In-situ fabrication of nanosheet arrays on copper foil as a new substrate for binder-free high-performance electrochemical supercapacitors

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ABSTRACT

A facile hydrothermal method and subsequent electroactivation have been developed to fabricate three-dimensional (3D) CuO nanosheet arrays on the copper foil substrate, which can be used directly as a binder-free electrode for supercapacitor applications. Under optimum conditions, by using this facile method, a high capacitance of 125 mF/cm^2 at a current density of 0.3 mA/cm^2 is obtained. The prepared supercapacitor showed a good rate capability (46.4% capacitance retention, when the current density is increased to more than 30 times) and an excellent cyclability (more than 88% capacitance retention after 3000 cycles).

1. Introduction

The rapid depletion of fossil fuels and increasing environmental issues have encouraged researchers to develop clean and sustainable energy sources for different applications [1,2]. Among various energy storage devices, supercapacitors, also known as electrochemical capacitors have attracted great attention due to their high power capability, long cycle life time, and fast charge/discharge rates with a broad range of applications [2–5]. Based on the charge storage mechanisms, supercapacitors can be divided into two major categories, electric double layer capacitors (EDLCs) and pseudocapacitors [3,6]. The capacitance of the EDLCs materials comes from the charge accumulation at the electrode/electrolyte interface. Pseudocapacitors on the other hand, are dominated by reversible and fast Faradaic reactions on the surface of electrode materials. Compared with EDLCs, pseudocapacitors exhibit higher specific capacitances and energy densities; but usually suffer from poor electrical conductivity [7–9]. To address this issue, various methods such as a) tuning morphology and the pore size of the active material, b) using core-shell assemblies, and c) adjusting the contact between the active material and current collector have been explored [10]. Generally, the material constituents of supercapacitors can be divided into three main categories: (1) carbon materials such as activated carbon, carbon nanotubes, graphene and etc. [11,12], (2) electrically conducting polymers, such as polyaniline and polypyrrole [13–15] and (3) transition metal oxides and hydroxides, such as RuO$_2$, V$_2$O$_5$, Ni(OH)$_2$, Cu(OH)$_2$ NiO, MnO$_2$, V$_3$S$_4$, Co$_3$O$_4$ and CuO [16–21]. During the last decade, copper oxide (CuO) is considered extensive

attention because of the abundant resources, low cost, environmental compatibility and ease of preparation [22,23].

Copper oxide nanostructures have been prepared by various methods, such as anodizing, sol-gel, chemical deposition, solvothermal coating and electrochemical deposition [10,24,25]. Among these methods, the hydrothermal route is attracted great attention due to its simplicity, ease in adaptation to large-scale production and high potential for synthesis of nanomaterials. Moreover, films can be deposited at low temperatures on the surface of various substrates and the thickness and quality of the deposited layers may be easily controlled by adjusting the bath chemical composition, deposition time and hydrothermal treatment temperature [26]. Some attempts are reported for increasing the capacitance performance of CuO nanostructures. Chen et al. synthesized Cu(OH)$_2$ nanoporous nanorods by anodizing copper foil in 1 M NaOH solution at a constant current density of 1.5 mA/cm^2 [10]. Under optimum conditions, they obtained the highest areal capacitance of 213 mF/cm^2. Shinde et al. have reported a specific capacitance of 459 F/g at 5 mV/s for CuO/Cu(OH)$_2$, synthesized by Successive Ion Layer Adsorption (SILAR) method in 2 M KOH electrolyte [27]. Navate et al. synthesized copper oxide nanostructures by hydrothermal method [28]. They attained the highest specific capacitance of 60 F/g at the scan rate of 10 mV/s in a series of ionic liquid electrolytes. Pawar et al. synthesized granular Cu$_2$O and CuO on stainless steel substrate using reactive radio-frequency magnetron sputtering at room temperature. They reported the specific capacitances of 215 and 272 F/g in 6 M KOH solution for Cu$_2$O and CuO electrodes, respectively [22]. CuO/Cu(OH)$_2$ lotus-like structures have been fabricated by CBD

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method on copper foil electrode. The highest specific capacitance 278 F/g is attained at a current density of 2 mA/cm^2 [29]. Li et al. found that the CuO nanosheets can directly grow onto copper foam, exhibited a specific capacitance of 212 F/g at a current density of 0.41 mA mg^{-1} in 6.0 M KOH electrolyte [30]. Zhang et al. have reported a specific capacitance of 88.5 F/g at the scan rate of 2 mV/s for the synthesized CuO nanostructures with different morphologies using a controlled method in the presence of tetraoctylammonium bromide (TOAB) at room temperature [31]. Huang et al. prepared CuO nanowires on the Cu foam substrate by using CBD in Ammonium peroxy disulfate (APS)/NaOH solution mixture followed by annealing at 190 °C [32]. They obtained a specific capacitance of 608 mF/cm^2 at the scan rate of 2 mV/s. Nawanya et al. have reported a specific capacitance of 566.33 F/g at the scan rate of 5 mV/s by synthesis of Nanosheet-like CuO Film on ITO substrate using SILAR method [33]. However, to the best of our knowledge, there is no report on preparing CuO nanosheet arrays by etching the Cu foil in acidic media.

Driven by the above motivations, for the first time; a facile hydrothermal method was employed here, didn't have the complexity and maintenance of the electrochemical device [10,30], reactive radio-frequency magnetron sputtering [22] and also the SILAR set-ups [27,33]. However, all the above methods suffer from the introduction of other copper sources [28] and even the use of strong alkaline oxidants [29,32–33] or the use of polymers such as PVDF or PTFE as binder for adhering electroactive material to the surface of substrate which really in this case results in increasing the internal resistance of final electrode [31]. We herein, presents the simple hydrothermal route in HCl acidic solution to synthesize 3D CuO nanosheet arrays on the surface of Cu foil. Integrated as free-standing electrodes, the electrodes showed promising performance for pseudocapacitive energy storage. The electrochemical results revealed that 3D CuO nanosheet arrays have superior electrochemical properties including high capacitance, high cycling stability and good rate capability performance.

2. Experimental

2.1. Materials

All chemicals were of analytical reagent grade and purchased from Sigma-Aldrich and Merck companies and used as received without any further purification. Cu foils were purchased from Merck Company. Also, all aqueous solutions were prepared with DI water (Millipore Water Purification, 18.2 MΩ).

2.2. Preparation of electrodes

First, Cu foil was cleaned in HCl (3 M), deionized water and ethanol for 10 min, 2 min and 5 min, respectively. Then, a piece of Cu foil (1.5 cm × 1 cm) was immersed into a solution containing 3 M HCl and then transferred to the stainless steel autoclave and maintained for 6 h at various temperatures between 70 and 130 °C. After that, the autoclave naturally allowed to cool down to room temperature and then Cu foil rinsed sufficiently with deionized water and finally dried at 60 °C for 3 h.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded with an X-ray diffractometer (GBCMMA, Instrument) in the 2θ range from 10° to 80° using Cu Kα radiation. The structure and surface morphology of electrodes were studied by a field-emission scanning electron microscope (FE-SEM MIRA 3 TESCAN, 15 kV, Czech). FT-IR spectra were obtained by using a Perkin Elmer FT-IR spectrometer (spectrum 100). The specific surface area and pore size distribution of the CuO electrode was estimated by the multipoint Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) procedures at 77 K from N$_2$ adsorption-

desorption isotherm using a PHS-1020 (PHSCHINA) apparatus, respectively.

2.4. Electrochemical measurements

Electrochemical experiments were performed in 2 M NaOH solution with an Autolab PGSTAT 101 (Metrohm, Netherlands) in a conventional three-electrode system with Cu foil, Pt foil (1 cm × 2 cm) and Ag/AgCl, as the working, auxiliary and reference electrodes, respectively. The Cu foil samples with an exposed area of approximately 1 cm^2 were used for electrochemical measurements. All potentials were quoted versus Ag/AgCl (3.5 M). Electrochemical impedance spectroscopy (EIS) measurements were carried out with a galvanostat/potentiostat EG & G model 273A (Princton Applied Research, USA) equipped with a frequency response detector, superimposed with a sinusoidal voltage with an amplitude of 10 mV in the frequency range of 100 kHz to 10 mHz. All EIS measurements were performed at an open circuit potential (OCP). The voltammetric charge (q) integrated from cyclic voltammograms can be used as an effective criterion for determining the pseudocapacitance using the following equation:

$$C_s = \left(\left(\int i*dv\right)\Big/2*(S*\upsilon*\Delta V)\right)$$

where, i is the current in A, S is the geometric surface area in cm^2, υ is the potential scan rate (V/s) and ΔV is the investigated potential window (V). The number 2 is included in the denominator to eliminate the contribution from the charging current (anodic scan).

The areal capacitance of the electrode was also derived through galvaonostatic charge/discharges measurements (GCD) using the following equations:

$$Cs = {i \times \Delta t}\Big/{S \times \Delta V}$$

where C$_s$ is the areal capacitance in F/cm^2, Δt is the discharge time (s), i is the discharge current (A), ΔV is the GCD applied potential window in V, and S (cm^2) is geometric surface area of the Cu foil, which is 1 cm^2 in all experiments.

3. Results and discussions

3.1. Mechanism of nanosheet arrays formation

Starting from the acidic conditions for hydrothermal procedure, a dissolution–precipitation mechanism is proposed to elucidate the nanosheet arrays growth on the copper foil. Acid etching of the copper foil surface results in the dissolution of copper element to form Cu^{2+} ions, which is confirmed by changing the color of the HCl solution, leading to formation of nano-pits on the surface of foil at the early stages of the reaction. By increasing the time, H$^+$ ions are consumed and hydrolysis of the Cu^{2+} ions is occurred. Because the nano-pits have high surface energy, it is anticipated that these nano-pits can act as nucleation sites for the precipitation of CuO structures, leading to preferential deposition of CuO on the copper foil. Regarding the nano-pits on the surface of copper foil, newly formed Cu^{2+} ions reacted immediately with the oxygen in the media and results in the formation of CuO structures on the surface of Cu foil after hydrothermal treatment and electrochemical activation in alkaline media. The color of the Cu foil turned from red to black after hydrothermal treatment and subsequently electrochemical activation in 2 M NaOH solution, indicating the formation of copper oxide nanostructures on the foil [34,35].

3.2. Structural and morphological characterizations

Fig. 1 shows the typical FT-IR spectrum of CuO sample. The absorption peaks around 430, 504, 609 and 874 cm^{-1} are attributed to the metal-oxygen stretching vibrations of CuO. Strong bands obtained at about 609 and 504 cm^{-1} are assigned to the characteristic stretching