Short communication

A hybrid of MnO_2 nanowires and MWCNTs as cathode of excellent rate capability for supercapacitors

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ABSTRACT

A hybrid of MnO_2-nanowires and MWCNTs to be used as cathode in a supercapacitor with good electrochemical performance was prepared by a facile hydrothermal method. In this hybrid the α-MnO_2 nanowires are well entangled with MWCNTs. The MWCNTs provide a network for fast electron transport whereas MnO_2 nanowires show a fast redox response. Since gain/loss of both electrons and ions can be realized very rapidly at the same time, the hybrid has an excellent rate capability and delivers an energy density of $17.8\,W\,h\,kg^{-1}$ at $400\,W\,kg^{-1}$, which is maintained almost constant even at $3340\,W\,kg^{-1}$ in 0.5 M Li_2SO_4 aqueous electrolyte. The cycling behavior is very good even in the presence of oxygen. The data present great promise for the hybrid as a practical cathode material for aqueous supercapacitor.

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1. Introduction

Supercapacitors are energy storage devices which can provide higher power density as compared to batteries and higher energy density than conventional capacitors such as electrolytic capacitors or metal film capacitors [1,2]. Numerous oxides such as RuO_2, PbO_2, $NiOOH$, $Ni(OH)_2$, NiO, MnO_2, $MnOOH$ and V_2O_5 could be used as the cathode materials of aqueous supercapacitors [3–12]. Among them, manganese oxides have attracted a lot of attention because of their multi-valence characteristics, easy preparation, environmental friendliness and relatively low cost. However, MnO_2 has low electronic conductivity, which severely limits its fast charge/discharge behavior. One effective approach to overcome this disadvantage is to mix it thoroughly with electronically conductive materials such as carbon black or carbon nanotubes (CNTs).

CNTs possess high electronic conductivity and good mechanical strength [13–16]. Recently, various MnO_2/CNTs nanocomposites obtained via different methods were investigated [17–22]. The results show that the electrochemical performance of electrodes or devices can be significantly enhanced. However, it is still hard to synthesize highly-homogeneous nanocomposites with better electrochemical performance for supercapacitors especially with high rate capability and good cycling performance in the presence of oxygen. In addition, their energy density is still small at high power density [23]. In this paper, we report a facile hydrothermal method to prepare a hybrid of MnO_2-nanowires and MWCNTs, which can be used as cathode material for aqueous supercapacitors with super-fast rate capability and good cycling behavior.

2. Experimental

Commercial MWCNTs (multiwall CNTs, outer diameter × inner diameter × length: 40–50 nm × 10–15 nm × 0.1–10 μm, purity: >90%) were treated in 6 M HNO_3 for 2 h with sonication to remove the impurities and endow the surface with hydrophilic groups such as –OH and –COOH. The treated MWCNTs (10 mg) were mixed with 40 ml aqueous solution of $MnSO_4$ (analytical grade, 5 mmol), $(NH_4)_2S_2O_8$ (analytical grade, 5 mmol) and $(NH_4)_2SO_4$ (analytical grade, template for nanowires, 20 mmol). After sonication for 3 h, the mixture was transferred to a 50 ml Teflon-lined stainless steel autoclave and hydrothermally reacted at 80 °C for 24 h. Then, the reaction product was washed with distilled water and ethanol. After drying at 100 °C for 12 h, a hybrid of α-MnO_2-nanowires and MWCNTs was obtained. α-MnO_2-nanowires were also prepared by the same method without adding MWCNTs as a control. After
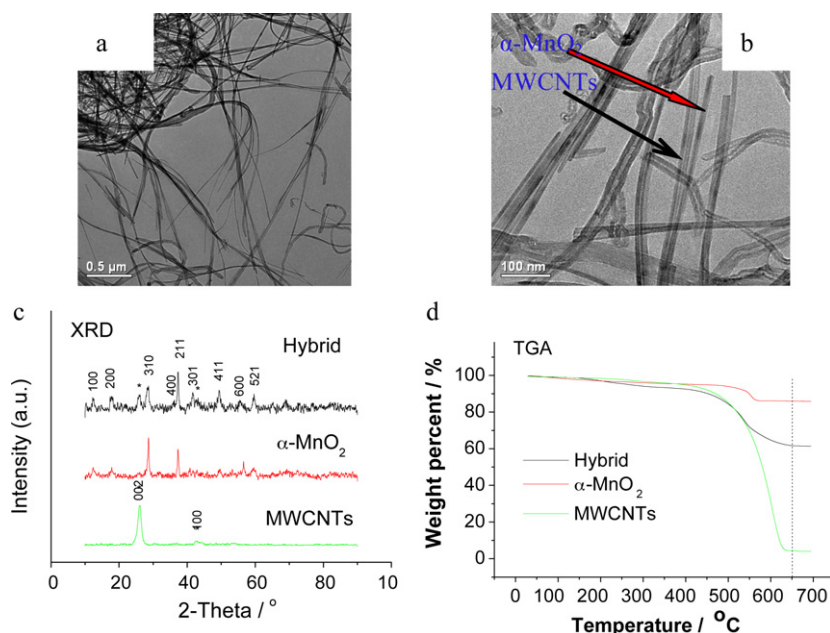
Fig. 1. TEM micrographs of (a) the virginal MnO_2 and (b) the hybrid of α-MnO_2 nanowires and MWCNTs, (c) X-ray diffraction patterns and (d) thermogravimetric analysis (TGA) of the hybrid.

pulverizing, the obtained particles were analyzed with X-ray diffraction (XRD) on a Bruker D4 X-ray diffractometer with Ni-filtered CuK$_\alpha$ radiation. The amount of MWCNTs in the composite was estimated using a Perkin Elmer TGA-7 Stare System from room temperature to 700 °C at 10 °C min^{-1}.

The as-prepared hybrid of α-MnO_2-nanowires and MWCNTs was mixed with acetylene black and poly(tetrafluoroethylene) (PTFE) in a weight ratio of 7.5:1.5:1 with the help of ethanol. After drying, the mixture was pressed into a film. The film was cut into disks of about 1 mg weight and 1 cm^2. These disks were pressed onto Ni-grids at a pressure of 10 MPa and then dried at 80 °C for one night and used as working electrodes. Cyclic voltammetric (CV) data were collected at different scan rates on an electrochemical work station of CHI660C (Chenhua).

Activated carbon (AC) with a specific surface area of about 2800 m^2 g^{-1} measured by the BET method was purchased from Ningde Xinseng Chemical Industrial Co., Ltd. and used as received without further treatment. The AC electrode was prepared in the same way as the hybrid electrode with the same amounts of acetylene black and PTFE. A two-electrode cell consisting of the above hybrid cathode and the AC counter electrode (weight ratio 0.45:1 for the hybrid vs AC) with electrode separation of 1 cm was used to test the cycling behavior of the hybrid in 0.5 M Li_2SO_4 solution on a cell tester (Land).

3. Results and discussion

TEM micrographs of the pristine MnO_2 and the hybrid of α-MnO_2-nanowires and MWCNTs, X-ray diffraction patterns and thermogravimetric analysis (TGA) of the hybrid are shown in Fig. 1. The pristine MnO_2 exists in the form of nanowires due to the use of the template, $(NH_4)_2SO_4$ (see above for details of our method). Since the surface of the MWCNTs is hydrophilic after the oxidation and our method is different from the reported ones such as by encasing MnO_2 particles or smearing MnO_2 layer on MWC-NTs [17–22], the prepared MnO_2-nanowires with about 10 nm in diameter are homogeneously entangled with MWCNTs to get a three-dimensional network structure. This is expected to provide a

large interface with an electrolyte solution for facile ion transportation and a conductive network with high electronic conductivity. MWCNTs has diffraction peaks at 26° and 42° corresponding to its (0 0 2) and (1 0 0) planes, respectively [24]. The other peaks of the XRD patterns of the hybrid are indexed to the tetragonal phase of α-MnO_2 (JCPDS No. 44-0141). The pristine MnO_2 sample without adding CNTs also confirms the formation of pure α-phase. Both α-MnO_2 and the hybrid start to decompose or oxidize slowly in air at temperature above 300 °C, and rapidly above 450 °C. The retained weight ratios of the α-MnO_2 powder, MWCNTs and the hybrid were 13.7, 95.8 and 38.2 wt.% after 650 °C, respectively. According to a method reported elsewhere [25], it was estimated that the amount of MWCNTs in the hybrid is approximately 31 wt.%. Its high amount in the hybrid provides numerous knots or binding sites with the MnO_2 nanowires, ensuring excellent electronic conductivity of the hybrid.

CVs of the hybrid electrode at the scan rates of 100, 300 and 600 mV s^{-1} are shown in Fig. 2a. The shapes of the CVs are close to rectangular for the hybrid even at the very high scan rate of 600 mV s^{-1}, showing a nearly ideal capacitive behavior. The specific capacitance of the hybrid calculated by integrating the CV curves is presented in Fig. 2b. All capacitance data were calculated based on the total mass of the hybrid in the electrode. The hybrid has an initial specific capacitance of 62 F g^{-1} at a scan rate of 50 mV s^{-1}. When the scan rate increases, the specific capacitance does not decrease much. This may be due to the unique three-dimensional network structure of α-MnO_2 with MWCNTs, providing a good electronically conductive network which could significantly facilitate the gain/loss of charges into/from the whole electrode matrix even at large scan rates [18,26]. Of course, some weight to the total weight of the hybrid is smaller than that reported for plain MnO_2 [8–12]. One reason is that the CNTs contributes to some weight of the hybrid, 31 wt.%. Another one is that MnO_2 exists in the form of its α-phase. It was reported that the contribution of CNTs to the capacitance could be neglected [21,22], which is consistent with our calculation, less than 5 F g^{-1} (not shown here). Nevertheless, further work on the increase of the capacitance of the hybrid is needed.
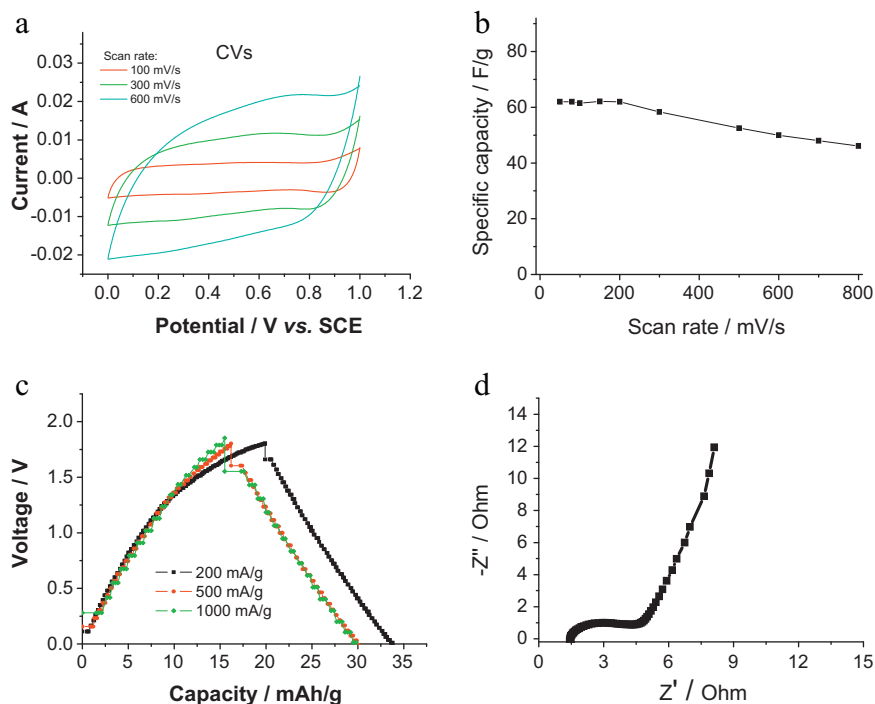
Fig. 2. (a) CV curves of at different scan rates, (b) specific capacitance with the scan rate, (c) charge and discharge curves at different current densities and (d) Nyquist plots of the hybrid electrode in 0.5 M Li_2SO_4 aqueous electrolyte.

The asymmetric aqueous supercapacitor based on AC anode and the hybrid cathode at different current densities shows an almost symmetric charge and discharge profile (Fig. 2c). The galvanostatic charge and discharge curves at 500 and 1000 mA g^{-1} almost overlap. The charge capacity is about 15 mAh g^{-1} from 200 to 1000 mA g^{-1}, indicating a good practical rate capability. This is consistent with the above-mentioned change of the specific capacitance with the scan rate. The Nyquist plot (Fig. 2d) shows that the charge-transfer resistance (R_{ct}) and the Warburg diffusion impedance are very small, leading to very small overpotentials during the charge and discharge process.

The Ragone plot of the asymmetric supercapacitor based on AC//hybrid in Fig. 3a shows clearly that it has a much higher energy density than the symmetric supercapacitor AC//AC. The energy density of the asymmetric supercapacitor based on AC//hybrid is 17.8 Wh kg^{-1} at 400 W kg^{-1} and stays almost constant with an increase of power density even at 3340 W kg^{-1}, which has been rarely reported. All other reported oxide materials or composites with CNTs show an evident capacitance fading with the power density [9–12,17–22]. At 3340 W kg^{-1}, its energy density is also much higher than other hybrid supercapacitors based on intercalation compounds and oxides [3–12,27–29]. The asymmetric supercapacitor based on the hybrid presents much better rate capability than the AC//AC system since the energy density of the latter still decreases with the power density though the decrease is much less than with other supercapacitors [3–12]. It is well known that MnO_2 shows a pseudocapacitance due to its redox behavior. In the case of a redox reaction, gain/loss of electrons and ions should happen at the same time. If not, the redox reaction will be hindered and the energy density will decrease with current or power density. In our hybrid material, MnO_2 nanowires are well entangled with the MWCNTs. MWCNTs are good electronic conductors much better than AC. The gain/loss of electrons can proceed very rapidly due to a lot of knots or binding sites with MnO_2 nanowires (the amount of MWCNTs in the hybrid is 31 wt.%). In the meanwhile, the diameter of the MnO_2 nanowires is very small, about 10 nm. The gain/loss of
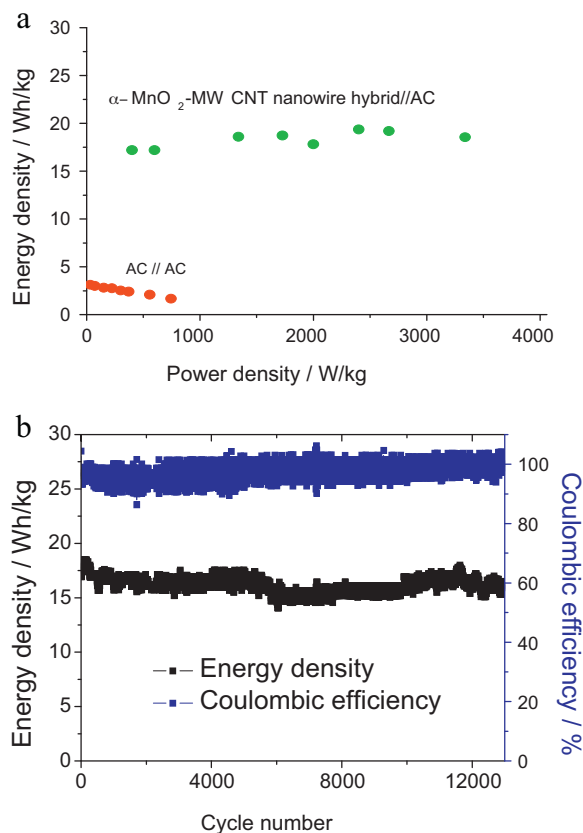

Fig. 3. (a) Ragone plot and (b) cycling behavior at 500 mA g^{-1} of the hybrid in 0.5 M Li_2SO_4 aqueous electrolyte solution.

Li$^+$ can also be realized very quickly. Since the gain and loss of both electrons and ions can be realized at the same time very rapidly, the energy density will not fade much with the power density. This is quite different from findings in former reports on composites of CNT with oxides [9–12,17–22]. This is similar to the initial stage of CV behavior in Fig. 2b. Due to the limited current range of our testing instrument, we could not get data at higher power density. When the power density is increased further, perhaps the energy density will also fade.

The capacity does not change much after 13,000 cycles even when oxygen is not removed (Fig. 3b). The excellent cycling performance of the hybrid cathode is due to the existence of MnO_2 nanowires in the hybrid, which greatly alleviates the stress or distortion during charge and discharge because of their excellent resilient property [30]. This excellent cycling behavior is similar to that of our formerly reported MnO_2 nanorods [9], which show energy density fading with energy density due to the lack of electronic conductive MWCNTs network.

4. Conclusions

A hybrid of α-MnO_2-nanowires well entangled with MWCNTs is prepared by a versatile hydrothermal method. The asymmetric supercapacitor based on AC and the hybrid can deliver a nearly constant energy density of 17.8 Wh kg^{-1} at different power densities. The capacitance shows only a small fading after 13,000 cycles when oxygen is not removed. The major cause is the uniform MWCNTs network in the hybrid providing good electronic conductivity and the small diameter of MnO_2 nanowires ensures fast gain/loss of Li$^+$ ions. In addition, the MnO_2 nanowire structure of good resilient property can keep structural stability during the charge and discharge processes even at very high current density.

Acknowledgements

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