZnO nanotubes for high-rate lithium storage

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ABSTRACT

ZnO is an important functional material, and a nanotube structure is beneficial for various applications. Here, we report the facile synthesis and electrochemical properties of carbon-coated ZnO nanotube materials as Li rechargeable battery anodes. ZnO nanorod was first synthesized via a simple hydrothermal method. Subsequently, the material was annealed with a carbon precursor, forming free-standing, carbon-coated ZnO nanotubes. The carbon-coated nanotube structure is beneficial to alleviate volume changes of the ZnO active material during Li insertion and extraction processes as well as to improve the electrochemical reaction kinetics. Electrochemical test results demonstrate that the carbon-coated ZnO nanotube electrodes deliver improved the cycling performance compared with ZnO nanorod electrodes. Better rate performance than carbon-coated ZnO nanoparticle electrodes was also achieved.

1. Introduction

Zinc oxide (ZnO) is an important functional material, which has a semiconducting property with a direct wide bandgap (3.37 eV) and a large exciton binding energy (60 meV) [1]. In addition, ZnO is cheap and chemically stable. Therefore, it has been widely used in various applications such as biosensors, semiconductors, optics, solar cells, and light emitting diodes [2–7]. Moreover, ZnO is also widely used in traditional industrial products such as white pigments, sunscreens, and rubber additives. Recently, ZnO has been considered as a candidate electrode material for electrochemical energy storage devices including lithium secondary batteries and hybrid supercapacitors [8–15].

For diverse industrial applications, one-dimensional (1D) nanostructured materials are beneficial because of their unique morphology and large surface area. In electrode materials for lithium storage, 1D structures such as nanowires and nanotubes enable fast electronic and ionic transport using their high surface area and unique structures [8,10,13]. When ZnO materials are used for Li-ion storage, volume changes during Li^+ insertion and extraction process should be considered for cycling stability. In this regard, nanotube structures that have inside pores are expected to be more effective than nanowires or nanorods because the extra inner space can accommodate the volume changes. In addition, the electrolyte can penetrate pores and facilitate the transportation of Li ions. ZnO nanotubes (ZNTs) can be synthesized via several methods such as the hydrothermal process [16–18], vapor phase growth [19,20], chemical-liquid phase deposition [21], and electrochemical method [22,23]. Some synthetic methods are not economical and moreover, the ZNT-based materials have been usually prepared on substrates, which is not suitable for practical Li storage applications because of the small amount of active materials.

For Li storage applications, low electronic conductivity of ZnO is still an issue. To solve this problem, carbon incorporation and/or carbon coating methods are commonly used [24]. In this study, we report a facile synthesis of free-standing, carbon-coated ZnO nanotubes. Here, we first prepared free-standing ZnO nanorod materials using a simple hydrothermal method. The nanorod structures were transformed into nanotubes via simultaneous carbon-coating process during annealing. The ZNT structure is very effective for alleviating volume changes during Li insertion and extraction cycling, and carbon coating facilitates fast electronic transport through the nanotube surface as well as a buffering effect for volume changes of the ZnO active material. The material characterization of ZNT was performed using analytical tools and the electrochemical test results demonstrate that the synthesized material can be a good candidate as Li storage electrodes.

2. Experimental

Zinc nitrate hexahydrate ($ZnNO_3{\cdot}6H_2O$, Samchun, 98.0%, 2.974 g) and sodium hydroxide (NaOH, Daejung, 97.0%, 8.000 g) were introduced in deionized water (20 ml), and the solution was

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ultrasonicated for 30 min. The mixed solution (9 ml), deionized water (9 ml), ethylenediamine (Junsei, 99.0%, 9 ml), and pure ethanol (Daejung, 99.5%, 90 ml) were mixed under ultrasonication for 40 min. This solution was transferred into a Teflon-lined steel autoclave (200 ml). After sealing, the autoclave was heated to 180 °C in an electric oven. The temperature was maintained for 20 h to enable the hydrothermal reaction [25]. The resulting product was centrifuged to obtain precipitates. After washing with deionized water and pure ethyl alcohol for several times, the powders were dried at 80 °C. The final product was identified to be free-standing ZnO nanorods. For carbon coating and morphology transformation, the ZnO nanorod powder (200 mg), polyvinylpyrrolidone (Sigma-Aldrich, 200 mg), and glucose (Sigma-Aldrich, 96.0%, 1.8 g) were added into 30 ml of deionized water. The solution was stirred for 24 h at room temperature and subjected to the hydrothermal reaction again at 180 °C for 4 h. After the product was centrifuged by pure ethyl alcohol for at least 5 times, it was heat-treated at 600 °C for 4 h under N_2 atmosphere to obtain carbon-coated ZNTs.

The morphology and microstructure of the synthesized materials were observed with a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7401F) and a high-resolution transmission electron microscope (HR-TEM, JEOL, ARM-200F) with an energy dispersive spectroscope (EDS). The crystal structures were investigated via X-ray diffraction (XRD, D/MAX-2500V with Cu Kα radiation). Raman spectroscopy (Raman microscope, Renishaw) was used to analyze the carbon-coating layer of ZNTs.

For electrochemical test, a slurry was prepared by dispersing 70 wt % of the active material (carbon-coated ZNT), 15 wt% of conducting agent (Denka Black), and 15 wt% of binder (polyvinylidene fluoride, PVDF) in a *N*-methyl-2-pyrrolidone (NMP) solution. The slurry was coated onto a current collector (Cu foil, 10-μm-thick) to prepare electrodes. After pressing, the electrodes were dried under vacuum at 120 °C for 12 h. Cell assembly procedures were performed in an Ar-

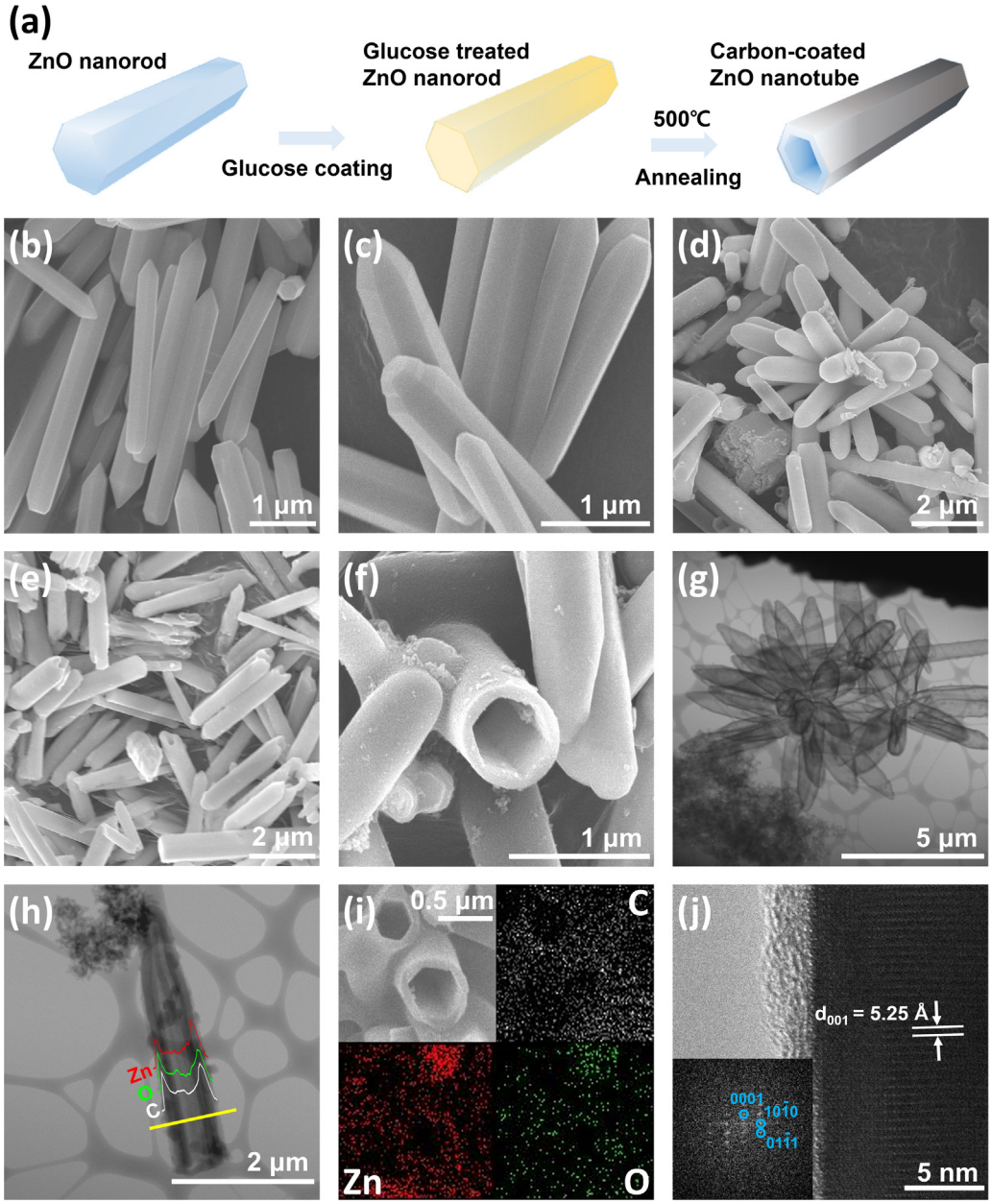

Fig. 1. (a) Schematic of the synthesis of carbon-coated ZNTs, (b–c) FE-SEM images of ZnO nanorods, (d) FE-SEM image of glucose-treated ZnO nanorods, (e–f) FE-SEM images of carbon-coated ZNTs, (g) TEM image of carbon-coated ZNTs, (h) TEM image with EDS line scan result, (i) EDS elemental mapping image, and (j) HR-TEM image with the FFT pattern of carbon-coated ZNTs.