



In-situ growth of self-assembled 3D Cu₂O@Cu foam with enhanced electrochemical properties



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ABSTRACT

Nanostructured Copper oxides are promising materials for supercapacitors due to their high theoretical capacitance, low cost and environment friendly properties, especially for those prepared via template-free method. In this work, an in-situ growth of self-assembled 3D Cu₂O@Cu foams nanocomposite without template has been developed and the synthesis mechanism has been discussed in detail. The electrode exhibits a high capacitance of 0.66 F cm⁻² (about 200 F g⁻¹) and significant stability (after 12000 times cycling, remaining 87.9% of the initial value). Extraordinary performances and relative cost of the raw material indicate its potential in commercial applications for energy storage.

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1. Introduction

Environmental pollution and the depletion of traditional energy have aroused more attention in finding developing clean and renewable energy [1]. Supercapacitors, regarded as novel energy storage equipment, have attracted public attention and gradually being commercializing and industrializing [2–5]. However, its large-scale industrialization is held up due to the really inferior electrochemical performances of the electrode materials. The main influencing factors may be the poor interface between the electrode materials and current collectors, since a binder has been used to bond each other, greatly reducing the conductivity, meanwhile increasing the resistance.

Cu₂O, as a p-type semiconductor, is considered as a promising material in sensors, Li-ion batteries and supercapacitors [6–8], due to their high theoretical capacitance, low cost and friendliness to environment [9–11]. However, the usage of its excellent physical properties in photocatalysis [12,13], antibacterial experiment [14–16], and supercapacitors has rarely been reported. For example, Chen et al. have developed a novel core-shell heterostructured Cu/Cu₂O nanowires as efficient visible-light photocatalysts [17]. Nevertheless, poor electronic conductivity of these oxides significantly restrict their specific capacitance, cycling stability and high-power applications [18].

Nanostructuring and/or hybridization with highly-conductive materials are common strategies to enhance the electronic

conductivity of metal oxides, increase their specific surface areas, and improve their capacitance. 3D Design enables traditional 2D or 1D material to perform in an all-dimensional scale, leading significant properties [19]. For example, Dubal et al. reported a copper oxide electrode material of 43 F g⁻¹ at 10 mV s⁻¹, while Yu et al. developed a 3D porous gear-like CuO on a Cu substrate electrode of 348 F g⁻¹ at 1 A g⁻¹ [9,20].

In recent years, there has been increasing focus on creating novel materials inspired by nature such as metal foams. Among those methods of preparation, in situ growth of electrode material on metal foams could dramatically enhance the electronic conductivity, increase their specific surface areas, and improve their capacitance. Besides, intimate interface contact between materials and electrode (or current collector) plays a critical role in the full using of active materials, and further enhancing cycling stability [21–24]. Wang et al. report the in-situ growth of CuO nanoparticles on nickel foam, which owns 569 F g⁻¹ at the current of 5 mA cm⁻², which is much larger than that of commercial CuO powder [24]. Dong et al. electrodeposit Cu₂O at copper foam to form a structure of nanoneedle arrays, exhibiting a high capacitance of 862.4 F g⁻¹ at 5 mV s⁻¹ [27]. However, the development of environmental-friendly commercial Cu oxides/hydroxides via a green and facile way with high specific capacitance, excellent cycling stability and high energy/power density is still challenging [27]. Herein, a green, low cost, environment-friendly and template-free method in situ growth of self-assembled 3D Cu₂O@Cu foams nanocomposites has been introduced. The Cu₂O@Cu foams exhibits extraordinary specific capacitance of 0.66 F cm⁻² (about 200 F g⁻¹) and significant stability (after 12000 times cycling, remaining 87.9% of the initial value). Furthermore, the formation

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mechanism in terms of all different reactors has been discussed in detail.

2. Experiment

3D Cu₂O@Cu foams nanocomposites were prepared by a one-step method. The growing solution was prepared by dissolving 0.01 M Cu(NO₃)₂ and 0.005 M cetyl trimethyl ammonium bromide (CTAB) in a mixture solution of alcohol and water. The copper foam was cut into 1 cm × 1 cm piece and then pretreated in acetone for 20 min under ultrasonic and rinsing with deionized water. The pretreated copper foam was then put in the growing solution with an amount of H₂O₂ dropped into the solution for 8 h at 30 ± 1 °C to lead the assembling of Cu₂O on copper foam. After growth, the piece was washed with deionized water and alcohol and dried in vacuum oven at 60 °C for 12 h to acquire the final electrode with about 3 mg Cu₂O.

X-ray diffraction (XRD) powder patterns were recorded on D/max-γB diffractometer using Cu Kα radiation at a 2θ range from 30° to 80° with a scan rate of 8°/min. The morphologies of the samples were investigated by scanning electron microscopy (SEM) on Tescan MAIA3 XMH. The energy dispersive X-ray spectroscopy (EDX) and EDX elemental mapping were conducted on Bruker Xflash 6160. Electrochemical tests as cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were conducted on Autolab PGSTAT128N electrochemistry workstation. Open-circuit potential and stability were investigated on Shanghai Chenhua 660E. The Brunauer-Emmett-Teller (BET) test of the Cu foam and Cu₂O@Cu electrode were invested on Tristar II 3020.

3. Result and discussion

The XRD results confirm the formation of Cu₂O on Cu foam (Fig. 1a). The diffraction peaks at 2θ of 36.5°, 42.4°, 61.5°, 73.7° are attributed to the (111), (200), (220) and (311) reflections of Cu₂O, in accord with the standard powder diffraction patterns of Cu₂O structure (JCPDS NO. 65–3288). While, the base Cu foam contributes to the diffraction peaks at 2θ of 43.3°, 50.5°, 74.2°, attributed to the (111), (200) and (220) planes, matching well with the standard XRD pattern of Cu (JCPDS no. 65–9026). Fig.S3 further

confirms the ratio of Cu and O on the surface is 2:1, indicating the formation of Cu₂O.

N₂ adsorption-desorption measurement is applied in the investigation of the specific surface area and porous structure of the as-synthesized Cu₂O@Cu electrode. A typical IV isotherm could be classified (Fig. 1c), which corresponds to the presence of mesoporous. Considered as a whole, the Brunauer-Emmett-Teller (BET) of the as-synthesized Cu₂O@Cu electrode exhibits a specific surface area of 2.99 m² g⁻¹, while the Cu foam only contributes to 0.19 m² g⁻¹ (Fig. S1), on the basis of the N₂ adsorption-desorption isotherm. The pore volume distribution could be calculated from the N₂ adsorption-desorption isotherm on the Barrett-Joyner-Halenda (BJH) method. The average pore volume distributed in the mesoporous region, is calculated as about 4.64 nm. In addition, the total pore volume of the pores with the diameter of from 1.7 nm to 300 nm is 0.00344 cm³ g⁻¹. Such a mesoporous structure allows the rapid accession to the electrode of the active materials and contributes to a better electrochemical behavior.

As schematically shown in Fig. 2a, the Cu₂O nanoparticles forms on the skeleton surface of Cu foam the self-assembled under the influence of static and micelle. Firstly, the surface of pretreated Cu foam still exists some grains, which act as the center of heterogeneous nucleation (Fig. 2c). After processing in the H₂O₂ solution, the free micelle of CTAB traced Cu²⁺ ions into a ball, and then attached to the grains (Fig. 2d), leading the surface to become rough and porous. During the first one hour, the Cu₂O nanoparticles tend to form in situ on cross growth, and no bare surface of the basic Cu foam could be observed (Fig. 2e). At the first stage, the growth rate of Cu₂O nanoparticles is rapid (Fig.S4). Right now the grain crystal will turn to center, and the growth will incline to longitudinal. Obviously the spherical structure has been covered with the Cu₂O nanoparticles with about 50 nm in width and 150 nm in length (Fig. 1b). As the time goes by, the nanostructure makes no odds (Fig. 2f), and the formation rate tends to be steady (Fig.S4). And clearly the growing Cu₂O nanoparticles shows polycrystalline, since the Cu₂O grows as accumulation in disorder (Fig. 2b).

To further discuss the mechanism, three control experiments have been performed. Obviously the impact of H₂O₂ is tremendous, as an oxidizing agent, H₂O₂ leads Cu²⁺ ions to crystallize quickly and lower the Gibbs free energy of crystallization, tending to form

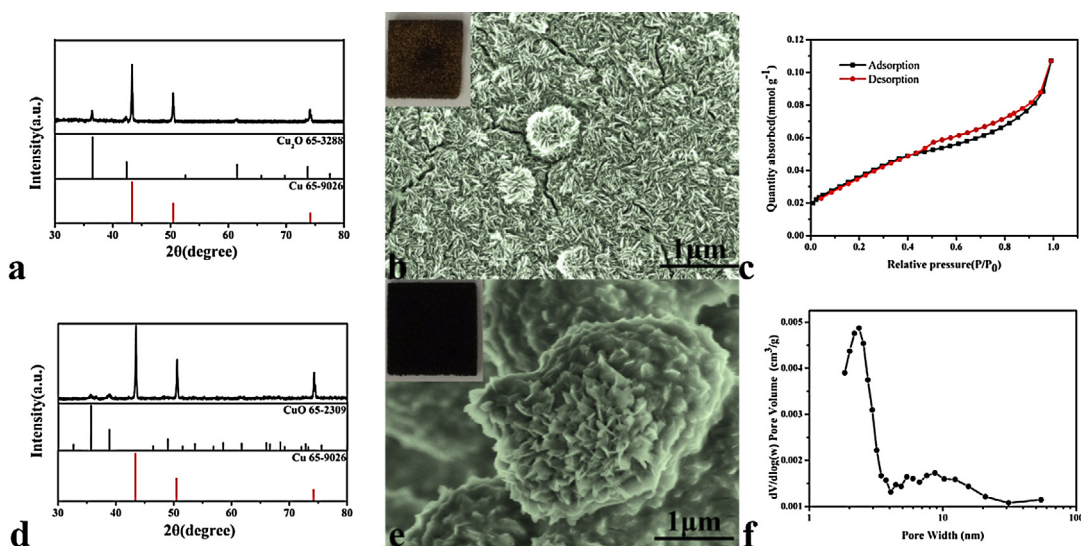


Fig. 1. (a) XRD patterns of as-synthesized Cu₂O@Cu electrode; (b) SEM images of Cu₂O@Cu foam and the photo of as-synthesized sample (inside); (c) N₂ adsorption-desorption isotherm of Cu₂O@Cu electrode; (d) XRD patterns of the electrode after being positively scanned to 0.5 V vs. Ag/AgCl during the CV process in 6 M KOH solution; (e) SEM images of Cu₂O@Cu foam after reaction and the photo of the sample (inside); (f) BJH adsorption pore volume distribution of Cu₂O@Cu electrode.

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