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Hierarchical dandelion-like copper oxide wrapped by reduced graphene oxide: Hydrothermal synthesis and their application in supercapacitors

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ABSTRACT

In this study, reduced graphene oxide (rGO)-wrapped dandelion-like CuO microspheres have been successfully synthesized using a one-step hydrothermal method without calcination. Characterization results demonstrate that dandelion-like CuO microspheres with sizes of 2.0 μm are well wrapped by ultrathin rGO nanosheets. Moreover, the introduced amount of GO dispersion in the reaction system was found to play a key role in tuning the phase compositions and microstructures of the resultant CuO-rGO composites. When used as electrode materials for supercapacitors, dandelion-like CuO wrapped by rGO nanosheets exhibited the best capacitive behavior with a specific capacitance of 296 F g^{-1} at 1.0 A g^{-1} and a retention of 96.1% after 2000 cycles at 2.0 A g^{-1}. Such excellent electrochemical performance might be mainly attributed to the rGO wrapping effect, efficiently providing higher electronic conductivity and buffering the volume changes.

1. Introduction

Graphene is an intriguing two-dimensional carbon nanomaterial which has received considerable attention in recent years owing to its remarkable properties such as electronic conductivity, good mechanical properties, strong adsorption, and high thermal stability [1,2]. Such superior performances endow it with exceptional application potential in many fields including catalysis [3–5], sensors [6,7], adsorption [8], energy storage [9,10], and so on. In particular, recent research has been focused on the graphene-based transition metal oxide composites due to the combination of remarkable unusual properties of graphene with metal oxides [11–13], and hence their synthesis and application have become of scientific and technological importance.

CuO as an important p-type transition-metal oxide semiconductor has received considerable attention due to its potential applications in many important fields such as heterogeneous catalysts [14,15], sensors [16,17], electrode materials [18–21], etc. Particularly, as the electrode materials used in Li-ion batteries and supercapacitor, however, its low electrical conductivity and destruction of the structure during charge-discharge process have hampered the electrochemical performance of CuO. Inspired by enhancement of the properties of combining metal oxides with graphene through the reinforcement or modification of each other, improved electrochemical performances for CuO-graphene composites can be expected because these composites may not only reduce the stacking degree of graphene nanosheets but also prevent the volume expansion of CuO during the cycling process. Up to now, CuO-graphene composites with different morphologies have been synthesized, and extensively studied for application as electrode materials [22–26]. For example, Purushothaman et al. prepared nanostructured CuO-graphene composites via anchoring CuO nanoparticles on graphene nanosheets, which exhibited the improved electrochemical performances as electrode materials for supercapacitors [23]. Wang et al. reported the synthesis of graphene-supported shuttle- and urchin-like CuO nano-composites with a higher-than-theoretical capacity [24]. Jiang et al. described the synthesis of nanoleaf-on-sheet CuO/graphene composites with higher specific capacitance and cyclic durability than pristine CuO [25]. Although great progress has been made, the construction of these above-mentioned CuO-graphene composites are characterized by anchoring different CuO nanostructures on

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the surfaces of graphene nanosheets. In comparison, to the best of our knowledge, there are few reports devoted to the synthesis of hierarchical CuO nano/microstructures wrapped by graphene nanosheets as electrode materials. It is believed that the wrapping of graphene nanosheets contribute to provide a highly conductive network to improve the electrical conductivity of the whole composites electrode. Meanwhile, the agglomeration or reassembly of graphene nanosheets.can be prevented by hierarchical CuO within the graphene matrix. As a consequence, superior electrochemical performance for graphene-wrapped hierarchical CuO composites can be also expected.

Herein, we reported a facile one-step hydrothermal synthesis of graphene-wrapped dandelion-like CuO microspheres for use in supercapacitors. In addition, CuO-graphene composites with different microstructures were also prepared for comparison. As expected, the graphene-wrapped dandelion-like CuO exhibited higher capacitive performance compared with other CuO-graphene composites and pure CuO microspheres, which would hold great promise for application in high-performance supercapacitors.

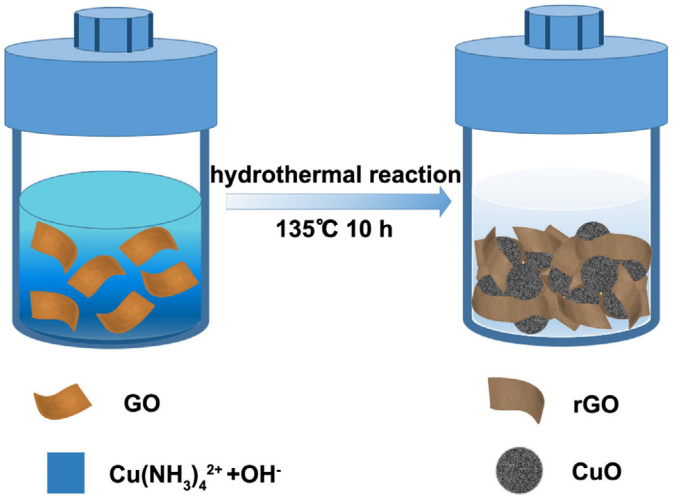
2. Experimental

All of the reagents were used without further purification. The GO suspension (2 mg/ml) was prepared from natural graphite by a modified Hummers method, as reported elsewhere [27]. To typically prepare dandelion-like copper oxide wrapped by reduced graphene oxide, firstly, 5.0 g of CuO powders and 7.5 g of $(NH_4)_2CO_3$ were added to 40 ml of deionized water at 40 °C. Then, 20 ml of $NH_3{\cdot}H_2O$ was introduced into the above mixture under stirring until CuO powders were dissolved into $[Cu(NH_3)_4]^{2+}$ solution (1.0 mol/l). Secondly, 3 ml of GO dispersion was added into 12 ml of deionized water to form a homogeneous dispersion by ultrasonication for 0.5 h. After that, 1 ml of $[Cu(NH_3)_4]^{2+}$ solution and 0.35 g of NaOH were sequentially added into the above GO dispersion. The solution mixture was stirred at 25 °C for 1 h and transferred into a 50-ml Teflon-lined stainless steel autoclave. The autoclave was then tightly sealed and heated at 135 °C for 10 h. After reaction, the autoclave was cooled to room temperature naturally. The products were collected by filtration, washed with deionized water and alcohol several times and dried by vacuum-drying. The obtained products were denoted as D-CuO-rGO. Moreover, by varying the volume of GO dispersion to be 1, 5 and 10 ml, CuO-rGO composites with different amounts of rGO are obtained using the same procedure, and labelled as CuO-rGO-1, CuO-rGO-5 and CuO-rGO-10 according to the corresponding volume of GO dispersion.

For comparison, CuO powders were prepared using the same procedure without GO.

2.1. Materials characterization

X-ray diffraction (XRD) patterns were recorded by a Bruker AXSD8 Advance X-ray diffractometer using Cu-Ka radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS, Kratos Amicus) was applied to determine the surface composition of the products. Raman spectroscopy was carried out by using a Bruker tensor27 micro Raman spectrometer. Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi SU8200 field emission instrument. High resolution transmission electron microscopy (HRTEM) images were recorded using a FEI Tecnai G20 electron microscope operating at 200 kV. Weight changes of the products were measured out on an EXSTAR TG/DTA 6300 using a heating rate of 5 °C min^{-1} in air (200 ml min^{-1}).



Scheme 1. Schematic illustration of the synthesis of D-CuO-rGO composite.

2.1.1. Electrochemical measurement

Typically, the obtained D-CuO-rGO powder, acetylene black and polyvinylidone fluoride (PVDF) binder (weight ratio of 80:10:10) were homogeneously mixed with a few drops of ethanol in an agate mortar until a homogeneous black slurry was obtained. After that, the resulting paste was immersed into a nickel foam (1 cm^2) under a pressure of 10 MPa. The used electrolyte was 2 M KOH aqueous solution. The capacitive performance of the samples was evaluated on a CHI 660E (Shanghai in China) electrochemical workstation. Cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy (EIS) measurements were measured with a three-electrode cell where Pt wire serves as the counter electrode and an Ag/AgCl electrode as the reference electrode. The specific capacitance of the electrode at different current densities can be calculated by using $C = It/\Delta Vm$, where C ($F\,g^{-1}$) is the specific capacitance, I is the discharge current, t is the discharge time, ΔV is the voltage interval, and m is the mass of the active material.

3. Results and discussion

The formation of D-CuO-rGO composites can be explained as follows (Scheme 1): the GO dispersion was firstly dispersed in $[Cu(NH_3)_4]^{2+}$ solution under ultrasonication. Then, the reduction of GO

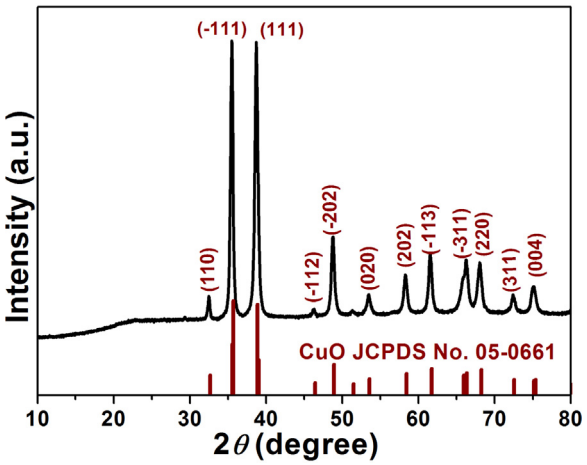


Fig. 1. XRD pattern of the obtained D-CuO-rGO product prepared by the hydrothermal method at 135 °Cfor 10 h.