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Cu superstructures hydrothermal-reduced by leaves and derived Cu-Co₃O₄ hybrids for flexible solid-state electrochemical energy

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Cu-Co₃O₄ hybrids and activated carbon were employed to fabricate flexible solid-state electrochemical energy storage device *via* facile processing. The resulting flexible devices showed a large specific capacitance of 530 mF cm⁻² with excellent mechanical flexibility, which offered a maximum volumetric energy density of 0.71 mW h cm⁻³, and delivered a maximum power density of 88.6 mW cm⁻³. What's more, the device showed an excellent cycling stability with only ~5.2% decay after 6000 cycles.

storage device

1. Introduction

Energy is regarded as the most important problem facing humanity nowadays. Electrochemical batteries, fuel cells and electrochemical capacitors (ECs) are the main modern electrochemical energy storage technologies.¹ According to charge storage mechanisms, supercapacitors (SCs) can be classified as 1) Pseudocapacitors based on the redox charge storage mechanism, and 2) Electric double layer capacitors (EDLCs) based on the electric double layer charge storage mechanism. SCs with a much higher power density are partly or completely replacing the common electrochemical batteries or fuel cells in many fields, thus attracting many countries' attention (especially the developed countries) on developing SCs. From the viewpoint of practical application, SCs have been widely used in large industrial equipment, hybrid electric vehicles, renewable energy power plants, and memory backup devices due to their qualities such as large life span, fast charge-discharge process, and rapid dynamics of charge propagation. Although SCs have many advantages than other electrochemical devices, they are also facing lower energy density in the current technical stage, which will seriously impede the practical application.²

In past years, electrochemical studies of cobalt based electrode materials were motivated since the chemical properties of cobalt is similar to those of nickel. In the 1990s, Conway and coworkers firstly reported the research based on transition metal oxides for electrochemical energy storage.³ Since then, studies about cobalt based materials, such as cobalt oxide,⁴ cobalt hydroxide,⁵ cobalt oxyhydroxides,⁶ cobalt carbonates,⁷ cobalt sulfide,⁸ cobalt-nickel oxide/sulfide,^{9,10} cobalt phosphate/ phosphite^{11,12} and cobalt compound related hetero-nanostructures/hybids,¹³⁻³⁴ have flourished to a point where these materials with tunable properties have been prepared for various energy storage applications. For example, Fan et al. mainly focused on the studies about the fabrication of hetero-nanostructures or hybrids employed as the electrochemical energy storage devices.¹⁷⁻¹⁹

In our previous work, we reported facile synthesis of Cu superstructures by hydrothermal-reduction of natural leaves and derived Cu-MnO₂ hybrids was used for high-performance of SCs.³⁵ In this work, Cu-Co₃O₄ hybrids were synthesized, and combined with activated carbon materials to fabricate flexible solid-state electrochemical energy storage (EES) device, exhibiting a large specific capacitance (530 mF cm⁻²). Interestingly, the device possessed a maximum volumetric energy density of 0.71 mW h cm⁻³ at a current density of 2.0 mA cm⁻² and delivered a maximum power density of 88.6 mW cm⁻³ at a current density of 9.0 mA cm⁻². Remarkably, the device showed excellent mechanical flexibility with a bending angle of 0° up to 180°. What's more, the device demonstrated little capacitance change after over 6000 charge/discharge cycles at a current density of 9.0 mA cm⁻², and showed an excellent cycling stability with only ~5.2% decay.

2. Experimental

2.1 Material preparations

Cu superstructures hydrothermal-reduced by leaves.³⁵ 0.20 g-CuSO₄ 5H₂O, 0.05 g-dry leaves (Leaves collected from magnolia grandiflora linn tree and washed with distilled water and ethanol, then dried in air), and 20 mL H₂O were mixed together. The above mixture was transferred into a Teflonlined stainless steel autoclave, and held at 200 °C for 24 h.

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After the reaction, the obtained samples were easily separated with the remaining organic compounds because of different densities. At last, the as-prepared Cu was carefully washed with distilled water and ethanol, and dried in air.

Cu-Co₃O₄ hybrids: 0.727 g Co(NO₃)₂·6H₂O, 0.70 g CO(NH₂)₂, and 50 mL H₂O were mixed together, and the obtained pink solution was transferred into Teflon-lined stainless steel autoclave lines with 0.1 g Cu superstructures dispersed into the above solution. The autoclave was heated at 95 °C for 8 h, and then cooled down to room temperature. The obtained sample was collected and rinsed with distilled water several times, followed by annealing at 350 °C in air gas for 3 h.

2.2 Electrochemical measurements

2.2.1 Fabrication of Cu superstructures-Co₃O₄ nanowire electrodes

The working electrode was made from the mixture of active materials, acetylene black, and polytetrafluoroethylene (PTFE) with a weight ratio of 80:15:5, which was coated on a piece of foamed nickel foam of about 1 cm², and pressed to be a thin foil at a pressure of 5.0 MPa. The weight of active sample is about 5 mg.

2.2.2 Electrochemical study on all the electrodes in a three electrode system

Electrochemical studies on Cu superstructures-Co₃O₄ nanowire electrodes were carried out on a CHI 660D electrochemical working stations (Shanghai Chenhua Instrument, Inc.). All electrochemical performances were carried out in a conventional three-electrode system equipped with platinum electrode and a Hg/HgO electrode as counter and reference Before the electrodes. respectively. electrochemical measurement, we purged out O_2 from the solution by the inert gas-Ar. The electrolyte was 3.0 M KOH solution. The capacitive properties of electrodes were determined by cyclic voltammetry (CV) and galvanostatic charge-discharge techniques.

2.2.3 Fabrication of the flexible solid-state EESs

The polyethylene terephthalate (PET) substrates were first covered with a layer of Pt film (\sim 3 × 5 nm thick) and then coated with the slurry containing the active materials. The Cu-Co₃O₄ hybrids and activated carbon materials were respectively prepared using a similar process to that in the three electrode system and were used as the working electrode after drying. The ratio of the mass of the positive electrode to that of the negative electrode is 1:4 (The specific capacitance of the Cu-Co $_3O_4$ hybrid electrode is 801 F g⁻¹ at 1.0 A g^{-1} , and that of the activated carbon is ~215 F g^{-1} at 1.0 A g^{-1} , and the ratio of the mass of the positive electrode to that of the negative electrode is 1:4,26 which makes the same capacitance of the electrode). The poly(vinylalcohol) (PVA)/KOH gel electrolyte was prepared as follows: the gel electrolyte (1.52 g PVA, 2.13 g KOH, and 15 mL H_2O) was prepared at 75 °C for 30 min and dropped onto the prepared sample to cover the active material after it was cooled naturally. Subsequently, two pieces of such electrodes were immersed in the PVA/KOH gel solution for 5-10 min to adsorb a layer of solid electrolyte. After the excess water was vaporized, two pieces of such electrodes containing electrolyte

were pressed together on a sheet out roller. In this way, the stacked all solid-state EESs were fabricated.

2.2.4 Electrochemical study of the flexible solid-state EESs

CV measurements were carried out between 0 and 1.50 V on a PARSTAT 2273 electrochemical work station. The flexible solidstate EESs were galvanostatically charged and discharged at the current density of 2.0-9.0 mA cm⁻² in the voltage range of 0-1.50 V on the Arbin BT2000 electrochemical instrument. All the electrochemical measurements were conducted at room temperature.

2.3 Characterizations

The morphology of the as-prepared samples was observed on a Hitachi S-4800 field-emission scanning electron microscope (FESEM) at an acceleration voltage of 10.0 kV. The phase analyses of the samples were performed by X-ray diffraction (XRD) on a Rigaku-Ultima III with Cu K_{α} radiation (λ = 1.5418 Å). Nitrogen adsorption-desorption measurements were performed on a Gemini VII 2390 Analyzer at 77 K using the volumetric method. The specific surface area was obtained from the N₂ adsorption-desorption isotherms and was calculated by the Brunauer-Emmett-Teller (BET) method. Transmission electron microscopy (TEM) images and high resolution TEM (HRTEM) images were captured on the JEM-2100 instrument microscopy at an acceleration voltage of 200 kV.

3. Results and discussion



Figure 1. XRD patterns of the as-prepared samples: a) Asprepared Cu superstructures, and b) The Cu-Co₃O₄ hybrids.

The crystallographic structure of the product was determined by X-ray powder diffraction (XRD). A typical XRD pattern of the product obtained from using sapless leaves from Magnolia grandiflora linn tree as the reducing agent is shown in **Figure 1**a. The strong diffraction peak is indexed to the cubic phase of Cu [Joint Committee for Powder Diffraction Studies File no. 04-0836]. The as-prepared Cu superstructures were reacted with cobalt nitrate hexahydrate under hydrothermal condition (Details seen the experimental section), and the hydrothermal product was calcinated at 350 ° in the air resulting in a black product. As shown in Figure 1b, no noticeable peak of Co₃O₄ phase is observed in the corresponding XRD pattern, indicating the small amount of Co₃O₄ coating.

The morphology of the as-prepared samples (Cu superstructures and Cu-Co₃O₄ hybrids) were characterized using FESEM and TEM. A panoramic view of the sample (**Figure**

2a) shows that these Cu superstructures are ten micrometers in size with smooth surfaces interconnected by many polygon nanoplates. Moreover, the thickness of the as-prepared Cu superstructures is about 500 nm (Figure 2b). As shown in the Figure 2c, the Cu superstructure- Co_3O_4 hybrid maintains the morphology of Cu superstructures, while possessing a rough surface due to the Co_3O_4 nanowire coating as shown in Figure 2d. Representative Co_3O_4 nanowires are clearly observed in



Figure 2. a, b) SEM images of as-prepared Cu superstructures; c-f) SEM images of the Cu-Co₃O₄ hybrids; g-i) EDS-mapping images of different elements; j, k) TEM images, Left of inset of k-the crystal lattice space, and Right of inset of k-corresponding SAED patterns.



Figure 3. As-prepared samples of a) N_2 adsorption-desorption isotherm curves, and b) The corresponding pore size distribution curves.

Figure 2e, manifesting the typical dimensions of 25-50 nm in length. The hybrid nature of the as-prepared Cu-Co₃O₄ superstructures can be further confirmed by elemental mapping images in Figure 2g-i, proving the generally uniform distribution of Cu, Co, and O elements within superstructures. The atomic percent of all the elements present in the sample from the EDX analysis is $Cu_{100}Co_{1.5}O_2$, in which the mass content of Co is only 1.36%. TEM was further used to characterize the structure of Co₃O₄ nanowires (Figure 2j), and the corresponding crystal lattice fringe spacing of 0.47 nm belongs to the (111) plane of the Co₃O₄ (JCPDS card: no. 43-1003) as shown in inset of Figure 2k. As demonstrated in large magnification (Figure 2k), the porous nanowire with a 2~4 nm pore size is composed of many Co₃O₄ nanocrystals. Consequently, the porous nature of the nanowire has provided sufficient surface/interface electroactive sites and facilitated the diffusion of ions/electrons, endowing the as-prepared Cu- Co_3O_4 hybrid with great potential in electrochemical capacitor.

The specific surface areas and porosity of the assynthesized Cu-Co₃O₄ hybrids were analysed by N₂ adsorptiondesorption measurements. As shown in **Figure 3**a, the N₂ adsorption-desorption isotherms can be ascribed to type IV, suggesting the presence of mesoporous in the Cu-Co₃O₄ hybrids, and the specific surface area of the Cu-Co₃O₄ hybrids is 45.7 m² g⁻¹, which is larger than that of the Cu superstructure (25.7 m² g⁻¹). The average pore size of the Cu-Co₃O₄ hybrids is 2~4 nm in Figure 3b, which is consistent with the HRTEM results in Figure 2k.

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Figure 4. a) Cyclic voltammetry experiments within the 0.0-0.48 V range at a scan rate of 5-50 mV s⁻¹ were performed on the Cu-Co₃O₄ hybrid electrodes in a 3.0 M KOH solution at room temperature; b) The galvanostatic charge-discharge curves of Cu-Co₃O₄ hybrid electrode at current densities of 0.5-5.0 A g⁻¹ in a 3.0 M KOH solution; c) Specific capacitances of Cu-Co₃O₄ hybrid electrodes derived from the discharging curves at the current density of 0.5-5.0 A g⁻¹ in a 3.0 M KOH solution; d) Cycling performance of the Cu-Co₃O₄ hybrid electrode at 3.0 A g⁻¹ for 6000 cycles.

The electrochemical properties of the as-prepared Cu- Co_3O_4 hybrids were investigated using CV and galvanostatic charge-discharge measurements. Figure 4a shows the CV curves of the electrode at different scan rates from 5.0 to 50 mV s⁻¹ within the potential window of 0.0 to 0.48 V in 3.0 M KOH solution. The shape of these CV curves are different from the electric double-layer capacitance. Each CV curve consists of a pair of large redox peaks, owing to the reaction of Co²⁺ to Co^{3+} occurring at the surface of the Cu-Co₃O₄ hybrid electrode. Interestingly, the redox current increases with the scan rate. Furthermore, it was found that the oxidation and reduction peaks shift toward higher and lower potential with a large potential separation, which was mainly attributed to the resistance of the electrode. Figure 3b presents the chargedischarge curves of the Cu-Co₃O₄ hybrid electrode at different current densities of 0.5 to 5.0 A g⁻¹. The shapes of the chargedischarge curves mainly is not the characteristics of a doublelayer capacitance in Figure 4b, which is in agreement with the CV tests. The specific capacitance of the electrodes was calculated from the discharge curves according to the following equation [Eq. (1)]:

$\mathsf{C} = (I \Delta t) / (m \Delta V) \quad (1)$

in which I, Δt , m, and ΔV are the discharge current [A], the time for discharge duration [s], the weight of the active materials [g] in the electrodes, and the voltage interval of the

discharge [V], respectively. A specific capacitance of 908 F g⁻¹ was obtained at a current density of 0.5 A g⁻¹. When the current density increased to 5.0 A g⁻¹, the specific capacitance still remained 467 F g⁻¹ as shown in Figure 4c. Cycling performance of the Cu-Co₃O₄ hybrid electrode at 3.0 A g⁻¹ for 6000 cycles is shown in Figure 4d, and it is seen that the specific capacitance is 583 F g⁻¹ even after 6000 cycles. The stable specific capacitance can be attributed to the large accessible surface area and porous structure, providing effective diffusion channels for the electrolyte ions and thus improving the diffusion of ions and the electrolyte. Furthermore, we have also prepared Co₃O₄ particles for comparison (Detailed information seen in Figure S1 and Figure S2). It is seen that the morphology of as-prepared Co₃O₄ particle is formless particles with sizes of 200-1500 nm in Figure S1. The specific capacitance of the as-prepared Co₃O₄ particle electrode is only 290 F g^{-1} at 0.5 A g^{-1} in Figure S2c. After 6000 cycles, the specific capacitance of as-prepared Co_3O_4 particle electrode is only 35 F g⁻¹ in Figure S2d. Electrochemical impedance spectra of the as-prepared Cu- Co_3O_4 hybrid, and Co_3O_4 particle electrode under room temperature is shown in Figure S3. Due to the good conductivity of the inner Cu superstructure, the Cu-Co₃O₄ hybrid electrode shows better conductivity than that of pure Co_3O_4 particle electrode, which can improve the electrochemical capacitor performance.

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Figure 5. a) CV curves; (b) Galvanostatic charge-discharge curves, and (c) Specific capacitances of the flexible solid-state EES (Cu- Co_3O_4 hybrids // activated carbons) with the increase of the potential.

To develop flexible power sources, flexible solid-state EESs (Cu-Co₃O₄ hybrids // activated carbons) were then fabricated based on the Cu-Co₃O₄ hybrids and activated carbon as active electrode materials with the aid of our previous method (see details in Experimental section). Figure 5a shows a series of CV measurements of the Cu-Co₃O₄ hybrids // activated carbons EES with different cell voltages varying from 0.0-1.0 V to 0.0-1.5 V. At 1.0 V, the presence of redox peaks (in the region between 0.0 and 1.0 V) indicates that the electrochemical energy storage properties of the cell originate from the positive electrode (the Cu-Co₃O₄ hybrids). The surrounding area from the corresponding CV curve is largest when the operating potential is increased to 1.5 V, denoting the potential at which most Faradic reactions will occur. More importantly, the charge-discharge curves of the flexible solidstate EES at a current density of 3.0 mA cm⁻² are nearly symmetric at an operating potential of 1.5 V (Figure 5b). This ideal capacitive characteristics with a rapid I-U response are probably attributed to the small equivalent series resistance of the device.³⁶ Figure 5c shows the specific capacitances of the flexible solid-state EES device calculated based on the discharge curves of Figure 5b. The specific capacitance increases from 35 to 484 mF cm⁻² with increasing the operating

potential from 1.0 to 1.5 V. According to the equation $E=CU^2/2$, the amount of the stored energy and delivered power of the flexible solid-state EES device (the potential window is 0-1.5 V) can be enhanced by at least 2.25-fold compared with those with the potential window of 0-1.0 V. As a result of the increased Faradaic reactions and the large voltage window, considerably improved energy density and powder density can be obtained.

CV curves of the flexible solid-state EES device (5, 10, and 50 mV s⁻¹) were also measured as shown in **Figure 6**a (the potential window is 0.0-1.5 V). According to the shape of the CV curves, a good electrochemical energy storage capacity is observed at all scan rates. Interestingly, the shape of the CV curve can still be well maintained even at the scan rate of 50 mV s⁻¹, indicating a good rate capability of the flexible solid-state EES device. Galvanostatic charge-discharge curves of the flexible solid-state EES device at different current densities are shown in Figure 6b, and the specific capacitance reached 530 mF cm⁻² at a current density of 2.0 mA cm⁻². Derived from the data in Figure 6b, other specific capacitances were plotted in Figure 6c, in which the flexible solid-state EES device exhibited good rate capability (62.2% retention at even 9.0 mA cm⁻²).

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Figure 6. (a) CV curves with scan rates between 5 and 50 mV s⁻¹; (b) Galvanostatic charge-discharge curves at current densities ranging from 2.0 to 9.0 mA cm⁻² of the device in the potential window of 0.0-1.5 V; (c) The specific capacitance was calculated based on the data in b, and (d) Cycling performance of the device at 9.0 mA cm⁻² for 6000 cycles.



Figure 7. Cyclic voltammetry within a 0-1.5 V range at a scan rate 30 mV s⁻¹ with four bended modes (Inset).

Interestingly, the stable cycling performance of the flexible solid-state EES device was also maintained at each current density, which further confirmed its good rate stability. 6000 charge-discharge cycling tests were carried out to examine the long-term cycle ability of the flexible solid-state EES device (Figure 6d). During the cycling process at a current density of 9.0 mA cm⁻², only a small decay of the capacitance was observed. In addition, the decay could be ascribed to the consumption of the gel electrolyte, originating from an irreversible reaction from active materials and electrolytes.³⁷ After 6000 cycles, the specific capacitance of the flexible solidstate EES device was still approximately 94.8% of its initial capacitance (330 mF cm⁻²), which strongly verified the good cycling performance of the flexible solid-state EES device. The morphology of materials affects the electrochemical activity. SEM images of the Cu-Co₃O₄ hybrid from the EES device recorded at 9.0 mA cm⁻² for 6000 cycles are shown in Figure S4. The outline of the superstructure was observed, however the Co_3O_4 nanorods disappeared and thus caused decay of the capacitance.

In order to test the flexibility of our solid-state EES, electrochemical tests were conducted with different bending

angles (**Figure 7**) at a scan rate of 30 mV s⁻¹. As shown in Figure 7, the CV curves with different bending angles only differed slightly. It is worthwhile to mention that the specific capacitance of the device was maintained throughout the bending process.



Figure 8. Ragone plots of the as-prepared device. The values reported for other previous devices are added for comparison.³⁸⁻⁴⁹

The energy and power densities of the flexible solid-state EES device measured at different scan rates are shown in Figure 8. A maximum volumetric energy density of 0.71 mW h cm⁻³ was achieved under an operating potential of 1.5 V. Additionally, the maximum power density of the flexible solidstate EES was 86.6 mW cm⁻³ at 9.0 mA cm⁻². These values of the as-assembled flexible solid-state EES device are comparable to the state-of-the-art devices reported recently as shown in Figure 8.³⁸⁻⁴⁸ The maximum energy density of our flexible solid-state $\ensuremath{\mathsf{EES}}$ device is larger than that of most devices in Figure 8, but is smaller than that of $Ni(OH)_2//FDU15$ (2.16 mW h cm⁻³).⁴⁵ Additionally, the flexible solid-state EES device exhibited much higher maximum power density than the recently reported devices: ZnO@MnO2,44 ZnO@MnO2// Graphene,⁴⁵ MnO₂//Fe₂O₃,⁴⁶ NiO//C,⁴⁷ and CoNiSiO_x//GO,⁴⁹ while possessing lower performance than other devices in Figure 8. Bearing all these results in mind, we can draw the conclusion that the Cu-Co₃O₄ hybrid is very promising as a high energy-density anode material for flexible solid state EES devices. It is noted that the improved performance can be attributed to the effect of high ion permeability of the porous structure and the abundant electron pathways within the inner Cu superstructures.

Conclusions

In summary, the Cu-Co₃O₄ hybrids were successfully prepared from Cu superstructures hydrothermally reduced by leaves and Co(NO₃)₂. Flexible solid-state EES devices based on the Cu-Co₃O₄ hybrid//activated carbon have demonstrated great performance, representing the first report of this material being applied for SCs. The flexible solid-state device showed little capacitance change after over 6000 charge/discharge cycles at a current density of 9.0 mA cm⁻², and exhibited an excellent cycling stability with only ~5.2% decay. Notably, the device shows excellent mechanical flexibility for bending angles between 0° and 180°. Because of the simplicity of synthesis and device fabrication processes, and the eco-friendly nature of the materials, this flexible solid-state EES hold great promise for being integrated into various flexible electronic systems such as power-on-chip systems, roll-up display panels and solar energy harvesters.

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The Cu-Co₃O₄ hybrid//activated carbon EES device is successfully assembled, and shows great performance, which represents the first report of this material being applied for supercapacitors.