Preparation, formation mechanism and performance of magnetic hollow coatings based on micro/nano cellulose fibers

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ABSTRACT

Micro/nano cellulose fibers were metallized via a simple electroless nickel (Ni) approach to construct hollow coatings (HCs) with improved lithium storage and catalytic properties. The magnetic HCs with uniform wall thickness were easily synthesized on cellulose fibers (CFs) surface via two depositions, and the morphology of the hollow metal coatings can be controlled by optimizing the experiment conditions. Composition elements of inner and outer walls were Ni, P and O. The mass fraction of Ni in inner and outer walls of HCs was found to be 51.39 and 87.59%, respectively. The mass fraction of CFs in magnetic HCs decreased from 16.30 to 4.56%, indicating that NaOH/thiourea aqueous solution dissolved the cellulose fibers. The formation mechanism of magnetic HCs was investigated. Compared with the electrode made from the nanowire electrode, the hollow composite materials displayed higher discharge capacity and better cycling reversibility, which may be a result of the hollow structure. The magnetic hollow materials shown here can be applied as catalysts compared with the lignocellulose/nano-montmorillonite composites. Herein, the catalytic capacity of hollow composite materials for Cu (II) was found to be 3776 mg·g^{-1}.

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1. Introduction

Magnetic hollow materials possess unique topology structure and properties, such as larger surface-to-volume ratios, lower density, larger interior space, better stability and excellent permeability [1–3]. Magnetic structure materials can be rapidly separated and driven in orienteering with the aid of an external magnetic field. Therefore, more attention is being focused on applications of magnetic hollow structure materials on biomedical, immobilized enzyme, magnetic separation and a variety of domains such as drug controlled release and targeted drug delivery [4–8]. Micro/nano scale hollow structure materials with size distribution between 10 nm and 10 μm were a kind of functional nano scale materials that had a secondary hollow cavity structure and single channel or hollow multi-channel structure with one dimensional or zero dimensional size, such as hollow nanotube, nano fiber and hollow microspheres, which were an indispensable material in nano-scale science and technology [9–11]. With the rapid

development of modern science, much literature reported preparation hollow structure methods including chemical and physical methods, such as template method, emulsion polymerization, spray drying, polymerization, and ultrasonic radiation. Many fabricated hollow materials have been widely applied in various fields [12–18].

However, the methods for preparation of hollow materials faced many problems. The removal of the templates via either thermal (sintering) or chemical (etching) methods was very complicated and energy-consuming [1]. The purity of prepared products via physical methods, such as smash and machine grinding was not high and the distribution of particle size was inhomogeneous. Furthermore, a higher precision for synthetic instruments was required [19], which greatly affected the preparation and practical value of hollow materials resulting in more attention for research focused on seeking a simple and controllable preparation method. There is little research focusing on the hollow magnetic materials based on micro or nano cellulose fibers via a simple electroless Ni-P strategy [20].

Herein, we developed a facile approach to prepare hollow magnetic materials. The rod-shaped Ni-P shells were synthesized based on micro or nano cellulose fibers bio-templates via electroless plating technique. The electroless deposition technique was investigated

to achieve uniform magnetic hollow metallic plating layers on micro or nano-sized cellulose fibers surface. The formation mechanism and catalytic performance of hollow magnetic metal coating on micro or nano cellulose fibers surface were analyzed. In addition, the electrochemical experiment was performed to compare the lithium storage capacity with different morphologies. The new process reported here affords the convenient optimization of the structure of the hollow material to achieve higher lithium storage.

2. Experimental

2.1. Preparation of magnetic hollow coatings

The process was as follows: 0.6 g lignocellulose (CB-204; Beijing building materials technique development center, Beijing, China) was dissolved in 300 mL distilled water to form a clear solution. Then, the ultrasonic (SM-1200-D ultrasonic signal generator, Nanjing, China) was used to disperse lignocellulose in an ice bath for 180 min and ultrasonic power of 960 W. Following this procedure, the cellulose fibers (CFs) were activated by solution A ($NiSO_4$ and HCl, analytically pure, Tianjin, China) and filtered until there was no liquid dripping from the CFs. The CFs were then activated in a solution of B which is made of $NaBH_4$ and NaOH ($NaBH_4$ and NaOH, analytically pure, Tianjin, China) and filtered until there was no liquid dripping from the CFs (Table 1). The electroless Ni was performed in the solution ($NiSO_4$, $Na_3C_6H_5O_7 \cdot H_2O$, $NaH_2PO_2 \cdot H_2O$, CH_4N_2S and $NH_3 \cdot H_2O$, analytically pure, Tianjin, China) under the conditions of pH 9 at 60 °C for 15 min (Table 2). The samples were washed with deionized water for 10 s. After cooling to room temperature naturally, the solid product was collected and dried at 100 °C for 30 min to obtain rod-shaped materials. The above-mentioned steps were repeated once and 0.6 g/L nano-TiO_2 (particle size 40 nm, Anatase, Aladdim Industrial Corporation) was added to the solution. The hollow coatings were obtained. Finally, the solids were dried for 30 min in a vacuum oven (DH-101-2-S thermostatic oven, Suzhou, China) in order to measure other properties by biological microscope (BK-5000), scanning electron microscope, transmission electron microscopy, ultraviolet-visible spectrophotometer, thermogravimetric analyses, electrochemistry workstation and vibrating sample magnetic flowmeter.

2.2. Characterization of structure and properties

2.2.1. Scanning electron microscope (SEM) and transmission electron microscope (TEM)

Samples were adhered with conductive adhesive and placed in the test-bed and observed by SEM(S-3400N and S-4800) and TEM (FEI Tecnai G20) to investigate the surface morphology and composition of MCFs.

2.2.2. Biological microscope (BMS)

Fifty milligrams of solids were dissolved in 30 mL distilled water to form a clear solution. Morphology was observed in droplets placed on a glass slide using an OPTEC-BK-5000 biological microscope at 400× magnification.

Table 1
Composition of activation solution.

Component	Content
$NiSO_4$ (analytically pure)	15 g·L^{-1}
HCl (analytically pure)	12 mL·L^{-1}
$NaBH_4$ (analytically pure)	15 g·L^{-1}
NaOH (analytically pure)	12 g·L^{-1}

Table 2
Composition of electroless plating bath.

Bath component	Content
Nickel sulfate (analytically pure)	0.1267 mol·L^{-1}
Sodium hypophosphite (analytically pure)	0.3267 mol·L^{-1}
Sodium citrate (analytically pure)	0.1033 mol·L^{-1}
Thiourea (analytically pure)	10 mg·L^{-1}
Ammonia (analytically pure)	30 mL·L^{-1}

2.2.3. Magnetic analysis

MPMS-XL-7 samples of vibration sample magnetic flowmeter (VSM) were supplied by the Quantum Design Company. The sensitivity of VSM was up to 5×10^{-9} emu, and magnetic field intensity was from -2 T $- +2$ T.

2.2.4. Thermogravimetric analyses (TGA)

Thermogravimetric analyses (TGA) measurements of the hollow materials were carried out via a TA-Q600 which was supplied from TA Company. Test conditions: nitrogen atmosphere, heating rate was 10 K/min between 293 to 1073 K. Calculation formula (Eq. (1)) was as follows:

$$W = \left(\frac{m_0 - m_1}{m_0} \right) \times 100\% \tag{1}$$

where, W represents weight loss ratio, m_0 is initial quality, m_1 is heating weight loss quality.

2.2.5. The description of the electrochemical experimental methods

The electrochemical performance of the as-prepared hollow coatings samples was tested by using them as an anode material for lithium ion batteries. Coin cell was assembled for the electrochemical measurements. The working electrode was fabricated by casting a slurry of 80 wt% hollow coatings material, 10 wt% conductive agent (acetylene black) and 10 wt% binder (polyvinylidene fluoride) in *N*-methyl-2-pyrrolidinone (NMP) on a Cu foil and then dried at 100 °C in vacuum for 12 h, and then compressed. The test cells were assembled in an argon-filled glove box, using a lithium foil as the counter and reference electrode, a microporous membrane (Celgard 2400) separator, and an electrolyte of 1.0 M $LiFP_6$ solution in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate. Galvanostatic charging and discharging between the voltage limits of 0.05 and 2.5 V was performed on a CT2001A Land Battery Testing System.

2.2.6. Photocatalytic performance analysis

6 g copper sulfate was dissolved in 50 mL distilled water to form a clear solution. Then, the catalyst was added into copper sulfate solution. The concentration of Cu (II) was measured via TU-1901ultraviolet-visible spectrophotometer every 20 min for 120 min. Calculation formula is (Eq. (2)) as follows:

$$\beta = \frac{(C_0 - C_1) \times V \times 64}{m_0} \tag{2}$$

where, β stands for catalytic amount, the initial concentration of Cu (II) was 0.7500 mol/L (C_0) and the solution volume is 50 mL (V), C_1 representing the concentration of Cu (II) after catalysis, m_0 stands for catalyst mass.