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Original Research

Three-dimensional interconnected cobalt oxide-carbon hollow spheres arrays as cathode materials for hybrid batteries

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ABSTRACT

Hierarchical porous metal oxides arrays is critical for development of advanced energy storage devices. Herein, we report a facile template-assisted electro-deposition plus glucose decomposition method for synthesis of multilayer CoO/C hollow spheres arrays. The CoO/C arrays consist of multilayer interconnected hollow composite spheres with diameters of ~350 nm as well as thin walls of ~20 nm. Hierarchical hollow spheres architecture with 3D porous networks are achieved. As cathode of high-rate hybrid batteries, the multilayer CoO/C hollow sphere arrays exhibit impressive enhanced performances with a high capacity (73.5 mAh g^{-1} at 2 A g^{-1}), and stable high-rate cycling life (70 mAh g^{-1} after 12,500 cycles at 2 A g^{-1}). The improved electrochemical performance is owing to the composite hollow-sphere architecture with high contact area between the active materials and electrolyte as well as fast ion/electron transportation path.

1. Introduction

Hybrid batteries HBs are considered as one of the most important power sources due to their fast recharge capability, high power density and long cycling life. Great efforts have been dedicated to searching for advanced cathode materials for high-performance hybrid batteries (HBs) with high energy/power density [1–5]. In recent years, the cathode materials of HBs was wrongly called as pseudocapacitive cathode in the literature [6–8]. Brousse et al. and Gogotsi group [6,7] pointed out that they belong to different categories because the cathode of HBs usually exhibit obvious redox couples with distinct charge/discharge plateaus, not liner behavior of capacitors. Accordingly, HBs usually consist of redox-reaction active cathodes (such as metal oxides/hydroxides [9–13], and metal sulfides [14]) and carbon materials anodes through electrochemical double layer [14,15]. Metal oxides/hydroxides are typical redox cathodes of HBs with high electrochemical reactivity, and good cycling life. But their low reaction kinetics greatly hinders their commercial application.

CoO is considered as one of the most promising cathode candidates because of its high specific capacity [1,8]. However, the practical application of CoO is still hampered by some issues (e.g., low electrical conductivity and slow ion diffusion), resulting in poor rate capability and reversibility, and unsatisfactory cycling life. To tackle the above problems, free-standing arrays electrodes has been constructed to enhance the power/energy densities and electrochemical stability [16–18]. Compared with the bulk powder counterparts, the integrated arrays electrodes present several advantages as follows: 1. The array structures possess combined properties of higher porosity and better electrical contact with the conductive substrates; 2. The arrays architecture can buffer large volume changes, leading to improved mechanical stability and cycling life; 3. No addition of polymer binders can reduce the inner resistance of electrodes; 4. Larger surface area and shorter ions/electrons diffusion path are obtained in the arrays electrodes. The integrated electrodes design has been verified successful in lots of metal oxides (e.g., CoO [18,19], Co_3O_4 [20,21], CoO [22,23]) nanostructure systems and noticeable electrochemical enhancements are achieved for Li ion batteries and supercapacitors.

Currently, integrated hollow nanosphere arrays have been investigated due to their unique geometry and porous configuration [24]. Currently, there has been no research about fabrication of 3D multilayer interconnected CoO/C hollow spheres arrays and their application for HBs. In this work, we report 3D porous multilayer CoO/C hollow sphere arrays (HSAs) by a facile combination of template-assisted electro-deposition (ED) and glucose carbonization method. Porous structure with hollow cores and interconnected nanowalls is achieved in one electrode. As cathodes of HBs, the designed CoO/C HSAs exhibit high discharge capacities and good high-rate properties owing to the unique hollow sphere array structure with faster ions/electrons transfer and large

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contact area. The proposed method is applicable for preparation of other high-performance hierarchical porous arrays for applications in energy storage and conversion.

2. Experimental

The multilayer CoO/C HSAs were prepared by a polystyrene sphere (PS) template-assisted ED method plus glucose decomposition. The simplified growth process was shown in Fig. 1a. The PS (particle size of ~300 nm) spheres template was assembled on the nickel substrate described in detail in the previous work [25]. Then, the CoO was prepared through a simple cathodic ED method, which was conducted in a three-electrode cell, the above PS spheres template electrode as the working electrode, saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter electrode. The electrolyte consisted of 0.5 M $Co(NO_3)_2$ +0.1 M $NaNO_3$. The ED was performed at a cathodic current density of 1.5 mA cm^{-2} for 30 min. Then, PS spheres template was etched by immering the sample in toluene for 12 h. Then, the sample was annealed at 400 °C in argon for 2 h to form the CoO HSAs. After that, the sample was immersed into 0.05 M glucose for 12 h plus an annealing process at 500 °C for 2 h in argon to form porous CoO/C HSAs. The mass of CoO and C was about 2.1 and 0.1 mg cm^{-2}, respectively.

The morphology and microstructure of the samples were characterized by X-ray power diffraction (XRD, Rigaku D/max 2550 PC, Cu Kα), a scanning electron microscopy (SEM, Hitachi S-4700 and FESEM, FEI Sirion-100), transmission electron microscopy (TEM, JEM 200CX at 160 kV, Tecnai G2 F30 at 200 kV) and Raman spectroscopy (WITec-CRM200 Raman system with a laser wavelength of 532 nm).

The electrochemical performances were tested in full HBs. The devices were assembled based on the CoO/C HSAs as the positive

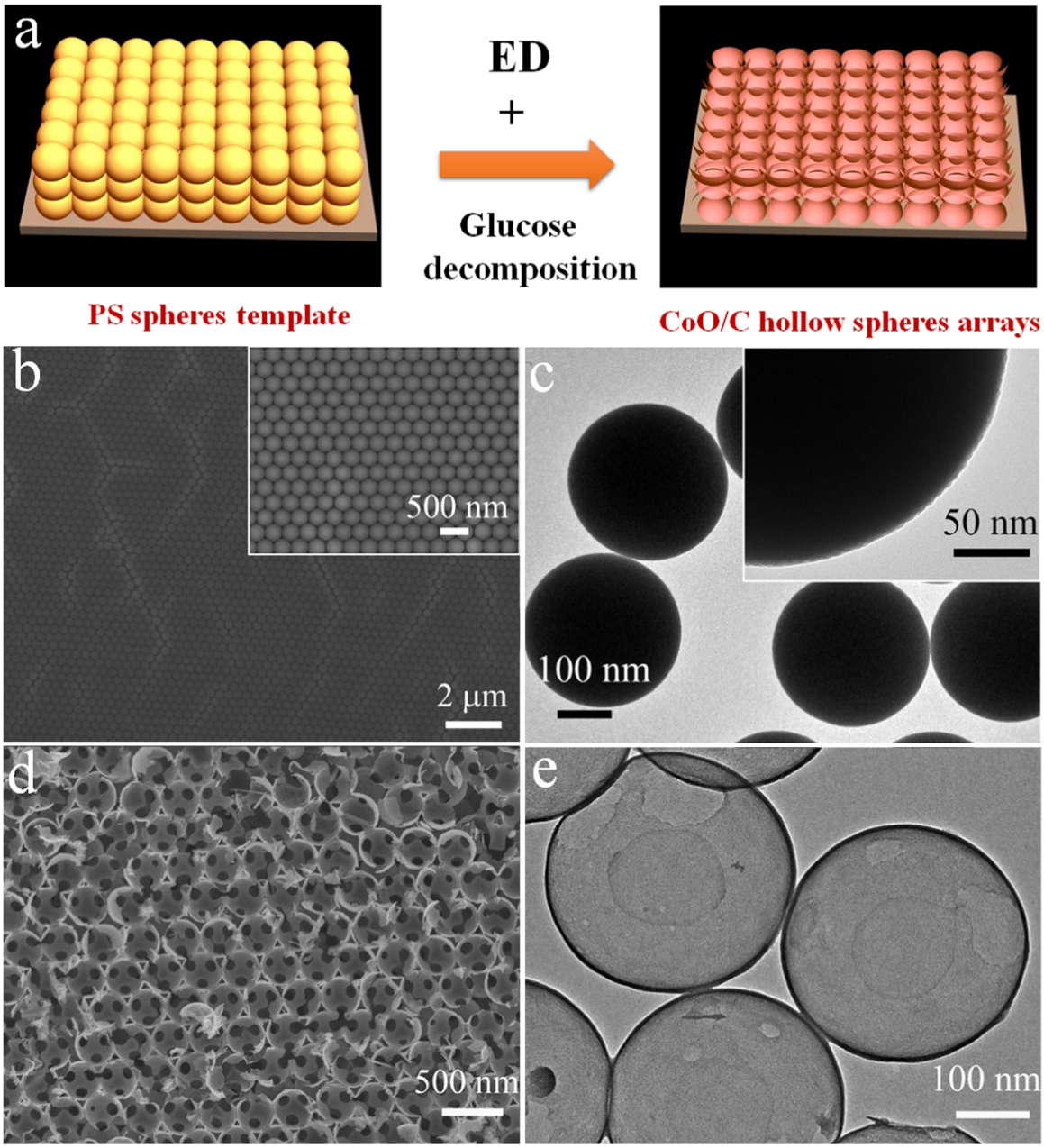

Fig. 1. (a) Schematics of growth of CoO/C hollow sphere arrays. SEM-TEM images of (b,c) polystyrene sphere template (high magnification images in inset) and (d,e) CoO/C hollow sphere arrays.