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Facile synthesis and magnetic study of Ni@polyamide 66 coaxial nanotube arrays

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ABSTRACT

Ni@polyamide 66 (PA66) core/shell coaxial double-layer nanotube arrays have been prepared in the nanopores of anodic aluminum oxide templates (AAO). The shell of PA66 nanotubes were formed first and then served as templates to deposit Ni nanotubes used as the core. The morphology, structures of the obtained arrays were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The formation of this unique coaxial nanotube structure was confirmed by SEM and TEM images and X-ray diffraction (XRD). We further explored the magnetic properties of the obtained coaxial nanotube arrays with vibrating sample magnetometer (VSM) and found that Ni@PA66 coaxial nanotubes exhibited higher remanence ratio than that of Ni nanotubes. These Ni@PA66 coaxial nanotubes are promising to be used as templates to fill in other materials.

1. Introduction

Making heterogeneous nanomaterials is an effective strategy for enhancing the chemical stability and mechanical strength of individual nanomaterial. In recent years, one-dimensional (1D) coaxial nanocables have attracted intense interests due to their versatile properties and functionalities derived from integration of different materials for applications in field-effect transistors (FETs), quantum wire lasers, sensors and nanoscale electronic devices [1–6]. Various coaxial nanocables with core/shelled structures have been successfully prepared, such as Cu/Ni [7], SnO_2–ZnO/PPy [8], NiO/Ni [9], CoP/C [10], and Sb_2S_3/TiO_2 [11].

Besides those nanocables, coaxial 1D nanotubes have also been prepared and exhibited unique properties for the applications in catalysis and energy. For example, Ding et al. prepared the Ni/Pt core/shell nanotube arrays showing remarkably enhanced electrocatalytic activity and stability for methanol oxidation [12]. Coaxial Pt/NiN nanotube arrays were synthesized and they showed improved electrocatalytic performance for the oxygen reduction reaction in Li-air batteries [13]. TiO_2/PbS (ZnS) coaxial nanotubes showed improved photocatalytic properties and analysis [14]. Novel MnO_2/PPy coaxial nanotubes demonstrated better rate capability, larger specific capacitance, and therefore, can be used as electrode material for supercapacitors [15]. Wu et al. [16] reported that $SnO_2@TiO_2$ coaxial nanotube arrays were prepared inside the open volume of a nanoporous template, and found the coaxial nanotubes could enhance Li^+ ion storage performance.

Polymers have also been used as shell materials for protecting the inner materials from oxidation, and metals, semiconductors, carbon or polymers et al. have been used as cores to generate different coaxial nanotubes: such as multiwall carbon nanotubes/polypyrrole [17], multiwall carbon nanotubes/polyaniline [18], Ag/polypyrrole [19], polypyrrole/polyaniline [20], and ZnO/poly(N-vinylcarbazole) [21]. Although these coaxial nanotubes have been synthesized successfully individually, it remains challenging to assemble the coaxial nanotubes into well-ordered arrays.

In this work, we reported the facile synthesis of Ni@PA66 coaxial nanotube arrays by utilizing the nanopores arrays in AAO as templates. The shell of PA66 nanotube was first obtained in the AAO template and then served as the template to deposit the Ni nanotubes. The obtained Ni@PA66 coaxial nanotubes showed improved magnetic property than that in Ni nanotubes due to the effective protection of the Ni nanotubes from oxidation. Therefore, the arrayed structures of the Ni@PA66 coaxial nanotubes make them promising for the applications in magnetic storage medium and integrated circuit. Moreover, these Ni@PA66 coaxial nanotubes can be used as template to fill in other materials to produce coaxial triple layered nanostructures for exploring their novel fundamental properties and potential applications.

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2. Material and methods

2.1. Preparation of Polymer nanotubes

The anodic aluminum oxide (AAO) templates were used as purchased. The diameter of the pores in the AAO templates is marked 200 nm, and the depth is about 60 μm. Formic acid was employed to use as solvent to prepare 3 wt% of polyamide 66 (PA66) solution. A drop of PA66 solution was added on a glass slide, and then a piece of AAO template was covered on the PA66 drop. The PA66 nanotubes were obtained after the evaporation of the solvent.

2.2. Preparation of working electrode

The AAO template filled with PA66 nanotubes was washed with the solvent to make through holes in the nanotubes. Then a thin film of Au was sputtered on the AAO template to serve as the working electrode.

2.3. Preparation of Ni@PA66 nanotubes

Ni@PA66 nanotubes were synthesized by using the electrodeposition of Ni inside of the PA66 nanotubes. Electrolyte solution used for the electrodeposition of Ni is composed of 0.6 M $NiSO_4 \cdot 6H_2O$, 0.3 M H_3BO_3 and 0.3 M KCl.

The AAO/PA66 nanotubes composite membrane was used as the working electrode and also the template for the Ni deposition. A platinum plate was used as the counter electrode and an Ag/AgCl electrode in saturated KCl solution as the reference electrode. Direct-current (dc) electrodeposition at −1.2 V/SCE was employed to prepare Ni nanotubes in PA66 nanotubes for 20 min.

For comparison, Ni nanotubes were also prepared by the DC electrodeposition of Ni in the AAO template at −1.2 V/SCE for 20 min.

2.4. Characterization

Scanning electron microscopy (SEM; JEOL JSM-6390LV), transmission electron microscopy (TEM; CM200-FEG equipped with a GIF) were used to characterize the obtained nanostructures. For

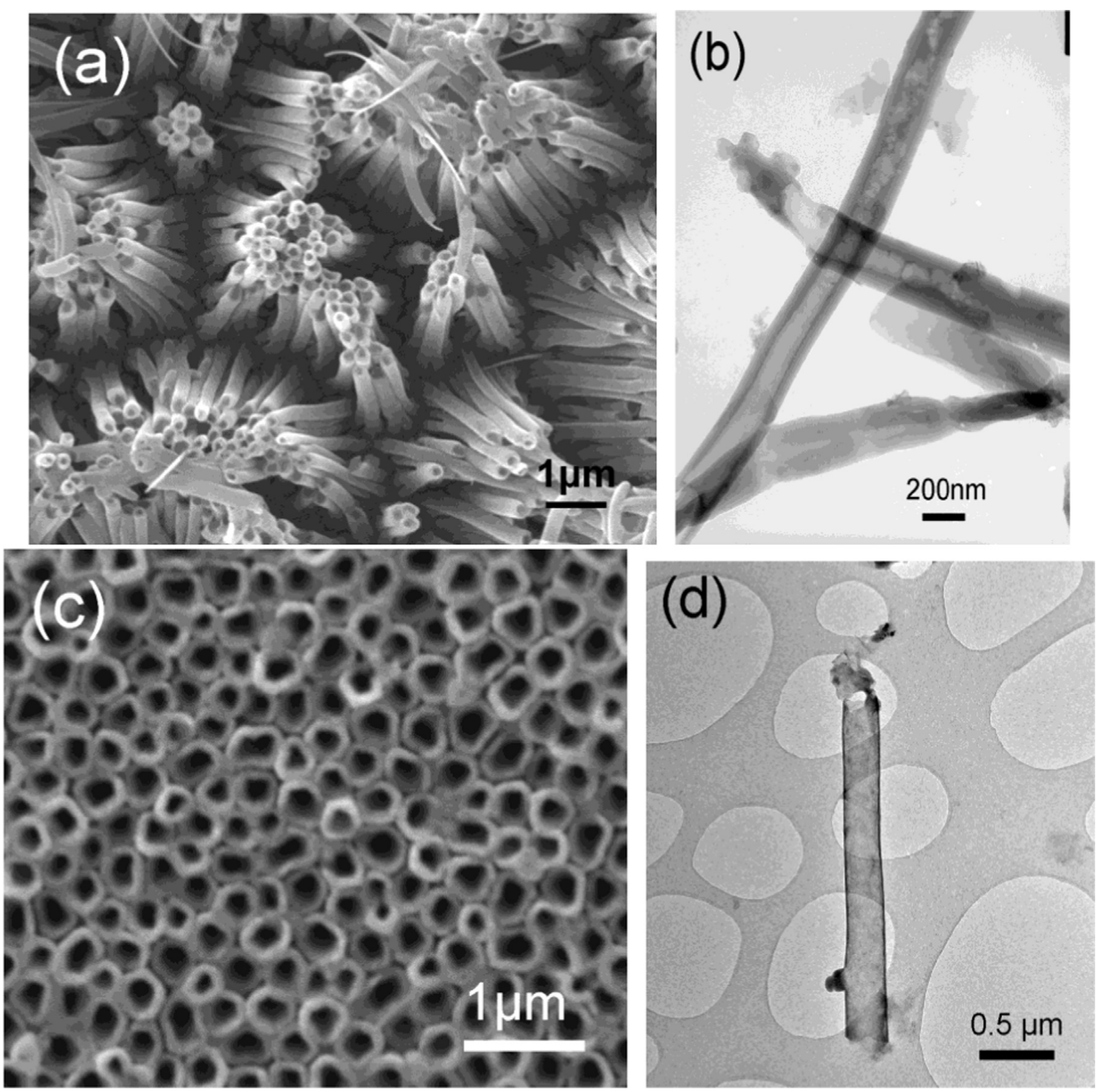

Fig. 1. (a) Typical SEM and (b) TEM images of PA 66 nanotube, (c) Typical SEM and (d) TEM images of Ni nanotube.