

Microwave-assisted synthesis of CuO/MnO₂ nanocomposites for supercapacitor application

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Copper oxide/manganese dioxide (CuO/MnO₂) nanocomposites were prepared by a facile microwave-assisted synthesis method in an ordinary household microwave oven and used for electrochemical supercapacitor. The nanocomposites were characterised by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Electrochemical results demonstrate that CuO/MnO₂ nanocomposites have better capacitance performance than pure CuO material. The CuO/MnO₂ nanocomposites have a high specific capacitance of 499.0 F/g at a current density of 0.5 A/g in 6 M KOH electrolyte. In addition, an asymmetric supercapacitor with activated carbon as a negative electrode and CuO/MnO₂ nanocomposite as a positive electrode was also successfully prepared. This asymmetric device exhibits a high energy density of 32.07 Wh/kg at a power density of 375.02 W/kg and fairly good cycling stability.

1. Introduction: As novel energy storage devices, supercapacitors have many advantages, such as high power density, fast charge-discharge rate, and good cycle stability [1–3]. However, compared with traditional capacitors or lithium-ion batteries, supercapacitors have lower energy densities. According to the formula $E = 0.5CV^2$ [4], energy density can be improved through the following strategies: enhancing specific capacitance and widening operating voltage. Therefore, an important factor for developing supercapacitors is a suitable electrode material with high specific capacitance. Copper oxide (CuO) is a promising material for realising supercapacitors with high energy densities because of its high theoretical specific capacitance (~1800 F/g) [5]. However, the charge transfer of a CuO electrode is seriously hindered by its intrinsic low conductivity, which often results in a low specific capacitance. This limitation can be addressed by combining CuO with other transition metal materials with good transfer abilities. This method enhances the capacitive performance. CuO. Manganese dioxide (MnO₂) is good material in combination with CuO because MnO₂ enables a fast redox process and the two components have synergistic effects. CuO/MnO₂ nanocomposites have a faster kinetic process and better electron conductivity than pure CuO and can afford a final assembly device high specific capacitance. For example, Zhang *et al.* [6] found that hollow dandelion-like CuO/MnO₂ nanocomposites had a specific capacitance of 240 F/g. Zhang *et al.* [7] found that hierarchical CuO/MnO₂ nanocomposites showed a specific capacitance of 228 F/g; Racik *et al.* [8] found that the CuO/MnO₂ nanocomposites exhibited a specific capacitance of 279.12 F/g.

In addition to electrode materials, the preparation method for developing supercapacitors is another important factor. Thus far, metal oxide electrode materials have been mainly prepared through hydrothermal [9–11], chemical deposition [12], sol-gel [13], and physical vapour deposition methods [14–18]. However, these methods have some disadvantages. For example, the hydrothermal method has a long reaction time and high energy consumption and is unsuitable for monitoring the growth process of oxide crystals [9–11]. The chemical deposition method often results in the production of impurities in oxide nanoparticles [12]. The sol-gel method requires expensive and organometallic solutions, which are also harmful to the environment [13]. The physical vapour deposition method requires expensive equipment and

harsh experimental conditions [14–18]. Therefore, a green, rapid, cheap, and effective method for preparing metal oxide electrode materials is necessary. Microwave-assisted synthesis methods for preparing metal oxide materials are efficient and environment-friendly [19, 20]. Microwave-assisted synthesis methods have shorter fabrication times, lower energy consumption, lower costs, and higher product purity than traditional wet chemical methods, such as the hydrothermal and sol-gel methods [19, 20]. In view of these advantages, we are going to use a simple and efficient microwave-assisted method to prepare CuO/MnO₂ nanocomposites and investigate their capacitive ability.

2. Experiment: Copper sulphate pentahydrate (CuSO₄·5H₂O), sodium hydroxide (NaOH), potassium permanganate (KMnO₄), and manganese acetate tetrahydrate [Mn(CH₃COO)₂·4H₂O] were obtained from Sinopharm Chemical Reagent, China. Potassium hydroxide (KOH) and activated carbon (AC) were obtained from Aladdin Industrial Corporation, China. All the chemicals and reagents were used as received without any further purification. All the solutions were prepared using deionised water.

The synthesis procedure of CuO was as follows: 20 ml of 0.2 M CuSO₄·5H₂O solution and 20 ml of 0.8 M NaOH solution were simultaneously added to a 130 ml crucible, then the mixing solution was immediately placed in a microwave oven (Panasonic NN-GF352MXPE). After microwave irradiation (300 W) for 5 min, the obtained product was filtered, then successively washed with deionised water, acetone, and ethanol, and finally dried at 60°C.

The synthesis procedure of CuO/MnO₂ nanocomposite was similar to that of CuO. In brief, 20 ml of 0.2 M Mn(Ac)₂·4H₂O solution, 20 ml of 0.2 M KMnO₄ solution, and 0.1 g of CuO obtained from the above process were simultaneously added to a 130 ml crucible. Then, the mixture was immediately placed in the microwave oven. After microwave irradiation (300 W, 3 min), the solid product was successively filtered, washed, and dried at 60°C.

Scanning electron microscopy (SEM) was performed with a JSM-7500F (JEOL) instrument. Transmission electron microscopy (TEM) was carried out with a Tecnai-G20 (FEI) instrument. The elemental valence state was determined with an Escalab 250 Xi X-ray photoelectron spectrometer (Thermo Fisher). X-ray

diffraction (XRD) was conducted with a Bruker D8 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

The active material, acetylene black, and polytetrafluoroethylene with the mass ratio of 75:10:15 were added to ethanol. The obtained homogeneous slurry was cast onto an acid-pretreated Ni foam ($1.2 \text{ cm} \times 1.0 \text{ cm}$). After drying at 70°C overnight, the loaded Ni foam was pressed under a pressure of 10 MPa and then used as a working electrode. All electrochemical measurements were performed with an MM-510 electrochemical workstation (Materials Italia), and 6 M KOH solution was used as an electrolyte. In a three-electrode electrochemical cell, Pt foil is the counter electrode, and a saturated calomel electrode is the reference electrode. An asymmetric supercapacitor (ASC) was assembled using a CuO/MnO₂ nanocomposite as a positive electrode, AC as a negative electrode, polypropylene as a separating membrane, and a 1 M KOH solution as the electrolyte. This ASC was labelled as CuO/MnO₂//AC ASC.

The capacitive behaviour was investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements. The specific capacitance (C_{sp} , F/g) was calculated with the following equation [21]:

$$C_{\text{sp}} = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

where m , ΔV , I , and Δt are the mass of active materials (g), potential window (V), discharge current (A), and discharge time (s), respectively.

The energy density (E) and power density (P) of the ASC device were calculated using the following equations [21]:

$$E = \frac{1}{2 \times 3.6} C_{\text{sp}} (\Delta V)^2 \quad (2)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (3)$$

3. Results and discussions: Fig. 1 shows the XRD patterns of CuO and CuO/MnO₂ nanocomposites. Apart from the diffraction peaks of CuO (JCPDS Card No. 45-0937) [10], the diffraction peaks of MnO₂ can be clearly observed in the pattern of the CuO/MnO₂ nanocomposite. Specifically, the peaks at 22.4° , 32.2° , 37.1° , 48.9° , and 65.5° can be assigned to the (200), (310), (211), (411), and (002) crystal planes of MnO₂ (JCPDS Card No. 44-0141) [22], respectively. No impurities, such as Cu(OH)₂ or Cu₂O, appear in both XRD patterns.

Fig. 2a shows the core level X-ray photoelectron spectroscopy (XPS) spectra of the Cu 2p state. The main Cu 2p_{3/2} and Cu 2p_{1/2} peaks, together with their satellite peaks, can be observed clearly, indicating the valence state of +2 [8]. Although,

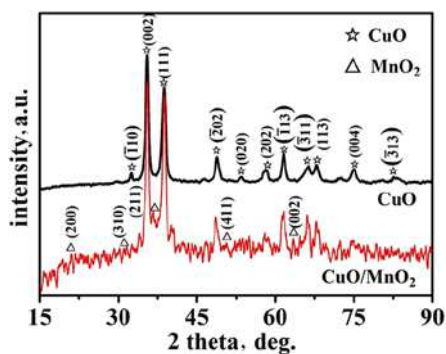


Fig. 1 XRD patterns of CuO and CuO/MnO₂ nanocomposite

these two main peaks show slight blue shifts in the spectra of the nanocomposite, the differences of the peak positions remain the same, indicating that the presence of Mn element has no obvious effect on the valence state of Cu. In Fig. 2b, the peaks of Mn 2p_{3/2} (642.2 eV) and Mn 2p_{1/2} (654.0 eV) can be clearly observed. The difference in peak position is 11.8 eV [23, 24], indicating a valence state of +4.

The SEM and TEM pictures are shown in Fig. 3. Figs. 3a and b show that CuO exhibits nanosheet-like structures, which facilitate electron transfer during the charge/discharge process [25, 26]. The lattice distance is 0.23 nm, corresponding to the (002) plane of tenorite-type CuO [10]. The addition of MnO₂ has no obvious effect on the structure of CuO (Figs. 3c and d).

Fig. 4 shows the Nyquist plots of CuO and CuO/MnO₂ nanocomposite. Both plots have two parts: a semicircle in the high-frequency region and a line in the low-frequency region. The semicircle and line indicate a charge transfer-controlled process and mass transfer-controlled process, respectively, on the electrode–electrolyte interface [7, 10]. The CuO/MnO₂ nanocomposite has a smaller semicircle than CuO, indicating that the nanocomposite has a smaller charge transfer resistance than CuO. The reason is the presence of a MnO₂ component, which can enhance the charge transfer ability of the whole nanocomposite. Nevertheless, a steep line in the low-frequency region suggests that electrolyte diffusion is fast within the two electrodes.

Fig. 5a shows the CV curves of the CuO and CuO/MnO₂ electrodes at 10 mV/s. Electrochemical capacitance increases with the size

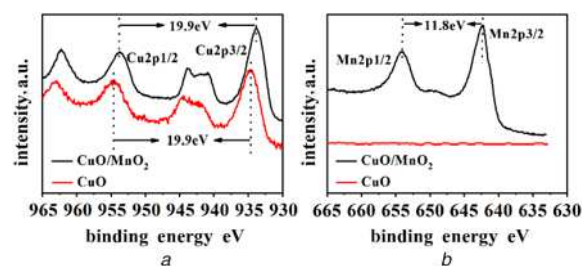


Fig. 2 Core-level XPS spectra of
a Cu 2p state
b Mn 2p state

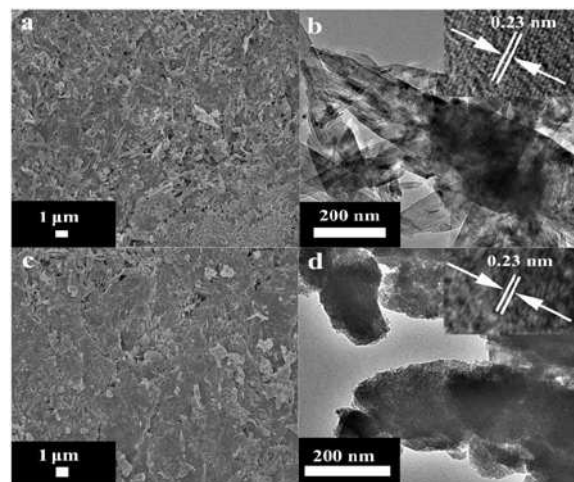


Fig. 3 SEM and TEM images of samples
a SEM of CuO
b TEM of CuO
c SEM of CuO/MnO₂ nanocomposite
d TEM of CuO/MnO₂ nanocomposite

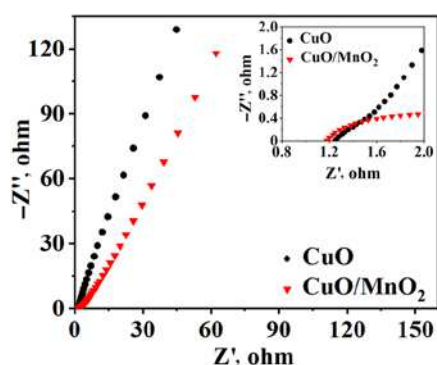


Fig. 4 Nyquist impedance plots of CuO and CuO/MnO₂ nanocomposite. Inset shows the Nyquist impedance plots at high frequency region

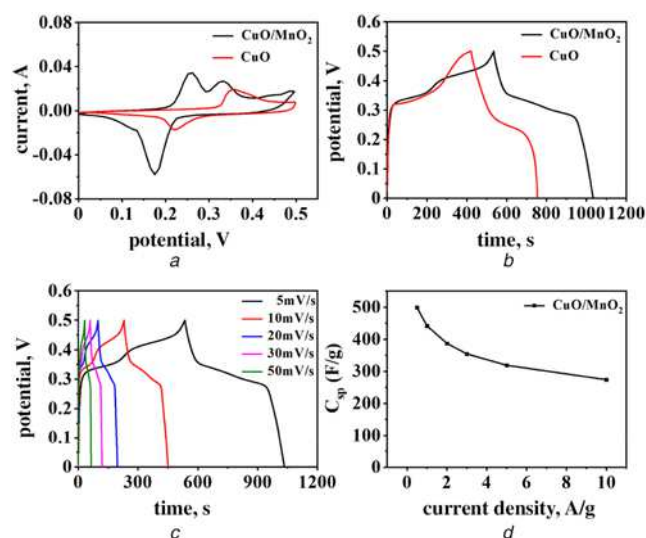


Fig. 5 Electrochemical measurements of CuO and CuO/MnO₂ electrodes
a CV curves at 10 mV/s
b GCD curves at 0.5 A/g
c GCD curves of CuO/MnO₂ electrode at various current densities
d The rate capability of CuO/MnO₂ electrode

of the enclosed area. Fig. 5b shows the GCD curves of the two electrodes at 0.5 A/g. The discharge time of CuO/MnO₂ electrodes is obviously longer than CuO. The calculated C_{sp} values of CuO/MnO₂ and CuO are 499.0 and 333.2 F/g at 0.5 A/g, respectively. The enhancement of C_{sp} is related to the increase in the number of Faraday active sites after the introduction of MnO₂ [27]. Fig. 5c shows the GCD curves of the CuO/MnO₂ electrode at various current densities in a voltage range of 0–0.5 V. The shape of the curve is a typical pseudocapacitor curve [28]. With increasing current density, charging and discharging times decrease because of electrode polarisation. Fig. 5d is the rate capability of the CuO/MnO₂ electrode at different current densities. C_{sp} can retain 54.9% of its initial value (from 499.0 to 274.0 F/g) as the current density increases from 0.5 to 10.0 A/g.

Fig. 6a shows the CV curves of the CuO/MnO₂ electrode at various scan rates from 5 to 50 mV/s in a voltage range of 0–0.5 V. The enclosed area of the CV increases with scan rate. The reactions in this process are expressed as follows [29, 30]:

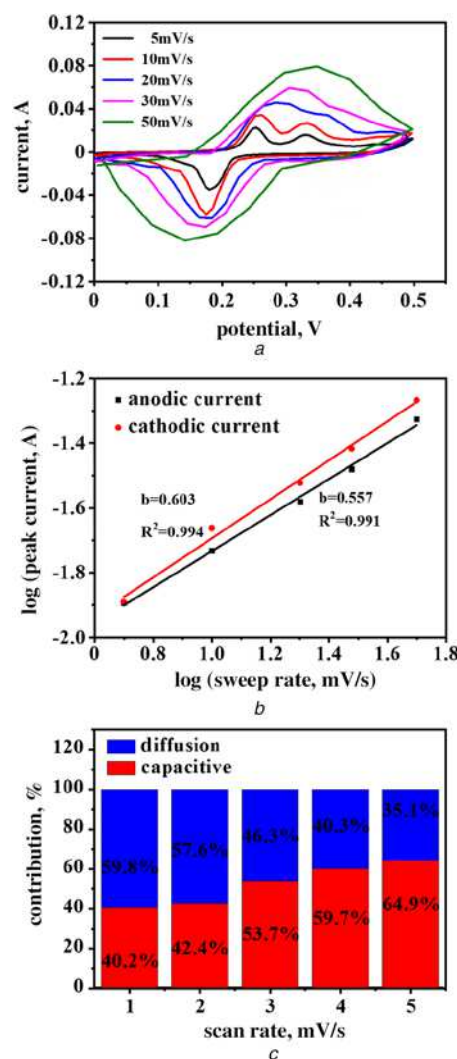
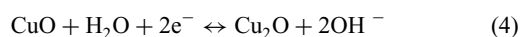


Fig. 6 Scan rate-dependent characteristic of CuO/MnO₂ electrode
a CV curves versus scan rates
b Logarithmic relationship between the peak current and scan rates
c The contribution proportions at various scan rates

The relationship between the peak current (i , A) and scan rates (v , mV/s) can be expressed:

$$\log(i) = b \log(v) + \log(a) \quad (6)$$

where a is a constant. The b -values of cathodic and anodic peaks can be calculated according to (6). When $b=0.5$, the reaction process is mainly controlled by a diffusion-controlled redox reaction. When $b=1$, the reaction process is mostly controlled by a surface-controlled capacitive reaction [31]. The b -values of cathodic and anodic peaks are 0.603 and 0.557, respectively, indicating the diffusion-dominated reactions of the CuO/MnO₂ electrode (Fig. 6b).

The capacitive-controlled (k_1v) and diffusion-controlled ($k_2v^{1/2}$) reaction processes for the electrode are expressed as follows [31]:

$$i(v) = k_1v + k_2v^{1/2} \quad (7)$$

$$i(v)/v^{1/2} = k_1/v^{1/2} + k_2 \quad (8)$$

where k_1 and k_2 are constants. The k_1 (slope) and k_2 (intercept) can be obtained from the linear relationship between $i(v)/v^{1/2}$ and $v^{1/2}$ at different scan rates [31]. Fig. 6c shows the capacitive-controlled and

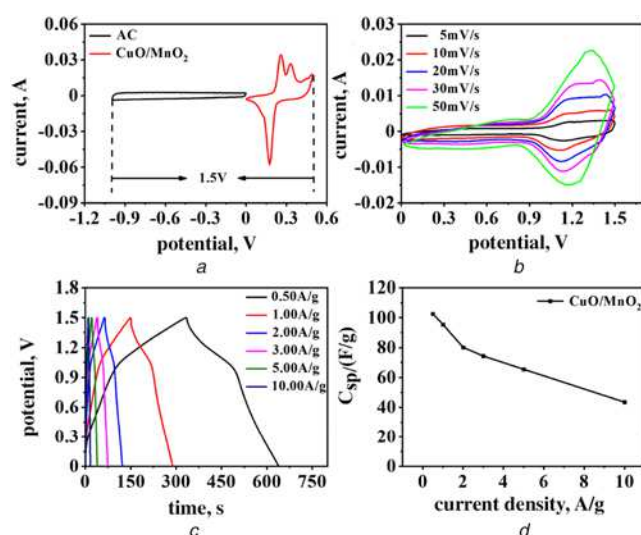


Fig. 7 Electrochemical performance of electrodes and ASC device
 a CV curves of AC and CuO/MnO₂ at 10 mV/s
 b CV curves of CuO/MnO₂//AC ASC at various scan rates
 c GCD curves of CuO/MnO₂//AC ASC at various current densities
 d The rate capability of and CuO/MnO₂//AC ASC

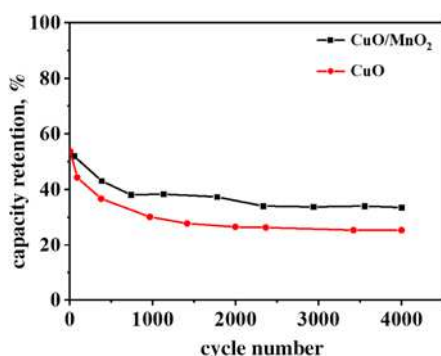


Fig. 8 Cyclic stability of CuO/MnO₂//AC ASC at 3 A/g

diffusion-controlled contributions for CuO/MnO₂ electrode at different scan rates. As the scan rate increasing, the redox reaction time decreases. Most of the ions have insufficient time to enter the inside and only react near the surface and thereby, the capacitance contribution gradually increases.

Fig. 7 shows the capacitive behaviour of an asymmetric capacitor. The voltage windows of CuO/MnO₂ and AC are 0–0.5 V and –1.0–0 V, respectively, indicating that the working potential of CuO/MnO₂//AC ASC may reach up to 1.5 V (Fig. 7a). Fig. 7b shows the CVs of the CuO/MnO₂//AC ASC at different scan rates. All CV curves have the Faradaic and non-Faradaic contributions, which confirms the asymmetric capacitive behaviour of ASC. As the scan rate increases, the anodic and cathodic peaks move to more positive and negative potentials, respectively. This is consistent with CVs investigated in the three-electrode system (Fig. 6a). Besides, the quasi-rectangular shape of CV can still remain at high scan rate, indicating an outstanding charge/discharge performance.

Fig. 7c displays the GCD curves of CuO/MnO₂//AC ASC at different current densities. The GCD curves are almost symmetrical, suggesting that the electrochemical reactions are fairly reversible. The C_{sp} of the CuO/MnO₂//AC ASC are 102.61, 95.49, 80.17, 74.34, 65.47, and 43.47 F/g at 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0 A/g, respectively. The C_{sp} of CuO/MnO₂//AC ASC device retains 42.36% of its initial value (from 102.61 to 43.47 F/g) when current density increases from 0.5 to 10 A/g (Fig. 7d).

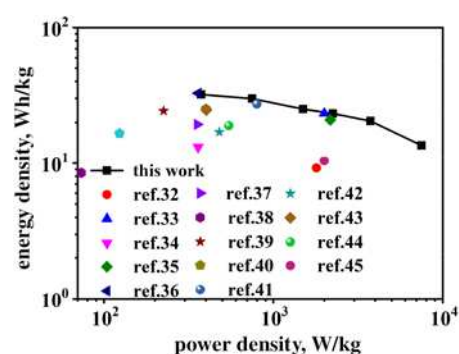


Fig. 9 Ragone plot related to energy and power densities of CuO/MnO₂//AC ASC

The cycling stability of ASC devices is shown in Fig. 8. The capacitance retention of CuO/MnO₂//AC ASC is ~65% of its initial value after 4000 cycles, indicating the fairly good stability of the CuO/MnO₂//AC ASC. The Ragone plot of the CuO/MnO₂//AC ASC device is presented in Fig. 9. The CuO/MnO₂//AC ASC device demonstrates a high energy density of 32.07 Wh/kg at a power density of 375.07 W/kg and maintains 13.58 Wh/kg at 7500.53 W/kg, which are better than the values in some previous reports [32–45].

4. Conclusions: CuO/MnO₂ nanocomposites can be successfully prepared through a microwave-assisted preparation method with a normal household microwave oven. The CuO/MnO₂ nanocomposite electrode prepared in this work exhibits better performance than the CuO/MnO₂ nanocomposite electrodes prepared through conventional wet chemical methods, such as the hydrothermal method or sol–gel methods. Specifically, the CuO/MnO₂ nanocomposite has a high C_{sp} of 499.0 F/g at 0.5 A/g. The assembled ASC device with CuO/MnO₂ nanocomposites as a positive electrode and AC as a negative electrode displays a high C_{sp} of 102.61 F/g at 0.5 A/g, an energy density of 32.07 Wh/kg at a power density of 375.07 W/kg, and a fairly good cyclic stability. The high C_{sp} suggests that CuO/MnO₂ nanocomposites are promising materials for energy storage application. Moreover, in view of the advantages of the microwave-assisted preparation method, future work should focus on optimising fabrication conditions and the synthesis of other metal oxide electrodes.

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6 References

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