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Electrochemical capacitive studies of cadmium hydroxide nanowires grown on nickel foam

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ABSTRACT

$Cd(OH)_2$ nanowires have been synthesized on nickel foam by a simple template-free growth method. Structural characterization by SEM and TEM indicated that the $Cd(OH)_2$ formed a porous film on the surface of the nickel foam skeletons. The thickness of the film reached approximately 25 μm and the nanowires have diameters of around ~100 nm. The nanowires is confirmed to be pure phase hexagonal $Cd(OH)_2$ by X-ray diffraction. The electrochemical capacitance behaviors of the $Cd(OH)_2$ nanowires electrode are investigated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy tests. The $Cd(OH)_2$ electrode performed in different electrolyte demonstrates that nanowires possess supercapacitance properties in the presence of high concentration OH^- ion. The specific capacitances as high as 1164.8 F g^{-1} at 1 A g^{-1} and 257.6 F g^{-1} at 10 A g^{-1} are obtained in 6 mol dm^{-3} KOH solution. The remarkably high capacitance of the $Cd(OH)_2$ nanowire electrode might be attributed to its unique 3D open structure for easy access of electrolyte ions, large surface area and high electrochemical activity. This work demonstrates that $Cd(OH)_2$ nanowires electrode has potential application in electrochemical capacitors.

1. Introduction

Electrochemical capacitors (ECs), also called supercapacitors, have attracted considerable attention over the past decade because of their higher power density and longer cycle life than secondary batteries and higher energy density than conventional electrical double-layer capacitors [1,2]. ECs can be categorized into two main types on the basis of their charge-storage mechanisms: (1) Electrical double layer capacitors (EDLCs), where the electrical charge is stored at the interface between the electrode and the electrolyte; (2) Redox electrochemical capacitors, where capacitance arises from faradic reactions taking place at the electrode/electrolyte interface [2–4]. For EDLCs, the most common supercapacitors at present, use carbon-based materials (activated carbons, carbon nanotubes, and reduced graphene oxide) [5–8] with high surface area as the electrode materials. However, carbon material has high power density and long life cycle, but the small double-layer capacitance limits its application. In order to improve the specific capacitance of ECs, lots of researches have been dedicated to the investigation of metal oxides/hydroxides pseudocapacitive materials, which produce higher capacitance than double layer carbonaceous materials. RuO_2 is the well studied pseudocapacitive electrode materials with remarkable performance [9,10]. The use of this material, however, is limited due to their high cost. Therefore, the development of high performance and low cost electrode materials for supercapacitors has attracted increased interest in recent years. Transition metal oxides/hydroxides (e.g. $Ni(OH)_2$ [11,12], Co_3O_4 [13,14], CuO [15,16], FeO_x [17,18] and MnO_2 [19–21]), are generally considered as promising electrode materials for supercapacitors due to their favorable capacitive characteristics and low cost.

On the other hand, the microstructure and conductivity of electrodes play important roles in the capacitance enhancement. Electrodes with a porous structure and a large surface area usually show significantly improved ion transfer ability and specific capacitance. In recent years, different types of conductive substrates (e.g., Ni foam, Ti foil, stainless-steel foil, and flexible graphite paper) are used as current collector for ECs. Nickel foam, as a commercial material with high electronic conductivity and a desirable 3D structure was widely used as the electrode substrate material. It would not only improve the charge transfer but also reduce the internal resistance and maintain a rapid redox reaction.

$Cd(OH)_2$ (or metal Cd) was widely used as electrode material for cadmium nickel battery because of its high energy density, long lifetime and high discharge rates [22,23]. In recent years, the CdO has been reported as pseudocapacitive material by Han's group [24,25]. To the best of our knowledge, no reports have used

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$Cd(OH)_2$ as electrochemical pseudocapacitor material. Hence, in this study, we report, for the first time, the direct growth of $Cd(OH)_2$ nanowires on nickel foam via a simple hydrothermal process and the electrochemical behaviors of $Cd(OH)_2$ were investigated for ECs. Notably, the as-prepared $Cd(OH)_2$ nanowires electrode exhibits an excellent pesudocapacitive performance with a specific capacitance as high as 1164.8 F g^{-1} at 1 A g^{-1} in 6 mol dm^{-3} KOH solution, suggesting this unique electrode has potential application in ECs.

2. Experimental

All the chemicals are of analytical grade and were used without further purification. The electrode of $Cd(OH)_2$ nanowires on nickel foam were synthesized according to the similar formation mechanism described before in our articles [13,15]. Briefly, a growth solution was prepared by dissolving 3.085 g $Cd(NO_3)_2{\cdot}4H_2O$ and 0.4 g NH_4NO_3 into 30 cm^3 ammonia (25–28 wt%) + 35 cm^3 H_2O. The pretreated nickel foam was immersed into the growth solution for 14 h at 90 °C to allow the growth of $Cd(OH)_2$. After growth, the electrode was washed with H_2O and heated at 60 °C for 2 h to obtain the final electrode. The morphology of $Cd(OH)_2$ nanowires was examined by scanning electron microscope (SEM, JEOL JSM-6480) and transmission electron microscope (TEM, FEI Teccai G2 S-Twin, Philips). The loading of $Cd(OH)_2$ was measured using inductively coupled plasma mass spectroscopy (ICP-MS, Thermo XSeries II) by dissolving the electrode in aqua regia. The mass loading of $Cd(OH)_2$ is around 2.048 mg cm^{-2}. The structure of nanowires was analyzed using X-ray diffractometer (XRD, Rigaku TTR III) with Cu Kα radiation (λ = 0.1506 nm). The 2θ ranges from 10° to 90° with a scan rate of 5° min^{-1} and a step width of 0.01°.

The cyclic voltammograms (CVs), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) measurements were performed in a conventional three-electrode electrochemical cell using a computerized potentiostat (VMP3/Z Bio-Logic) controlled by the EC-lab software. The as-prepared $Cd(OH)_2$ nanowires electrode (1 cm^2 nominal planar area) acted as the working electrode, a platinum foil (1 × 2 cm^2) served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The cycle life tests were conducted on a LAND battery program-control test system. The solutions were made with analytical grade chemical reagents and Milli-Q water (18 MΩ cm, Millipore). EIS measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at the open circuit potential.

3. Results and discussion

3.1. Characterization of $Cd(OH)_2$ electrode

Fig. 1a and b shows the SEM images of the $Cd(OH)_2$ nanowires electrode. The SEM image at low magnification (Fig. 1a) shows that the $Cd(OH)_2$ nanowires formed a porous film on the surface of the nickel foam skeletons and the thickness of the film reached approximately 25 μm. A few nanoparticles adsorbed on the surface of nanowires did not affect the morphology of the nanowires electrode. The SEM image at high magnification (Fig. 1b) shows the $Cd(OH)_2$ film is composed of long nanowires grown in random direction and crossed each other. TEM image (Fig. 1c) further confirm that the nanowires have diameters of around ~100 nm and are formed by interconnected nanoparticles. This porous nanostructure can expand the electroactive area for pseudocapacitive reactions, provide effective electrolyte accessible channels for ion transportation, and shorten the distance for ion diffusion, leading to considerably reduced internal resistance and substantially improved power performances.

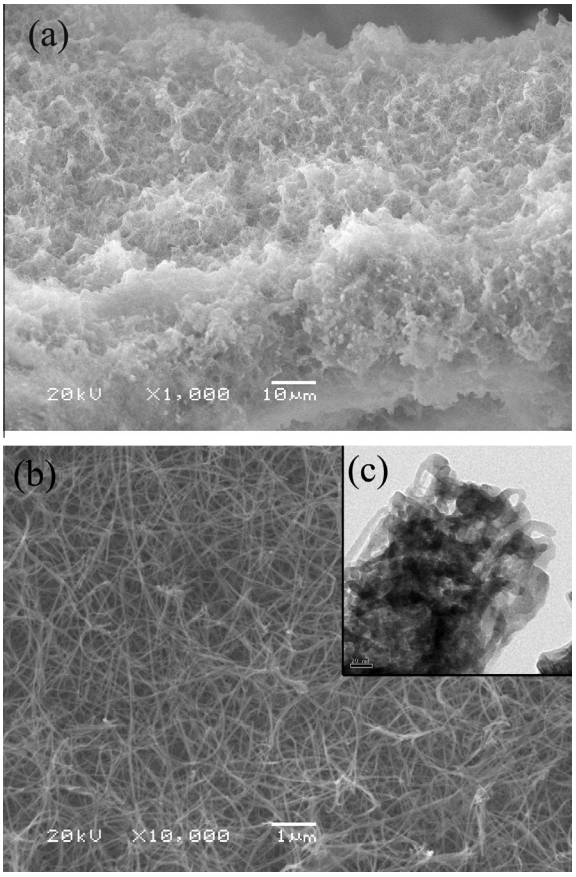

Fig. 1. SEM images of the $Cd(OH)_2$ film attached on nickel foam: (a) an overview and (b) an enlarge view. TEM image of $Cd(OH)_2$ nanowires (c).

Fig. 2 shows the XRD patterns of the $Cd(OH)_2$ powder sample scratched from nickel foam. Before the electrochemical tests, the nanowires is confirmed to be pure phase hexagonal $Cd(OH)_2$ because its XRD spectrum matched well with the standard XRD pattern (JCPDS 31-0228), and without peaks arising from impurity, such as CdO and metal Cd. The observed characteristic diffraction patterns at 2θ = 18.8, 29.4, 35.2, 48.9, 52.3, and 56.1° correspond

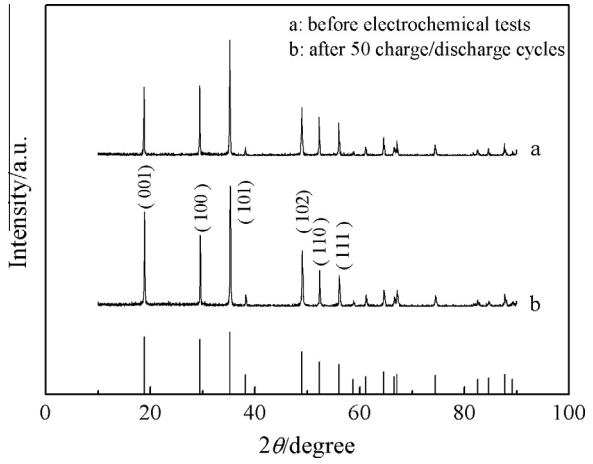

Fig. 2. XRD patterns of powder scratched down from the nickel foam. (a) Before electrochemical tests, (b) after 50 charge/discharge cycles).