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Incorporation of MWCNTs into leaf-like CuO nanoplates for superior reversible Li-ion storage

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ABSTRACT

CuO/MWCNT nanocomposite is prepared by a simple precipitation method. The MWCNTs are incorporated into the leaf-like CuO nanoplates and build up a network to connect the CuO nanoleaves. The as-prepared CuO/MWCNT exhibits superior reversible Li-ion storage, the capacity maintains 627 mAh g^{-1} at 60 mA g^{-1} even after 50 cycles. The improved capability is ascribed to the MWCNT network in the composite, which improves the electrical contact of CuO/CuO and CuO/current collector, facilitates the charge transfer on CuO/electrolyte interfaces, and compensates the volume change of CuO during cycling.

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1. Introduction

3d transition metal oxides (TMO) are considered as the promising anode materials for Li-ion batteries due to their high theoretic capacity, excellent reversibility of electrode reaction and low cost [1]. Most of them are typical semiconductors with poor electric conductivity, which makes cycling performance disappointing. In the past few years, surface coating on TMO with conductive additives [2] has been widely studied to improve their conductivity. These modifications generally involve multiple steps and seem a bit complex. Another effective way to improve cycling performance is synthesizing nanostructured materials for the short Li^+ diffusion route in nanostructures [3]. However, nanoparticles might pulverize seriously during cycling, which will negate the benefits of the decreasing particle size [4]. Therefore, it becomes urgent to develop a new approach to enhance the electric conductivity of TMO and decrease the pulverization induced by volume change as well.

MWCNT is well-known for its excellent electric conductivity and mechanical property, so it seems to be a promising additive to improve the electric conductivity and restrain the large volume change of TMO. Recently, CNT-modified CuO microspheres are synthesized by a refluxing method and the electrochemical properties are investigated [5]. However, the preparation is a little complex and the improvement of electrochemical performances is not obvious compared with previously reported CuO nanostructures [6,7]. In the present work, we firstly report a more facile precipitation synthesis of CuO/MWCNT composite with a network structure, where CuO nanoplates act as "leaves" and MWCNTs act as both "nerves" and "branches". This interesting network structure exhibits significantly improved electrochemical performances over recently reported CNT-modified CuO. The synthesis mechanism for the CuO/MWCNT nanocomposite is discussed and the effects of network structure on the enhanced electrochemical properties are investigated.

2. Experimental

0.15 M cetyltrimethylammonium bromide (CTAB) was dissolved in 100 ml deionized water with magnetic stirring at 60 °C. 0.01 g MWCNTs (prepared according to Ref. [8]) were ultrasonically dispersed in 5 ml dimethyl formamide (DMF), then the MWCNTs/DMF solution and 0.20 g $CuSO_4 \cdot 5H_2O$ were added to the CTAB solution, respectively. After 20 min, 20 ml NaOH solution (0.2 M) was dropped and subsequently stirred for 10 min. Finally, the precipitation was separated by centrifugation and dried at 60 °C. For comparison, pure CuO was prepared by the same procedures without introducing MWCNTs.

The structure, composition and morphology of the as-prepared particles were characterized by X-ray diffraction (XRD, Philips PC-APD with Cu Kα radiation), elemental analyzer (Flash EA 1112), field emission scanning electron microscopy (FESEM, Hitachi S-4800) and high resolution transmission electron microscopy (HRTEM, CM200UT and JEM 2010), respectively.

Test cells were assembled according to Ref. [9]. The galvanostatic charge–discharge tests were conducted on LAND battery-test system at different current densities from 3.0 to 0.02 V at room temperature (25 ± 1 °C). Cyclic voltammogram (CV) was performed on CHI660C

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electrochemical workstation at a scan rate of 0.1 mV s^{-1} from 0 to 3.0 V.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-prepared CuO and CuO/MWCNT. All diffraction peaks in Fig. 1a are indexed to monoclinic CuO (C2/c, JCPDS No. 48-1548). The broad peaks indicate the formation of CuO nanostructures. In Fig. 1b, in addition to the peaks of CuO, the wide peak at 25° is indexed to (002) plane of hexagonal graphite structure, which suggests that MWCNTs are successfully introduced in the composite. The content of MWCNTs in the composite is 11.1 wt.% characterized by elemental analysis.

The morphologies of as-prepared products are shown in Fig. 2. The CuO displays leaf-like structure with 400 nm in length and 100–200 nm in width (Fig. 2a, c and d). Each CuO leaf is self-assembled by several parallel thin pieces with a width of 10 nm. The selected area electron diffraction pattern (inset of Fig. 2c) displays regular diffraction spots, which indicates a thin piece is a single crystal. Several parallel single-crystalline pieces compose a polycrystalline CuO nanoleaf. Moreover, many tiny pores appear in the nanoleaves (Fig. 2d), which means there are a large number of crystal defects in the leaf-like CuO. The SEM and TEM images of CuO/MWCNT (Fig. 2b and e) show that incorporation of MWCNTs doesn't change the shape and size of CuO nanoleaves. And the MWCNTs are dispersed well in the composite, acting as branches to connect CuO nanoleaves. From the HRTEM image (Fig. 2f), the coexistence of MWCNTs and CuO is clearly seen. The 2.53 Å spacing and 2.32 Å spacing correspond to the (11-1) and (111) planes of monoclinic CuO. MWCNTs lie across CuO, which act as nervures of the leaves. Therefore, it is concluded that MWCNTs are indeed incorporated into CuO nanoleaves to form a CuO/MWCNT composite, not a simple mixture of CuO and MWCNTs. Moreover, MWCNTs built up a three-dimensional network, which act as "nervures" in CuO and "branches" among CuO nanoleaves.

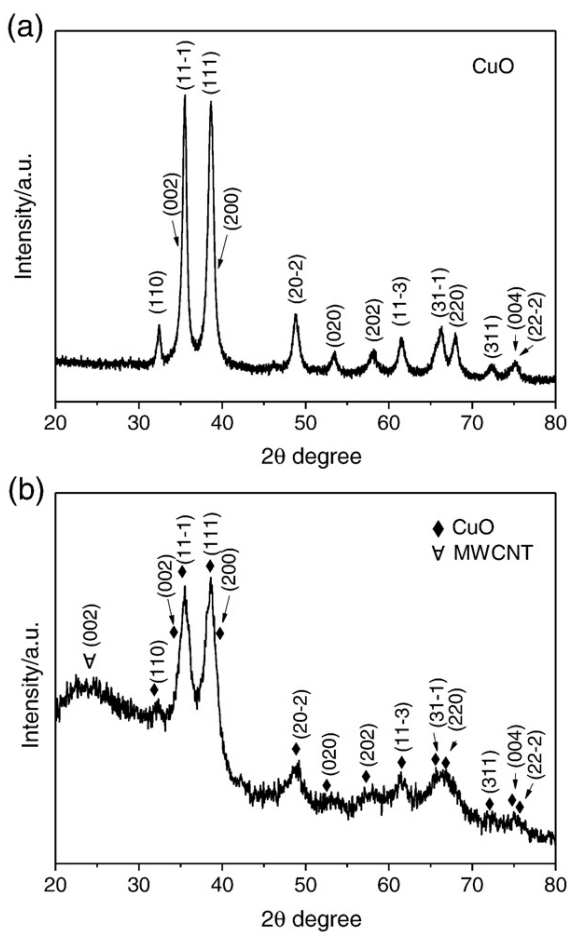

Fig. 1. XRD patterns of (a) CuO and (b) CuO/MWCNT composite.

The schematic illustration for the formation of CuO/MWCNT nanocomposite is presented in Fig. 2g. Once MWCNTs are added in the stirring CTAB solution, the cations are dispersed and attach randomly on the surface of MWCNTs (Step A). Due to the electrostatic effects, some Cu (II) ions added in the solution are absorbed in the outward end of the micelles while some are still dispersed in the solution (Step B). Once NaOH solution is dropped in, $Cu(OH)_2$ nanowires are immediately formed, some lie on MWCNTs while some are around MWCNTs (Step C). Then, $Cu(OH)_2$ nanowires dispersed in the solution self-assemble parallel to those lying on MWCNTs and become leaf-shaped nanoplates (Step D) [9]. After dehydration, a three-dimensional network of MWCNTs tightly connected with CuO nanoleaves is obtained (Step E).

The CV curves for pure CuO and CuO/MWCNT at a scan rate of 0.1 mV s^{-1} are shown in Fig. 3a and b. The CV curves for pure MWCNTs are also tested (inset of Fig. 3a). The peaks indexed to Li^+ intercalation/extraction of MWCNTs locate below 0.5 V, and the peak intensity is quite lower than that of CuO, which indicates the relative low Li^+ intercalation extent of MWCNTs. Therefore, the intercalation effect of MWCNTs on the CV curves of composite can be ignored. In the first cycle, three cathodic peaks at 1.7–1.8 V, 1.0 V and 0.65 V mainly correspond to reductive reaction from CuO to intermediate oxide, to Cu_2O and further decomposition into Cu and Li_2O, respectively [10]. The anodic peaks at 1.6 V and 2.6 V mainly result from the process $2Cu + Li_2O \rightarrow Cu_2 + 2Li^+ + 2e^-$ and oxidation of Cu_2O to CuO, respectively. The areas of all CV peaks of CuO/MWCNT are larger than those of pure CuO, indicating more reactions toward Li^+ occur in CuO/MWCNT. It is attributed to the MWCNT network, which acts as nervures to facilitate Li^+ transfer on active material/electrolyte interfaces, and also plays a role as branches to connect CuO nanoleaves, ensuring the improved electrical contact of CuO/CuO and CuO/current collector. The improved electric conductivity of CuO/MWCNT can enhance the kinetics and the extent of electrode reactions.

The positive effect of MWCNT network is still remarkable in the subsequent cycles (Fig. 3b). In addition to the larger peak areas of CuO/MWCNT, the separation between cathodic and anodic peaks of CuO/MWCNT is smaller than that of CuO, which reflects the decreasing polarization of CuO/MWCNT. MWCNTs incorporated into CuO nanoleaves can provide fast diffusion channel for Li^+, which decreases the transferring delay of Li^+ on CuO/electrolyte interfaces [7,11–13], so the polarization is reduced.

Fig. 3c and d show the cycling performances of CuO and CuO/MWCNT at different current densities. The Li^+ intercalation/extraction of MWCNTs is deducted when calculating the capacity of CuO/MWCNT according to Ref. [14]. The high initial discharge capacities of both CuO and CuO/MWCNT are ascribed to the 2D-nanostructured CuO with a large amount of lattice defects. The initial coulombic efficiencies of CuO/MWCNT are 72.1% and 70.2% at 60 mA g^{-1} and 600 mA g^{-1}, respectively, which are higher than those of CuO (64.6% and 58.6%). After 50 cycles, the charge capacity retentions of CuO/MWCNT and CuO are 63.2% and 50.1% at 60 mA g^{-1}, 53.3% and 26.3% at 600 mA g^{-1}, respectively. The cyclability of CuO/MWCNT is significantly improved, especially at high rate. Besides, the extra capacity of CuO/MWCNT compared to the theoretic capacity in the subsequent cycles can be ascribed to the partial reversible formation/decomposition of SEI due to the enhanced electrochemical activity after the incorporation of MWCNTs. Similar results are also shown in Ref. [15,16]. After 50 cycles, the discharge capacity of CuO/MWCNT still sustains 627 mAh g^{-1} (93% of the theoretic capacity), which indicates the excellent reversibility. The SEM images of pure CuO and

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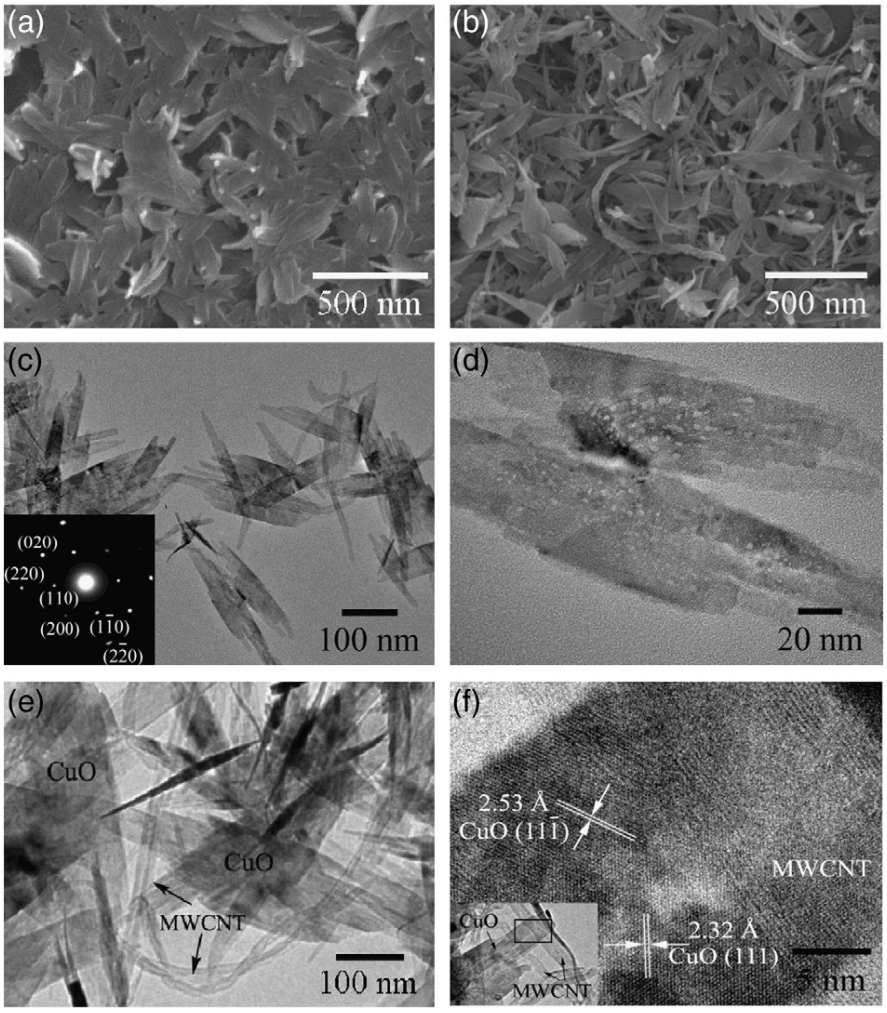

Fig. 2. SEM images of (a) CuO and (b) CuO/MWCNT; TEM images of (c), (d) CuO and (e) CuO/MWCNT; (f) HRTEM images of CuO/MWCNT; (g) schematic illustration for the formation of CuO/MWCNT composite.

CuO/MWCNT after cycling are shown in Fig. 3e and f. In the CuO electrode, the leaf-like CuO pulverizes and deteriorates seriously. But in CuO/MWCNT, the leaf-like morphology of CuO maintains well and the MWCNT network still well connected with CuO nanoleaves (Fig. 3f). It can be ascribed to the excellent mechanical property of MWCNTs, which absorbs the stress induced by volume change of CuO. Moreover, the as-prepared CuO/MWCNT exhibits significant improvement over recently reported CNT-introduced CuO microspheres, CuO nanowires, sisal-like CuO/C and hierarchical CuO hollow nanostructures [4–7] either in cycling performance or synthesis process. The detailed comparison is shown in Table 1. The enhanced capability and reversibility of CuO/MWCNT is attributed to the MWCNT network in the composite. Firstly, MWCNTs dispersed in the composite build up a network to connect CuO nanoleaves and ensure good electrical contact of active materials. Secondly, MWCNTs incorporated into CuO nanoleaves provide fast diffusion channels for Li^+ and facilitate the charge–transfer on CuO/electrolyte interfaces. Thirdly, MWCNTs with excellent mechanical property act as a soft matrix to buffer the volume changes and decrease the pulverization and deterioration of CuO during cycling.

4. Conclusions

MWCNTs are successfully incorporated into CuO nanoleaves by a facile precipitation method. The MWCNTs in the composite built up a three-dimensional network, which act as “nervures” in CuO and “branches” among CuO nanoleaves. The capability and reversibility of CuO/MWCNT shows a significant improvement over pure leaf-like CuO and previously reported CuO nanostructures. It is attributed to the three-dimensional MWCNT network, which improves the electrical contact of CuO/CuO and CuO/current collector, facilitates the charge transfer on CuO/electrolyte interfaces, and compensates the volume change of CuO during cycling. The proposed method can also be extended to other TMO to improve their cycling performances.

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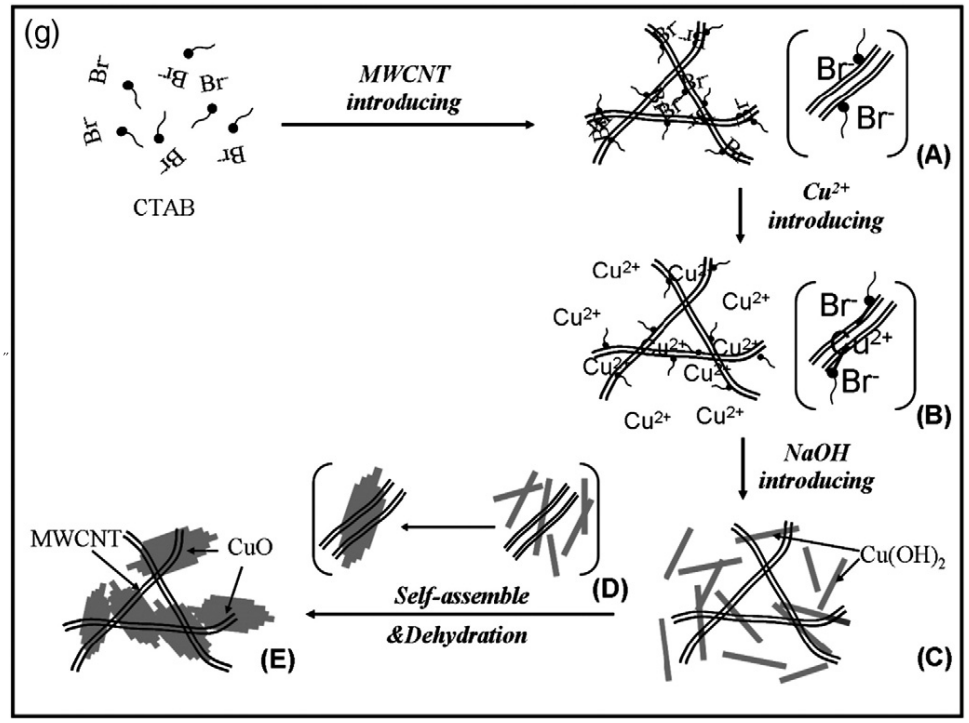

Fig. 2 (*continued*).

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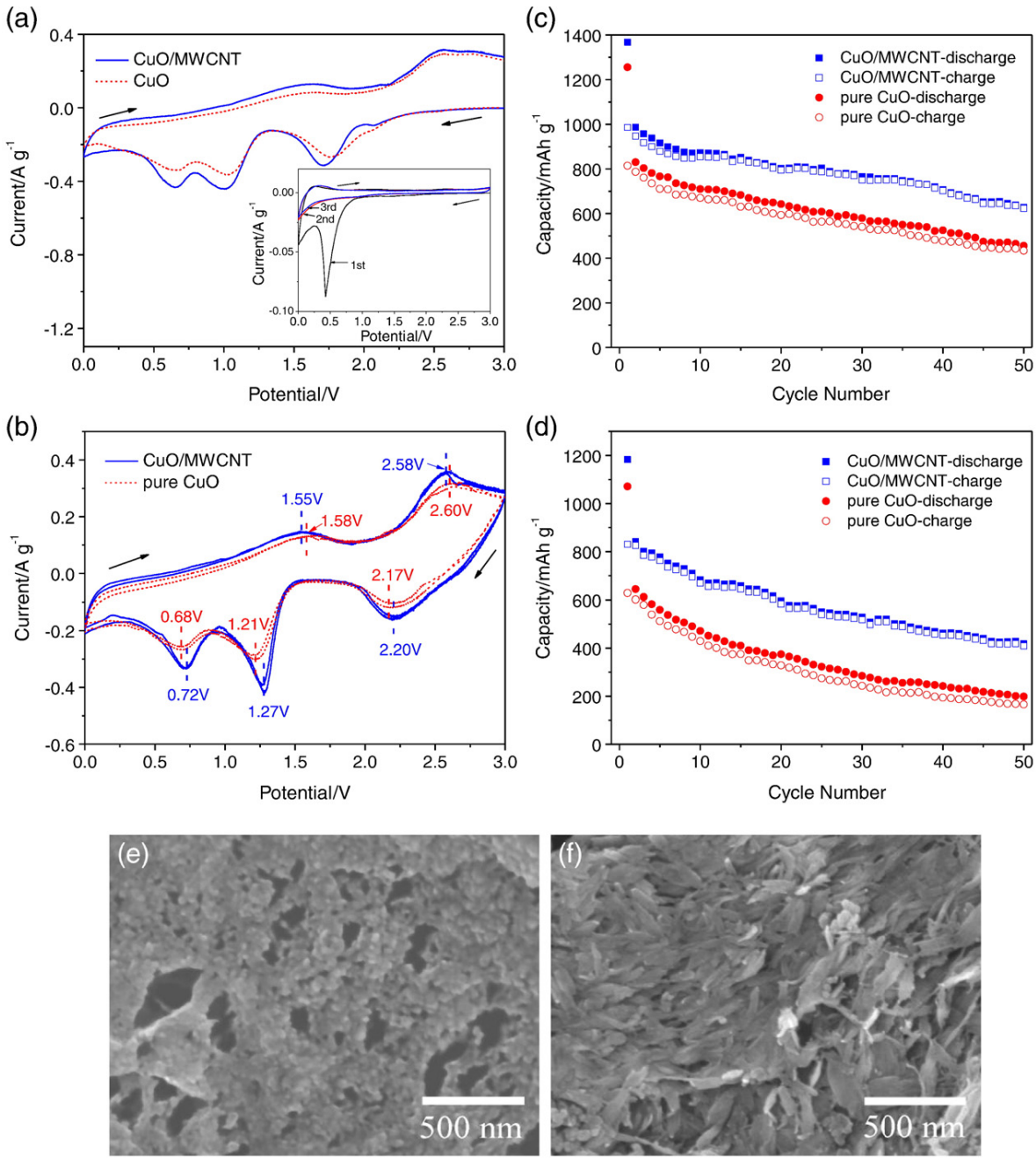

Fig. 3. Cyclic voltammogram curves at a scan rate of 0.1 mV s^{-1} from 0 to 3.0 V: (a) the first cycle, (b) the second and third cycles; cycling performances at current densities of (c) 60 mA g^{-1} and (d) 600 mA g^{-1}; SEM images of (e) CuO and (f) CuO/MWCNT after 50 cycles.

Table 1
Comparison between CuO/MWCNT and previously reported CuO nanostructures.

Material	Synthesis method	Thermal treatment	Initial coulombic efficiency	Reversible capacity	Rate	Ref.
Hierarchical hollow CuO	Hydrothermal method	130 °C/4 h	45.1%	300 mAh g^{-1}/20th cycle	0.1 C	[4]
CNT-introduced CuO microspheres	Reflux method	110 °C/2 h	52.3%	500 mAh g^{-1}/25th cycle	0.1 C	[5]
CuO nanowires	Wet chemical method	Below 20 °C/1 week	69.2%	600 mAh g^{-1}/50th cycle	0.5 mA cm^{-2}	[6]
Sisal-like CuO/C	Immersion and heat treatment	Room Temperature/96 h	46.3%	660 mAh g^{-1}/50th cycle	0.1 mA cm^{-2}	[7]
CuO/MWCNT	Precipitation method	60 °C/0.5 h	70.2%	627 mAh g^{-1}/50th cycle	60 mA g^{-1}	This work

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