



A novel material NiOOH directly grown on in-situ etched Cu(OH)₂ nanowire with high performance of electrochemical energy storage



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ABSTRACT

The 1D nanowire is prepared by in-situ etching current collector displaying faster electron transportation and better connection, plusing the directional charge transport properties, which could enable it become one of the most appropriate core of 3D core@shell structure. We apply novel nanowire-like Cu(OH)₂, which is synthesized by etching copper foil, as core structure to be coated by novel NiOOH with high theoretical capacity. The fast electronic conductive core structure and promising faradic electrode material candidate material enable the Cu(OH)₂@NiOOH/copper-foil electrode deliver high specific capacity of 1300 C g⁻¹ at current density of 10 mA cm⁻² and outstanding cycling stability of capacity retention of 88% after 10000 charge-discharge cycles, indicating the as-prepared Cu(OH)₂@NiOOH/copper-foil electrode has potential application in electrochemical capacitors.

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1. Introduction

With the increasing of population and economy, the demand for energy becomes stronger notably. The dwindling of traditional fossil fuels and the pollution of environment are the two thorny questions currently for human, luckily, which could be solved efficiently by electrochemical power source which could convert chemical energy to electrical energy. Because of the merits of higher power density, longer cycle life than batteries and simpler structure than fuel cells, supercapacitors have drawn great research interest [1–3].

Carbon materials, conductive polymer and transition metal oxide (TMO) are the most commonly used electrode materials for supercapacitor. While carbon materials show lower capacity and conducting polymer displays poor cycling stability, TMO has attracted more and more attention [4–7]. As to the present research situation of supercapacitor electrode materials, almost all the TMOs have been investigated, such as Ni(OH)₂ [8,9], Co(OH)₂ [10,11], CuO [12,13], Fe₂O₃ [14,15], V₂O₅ [16,17], and SnO₂ [18,19]. Therefore, many groups begin to focus on improving the

supercapacitor performance of TMOs. The typical approaches are (1) preparing binary or ternary TMOs composites; (2) compositing TMOs and carbon materials; (3) optimization the structure of electrode.

Obviously, modifying the contact type between active materials and current collector, namely avoiding usage of binder and conductive agent, is the simplest and effective strategies to improve the capacity. Hence, in-situ etching current collector to produce corresponding (hydro)oxides is very promising as supercapacitor electrode. For example, Li et al. prepared Ni(OH)₂ nanosheet via etching the nickel foam by H₂O₂ [20]; Tian et al. reported Fe₂O₃ nanowire by direct calcinating iron foil [21]; Wang et al. synthesized Cu(OH)₂ nanowire through etching copper foil in NaOH and (NH₄)₂S₂O₈ solution [22]. However, owing to the intrinsic inert ability of ions de-insertion, Fe₂O₃ or Cu(OH)₂ did not exhibit satisfactory specific capacity [22,23]. But it would be a great pity if we stop further investigating the application of Fe₂O₃ or Cu(OH)₂ nanowire in supercapacitor field, after all the nanowire morphology is very desirable for electrode materials, especially prepared in such simple way. We could make use of nanowire directly grown on current collector as substrate to support other materials to grow to prepare 3D core@shell electrode.

As we all know, this 3D core@shell structure has attracted great attention due to the enlarged surface area, guaranteeing more

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active materials contact electrolyte to take part in redox reactions to supply more faradic capacity [24,25]. Although various core@shell structure of TMOs have been reported, such as ZnO@NiHN [26], MnO₂@NiO [27], CoO@NiHON [28], and Co₃O₄@MnO₂ [29], et., it should be noted that among the reported structures (1) most nanowire cores are prepared by hydrothermal method, demanding high temperature and pressure, which is more expensive and complex than in-situ etching at room temperature [22]; (2) the nanowire core and substrate is heterogenous contact, which is less effective to shorten the path length of ions diffusion and electrons transportation than that synthesized by direct etching the current collector [21]. Plusing the directional charge transport properties of 1D nanowire, therefore, we could believe the above mentioned Fe₂O₃ or Cu(OH)₂ nanowire [21,22] will be a promising core materials. Tian et. al [21] and Liu et al. [30] has prepared electrodes of Ni(OH)₂ and PPY coating Fe₂O₃ nanowire, respectively, and shows good supercapacitor performance. To the best of our knowledge, there is no any reports core@shell structure about Cu(OH)₂.

In this work, we select NiOOH as the wrapped materials coating Cu(OH)₂ nanowire core, which mainly because the high specific capacity of nickel based (hydro)oxide as reported [31,32]. For the preparation of shell NiOOH, we also adopt the simplest strategy: chemical bath deposition at room temperature. It could be believed that this low-cost preparation route could be easily scaled up, and the unique structure design could make the electrode display more outstanding supercapacitor performance.

Our results shows that we successfully synthesized nanowire Cu(OH)₂ coated by spinous NiOOH on copper foil electrode (Cu(OH)₂@NiOOH/copper-foil). The electrode displays high specific capacity of 1300 C g⁻¹ at current density of 10 mA cm⁻² and perfect cycling stability of 88% capacity retention after 10000 charge-discharge cycles.

2. Experimental

2.1. The purity of the chemicals used in our experiment

Acetone (analytical purity, Tianjin City Fu Yu Fine Chemical Co., Ltd.), ethanol (analytical purity, Tianjin City Fu Yu Fine Chemical Co., Ltd.), HCl (analytical purity, Beijing chemical plant), NaOH (analytical purity, Tianjin kwangfu Technology Development Co. Ltd.), (NH₄)₂S₂O₈ (analytical purity, Tianjin Zhiyuan Chemical Reagent Co. Ltd.), Na₂SO₄ (analytical purity, Tianjin Zhiyuan Chemical Reagent Co. Ltd.), K₂S₂O₈ (analytical purity, Tianjin Zhiyuan Chemical Reagent Co. Ltd.).

2.2. Preparation and characterization of Cu(OH)₂@NiOOH/copper-foil electrode

We prepared the Cu(OH)₂@NiOOH array via two simple ways including in-situ etching copper foil and chemical bath deposition.

The first step is the preparation of Cu(OH)₂ nanowire via direct etching copper foil. Briefly, a fresh Cu foil (0.15 mm, 99.95%, Tianjin Hengxing Chemical Preparation Co., Ltd. China) was cut into 1 cm × 1 cm sheet. It was cleaned by a consecutive ultrasonication in acetone, ethanol, distilled water for 10 min., and then put it into 1.0 M HCl solution to remove any surface impurities and oxide layers. The Cu was then immersed in an aqueous solution consisting of 12 mL NaOH (10 mol dm⁻³), 6 mL (NH₄)₂S₂O₈ (1.0 mol dm⁻³) and 27 mL distilled water. After 30 min action, the copper foil was removed from the solution, rinsed with water and ethanol, and dried to obtain the Cu(OH)₂/Cu-foil electrode.

The second step is the preparation of Cu(OH)₂@NiOOH via chemical bath deposition. To grow NiOOH on Cu(OH)₂ nanowire cores, a solution was prepared by mixing 100 mL of 1 M

NiSO₄·6H₂O, 80 mL of 0.25 M K₂S₂O₄, and 20 mL of aqueous ammonia in a 250 mL Pyrex beaker. The Cu(OH)₂/copper-foil electrode was immersed into the aqueous solution. When the chemical-bath deposition of NiOOH was performed for 20 min, the NiOOH successfully uniformly coated the surface of nanowire Cu(OH)₂. The as-prepared Cu(OH)₂@NiOOH/copper-foil was dried at 60 °C for 12 h. NiOOH directly grow on copper foil was prepared in the same method.

The morphology was examined by scanning electron microscope (SEM, JEOL JSM-6480), transmission electron microscopy (TEM, JEOL 2010). The crystallographic phases of the sample were investigated by X-ray diffractometer (XRD, Rigaku TTR III) with K α radiation ($\lambda = 0.1506$ nm) with a scan rate of 10° min⁻¹ at a step width of 0.02°. X-ray photoelectron spectroscopy with Al K α radiation (XPS, Thermo ESCALAB250) was used to establish the valence states of Ni and Cu.

2.3. Electrochemical measurements

The supercapacitor performance is generally evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycling stability test. All tests are performed in 1 M KOH electrolyte. The CV, GCD and EIS are carried out using a computerized potentiostat (VMP3/Z Bio-Logic) controlled by the EC-lab software. The cycle life tests were conducted on a Land battery program-control test system. The single electrode is tested in a three-electrode system, including a platinum foil (1 × 2 cm²) as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, of which the potential value is 0.2412 V vs. SHE and the as-prepared electrode as working electrode.

3. Results and discussion

3.1. Characterization of electrodes

XRD analysis was first performed to study the crystal structure of the electrodes. The powder scratched from copper foil is used as samples for performing XRD. As shown in Fig. 1(a), all the diffraction peaks could be well indexed to orthorhombic Cu(OH)₂ (JCPDS file No. 35-0505), indicating the copper foil could generate pure Cu(OH)₂ after etched in NaOH and (NH₄)₂S₂O₈ solution. Fig. 1(b) shows the XRD patterns of the Cu(OH)₂/copper-foil after chemical bath deposition, from which it could be seen, firstly, the diffraction peaks from Cu(OH)₂ is still strong, indicating the high crystal quality of core material; secondly, the peaks located at 38.2 and 43.2 become obviously stronger, resulting from the coating of hexagonal NiOOH (JCPDS file No. 06-0075).

The Energy Disperse Spectroscopy (EDS) is used to detect the element composition and element distribution of the electrode. As shown in Fig. 1(b), Cu and Ni elements are tested and both the two elements are well distributed on the surface of the electrode, indicating well-proportioned growing of Cu(OH)₂ on copper foil and uniform covering of NiOOH on Cu(OH)₂.

X-ray photoelectron spectroscopy (XPS) is measured to determine the valence states of Cu and Ni elements. The full survey spectra in Fig. 1(c) further reveals the existence of Cu and Ni elements in active material. The detailed fitting peaks of Ni, Cu and O region are shown in Fig. 1(d)~(f), respectively. As shown in XPS spectra in Ni 2p region (Fig. 1(d)), two main peaks located at 873.9 and 856.3 eV can be assigned to Ni 2p_{1/2} and Ni 2p_{3/2} (with a spin energy separation of 17.6 eV) and two shake-up satellite peaks at 880.0 eV and 861.8 eV can be observed, which well indicate the existence of Ni³⁺ [33–35]. The XPS spectra in Cu 2p region shown in Fig. 1(e) exhibits two peaks at 954.4 and 934.4 eV (with splitting of 19.9 eV), corresponding to the Cu 2p_{1/2} and Cu 2p_{3/2}, respectively,

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