Research Article

Functional Carbon Nanotube/Mesoporous Carbon/MnO₂ Hybrid Network for High-Performance Supercapacitors

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A functional carbon nanotube/mesoporous carbon/MnO₂ hybrid network has been developed successfully through a facile route. The resulting composites exhibited a high specific capacitance of 351 F/g at 1 A g⁻¹, with intriguing charge/discharge rate performance and cycling stability due to a synergistic combination of large surface area and excellent electron-transport capabilities of MnO₂ with the good conductivity of the carbon nanotube/mesoporous carbon networks. Such composite shows great potential to be used as electrodes for supercapacitors.

1. Introduction

Supercapacitors have attracted significant attention over the past decades due to their great advantages such as high power supply, long cycle life, and low cost and, therefore, offer a promising approach to meet the increasing power demands for portable devices and automotive applications [1–3]. It is noteworthy that performances of supercapacitors depend strongly on the properties of the electrode materials they employ. As a type of good candidate, carbonaceous materials, transition metal oxides, and conducting polymers have always attracted great interest [4–6]. Among them, manganese dioxide (MnO₂) has been intensively studied as electrode material due to its outstanding capacitive properties and environmentally benignity, in addition to being cheap and largely available [7–9]. However, the poor electronic conductivity of MnO₂ has limited its application in high-performance supercapacitors. To enhance the desired properties, the combination of MnO₂ and other conductive electrode materials is reckoned to tackle this limitation.

On other hand, carbon materials, especially carbon nanotubes (CNTs), are promising materials as electrodes for supercapacitors because of their high conductivity and short diffusion path to ions and excitons. The supercapacitors based on CNTs exhibit excellent power density as testified in recent years. However, the specific capacitance and energy density

of CNTs are always lower than other carbon materials such as activated carbon (typical in the range of 15–200 F g⁻¹ for CNTs) due to the limited surface area (typically less than 200 m² g⁻¹), which restricts the usage of CNTs as electrodes for supercapacitors [10–12]. In comparison with CNTs, mesoporous carbon (MC) usually exhibits a better specific capacitance up to 200 F g⁻¹, because of their large surface area and suitable pore size distribution [13–15]. And, in our previously work [16], we reported the fabrication of uniform CNT/MC networks via a facile organic sol-gel chemical route, which exhibited greatly increased specific capacitance due to the favorable balance between specific surface area and pore size distribution, and a 3D, well-connected through-pore structure. However, the specific capacitance of CNT/MC networks is still poor relative to transition metal oxides such as MnO₂. Therefore, it has inspired attempts to develop novel electrode materials via the coupling of CNT/MC networks and MnO₂ as electrode for supercapacitor, which may exhibit huge potentials to combine the advantages of both of them.

Herein, we report a convenient preparation of well-designed uniform CNT/MC/MnO₂ hybrid networks by growing MnO₂ along the backbone of the CNT/MC networks. The resulting CNT/MC/MnO₂ hybrid network electrode, under preferred conditions, exhibits an outstanding specific capacitance of 351 F g⁻¹ at a scan rate of 10 mV s⁻¹

and retains the high values of 195 F g^{-1} even at a high scan rate of 500 mV s^{-1} . All the evidence indicates that the rational combination of CNT/MC networks and MnO_2 will greatly improve the electrochemical performance, where MnO_2 on the surface of CNT/MC networks is essential for high energy storage and interconnected porous channels and high electrical conductivity of networks can accelerate the kinetic process of ion diffusion.

2. Experimental Section

2.1. Synthesis of CNT/MC/ MnO_2 Hybrid Network. All the reagents used in the experiments were of analytical grade and used without further purification. Prior to use, purified MWCNTs (Alpha Nano Technology Co., Ltd., China) were treated with concentrated acids ($\text{H}_2\text{SO}_4/\text{HNO}_3 = 1/1$ (v/v)) for 3 hours under 60°C , washed with copious of water, and dried at 60°C . In a typical synthesis, the acid-treated CNTs (0.05 g) were suspended in deionized water and thoroughly dispersed using ultrasound (sonic power $\sim 100 \text{ W}$) for 2 hours. Once the CNTs were dispersed, P123 ((PEO-PPO-PEO), 0.248 g, 22.4 mmol), resorcinol (0.124 g, 11.2 mmol), formaldehyde (0.176 g, 22.1 mmol), and sodium carbonate catalyst (0.6 mg, 0.056 mmol) were added to the reaction solution. The P123 was chosen as the generation of mesoporous structures. After stirring for half an hour, carbon fiber papers (CFP) were put into the solution, and the sol-gel mixture was cured at 85°C for 72 hours. The CFP act as an electron collector, and CNT/MC networks directly grow on the CFP substrate to improve the contact between them. The resulting gels were washed with *tert*-butanol for 72 h to remove water from the pores of the gel network. The gels were subsequently dried with lyophilization (freeze-drying) and pyrolyzed at 950°C under N_2 atmosphere for 3 hours, and CNT/MC networks were obtained. Then, the obtained CNT/MC network was again dispersed in deionized water, and followed by adding KMnO_4 (CNT/MC and KMnO_4 mass ratio of 1:1) the suspension was stirred at room temperature for different times (10/20/30 min, resp.), filtrated and washed using deionized water, and dried in air at room temperature. CNT/MC/ MnO_2 hybrid network was finally obtained and named as CNT/MC/ MnO_2 -10, CNT/MC/ MnO_2 -20, and CNT/MC/ MnO_2 -30, respectively.

2.2. Characterization. The morphology of samples was characterized with scanning electron microscopy (FESEM; Hitachi S-4800) operated at 5 kV. The samples were also analyzed by a powder X-ray diffraction system (XRD, D/MAX 2550 VB/PC) equipped with CuK α radiation. N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using a Micromeritics ASAP 2100 surface area analyzer.

2.3. Electrochemical Measurements. All electrochemical measurements were done on an Ametek PARSTAT 2273 potentiostat in a three-electrode setup: the as-prepared products as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference

electrode. The electrochemical measurements included cyclic voltammograms (CVs) and galvanostatic charge/discharge (CD). All electrochemical measurements were carried out at room temperature in 1 M NaSO_4 aqueous electrolyte, under the potential range from -0.2 to 0.8 V .

3. Results and Discussion

Figure 1(a) shows the low magnification SEM image of the obtained CNT/MC networks. It can be seen that the CFP collector is covered with a layer of foam-like CNT/MC networks. We have reported that the network is comprised of random CNTs or CNTs bundles which interconnected by thin carbon sheets [5]. Figures 1(b) to 1(d) show the SEM image of the as-synthesized CNT/MC/ MnO_2 hybrid networks with different reaction time. It can be obviously seen that the MnO_2 nanoparticles assembled on the surface of the CNT/MC networks, owing to the reaction of MnO_4^- with less active carbons. And most of the nanosheets of MC in the CNT/MC networks disappeared, due to the reaction. The XRD patterns of CNT/MC networks, MnO_2 , and CNT/MC/ MnO_2 -10 sample are shown in Figure 2. It is clear that most MnO_2 is in amorphous nature, since the weak and broad peaks of MnO_2 in XRD analysis and the peaks at 2θ around 12° (0 0 1), 37° (1 1 1) and 66° (3 1 2) are indexed to poor crystallized birnessite-type MnO_2 . It has been reported that the amorphous parts are beneficial to increase the specific capacitance for the supercapacitors because the highly amorphous structure should favor the electrolyte to insert into or to expel out from the oxide matrix, which can enhance contact between the electrolyte and the electrode material and then improve the utilization ratio of the material. Comparing the samples with different reaction times, it is clear that the uniform MnO_2 coating has grown thicker with the increasing of reaction time. And for CNT/MC/ MnO_2 -30, there are too many MnO_2 nanoparticles on the CNT/MC network so that parts of the channel in the hybrid networks are blocked, which have influence on the electrochemical performance of the sample.

To examine the electrochemical performance of our present CNT/MC/ MnO_2 hybrid network materials, the samples were fabricated into the supercapacitor electrode, and cyclic voltammogram (CV) and galvanostatic charge-discharge (CD) measurements were carried out in 1 M NaSO_4 aqueous electrolyte, under the potential range from -0.2 to 0.8 V to avoid the electrolysis of water. Figure 3 shows the CV curves of CNT/MC/ MnO_2 hybrid networks at different scan rates (20, 50, 100, 200, and 1000 mV/s , resp.). CV curves of all CNT/MC/ MnO_2 hybrid networks are relatively rectangular in shape, proving the ideal pseudocapacitive nature at small scan rate. And under large scan rate (1000 mV/s), CV curves of CNT/MC/ MnO_2 -10 and sample CNT/MC/ MnO_2 -20 are still symmetrical, indicating excellent power capacitor behaviours; however, with MnO_2 loading increasing, the CV curves change into asymmetrical sharp. The low rate capability of CNT/MC/ MnO_2 -30 is caused by the poor conductivity of MnO_2 nanoparticles.

FIGURE 1: SEM images of (a) CNT/MC networks; (b) CNT/MC/MnO₂-10; (c) CNT/MC/MnO₂-20; (d) CNT/MC/MnO₂-30.

FIGURE 2: XRD patterns of CNT/MC networks, MnO₂, and CNT/MC/MnO₂-10.

Figure 4(a) shows the charge-discharge curves of all CNT/MC/MnO₂ hybrid networks and CNT/MC network at a current density of 1 A g⁻¹. The linear voltage-time profile and the highly symmetric charge-discharge characteristics also show good capacitive behavior of all samples. The discharge time for CNT/MC/MnO₂ hybrid networks is about two times larger than that of CNT/MC network, exhibiting an enhanced capacitance performance with the addition of MnO₂. The galvanostatic charge-discharge measurement is assumed to be the most accurate technique to estimate the supercapacitive performance. The specific capacitances C in this paper are calculated from galvanostatic charge-discharge curves according to $I t / m \Delta E$, where I is the

charge-discharge current, t is the discharge time, and ΔE is the voltage difference. The specific capacitance of CNT/MC network is only 159 F g⁻¹ at a current density of 1 A g⁻¹, while, for CNT/MC/MnO₂-10, its specific capacitance is 316 F g⁻¹. And CNT/MC/MnO₂-20 exhibits larger specific capacitance (351 F g⁻¹) compared to CNT/MC/MnO₂-10, due to the increasing loading of MnO₂. However, it is interesting to note that the specific capacitance of CNT/MC/MnO₂-30 is 339 F g⁻¹, which is smaller than CNT/MC/MnO₂-20. The enhanced specific capacitance of the CNT/MC/MnO₂-20 networks is mainly attributed to the effective utilization of active materials. CNT/MC/MnO₂-20 exhibits favorable balance between MnO₂ loading amount and unique interconnected network structures. The interconnected networks create hierarchical porous channels, which enable effective electrolyte transport and active site accessibility. And the poor conductivity of MnO₂ in the CNT/MC/MnO₂-30 sample decreased its electrochemical performance, due to the overloading of MnO₂ nanoparticles.

Figure 4(b) shows the relationships between specific capacitance and charge/discharge current density. CNT/MC/MnO₂-10 shows the best rate performance and the specific capacitance is still 183 F g⁻¹ (about 58% retention) at a current density of 20 A g⁻¹; as compared, CNT/MC/MnO₂-30 retained about 50% (171 F g⁻¹), while the specific capacitance of CNT/MC/MnO₂-20 is still 195 F g⁻¹ (about 55.6% retention). The superior power capability performance of CNT/MC/MnO₂ hybrid networks indicated that the high conductivity of CNTs skeleton provides quick electron transport channel, and, more importantly, the unique 3D-network configuration with short transportation pathway

FIGURE 3: CV curves of CNT/MC/MnO₂ hybrid networks at different scan rates: (a) CNT/MC/MnO₂-10; (b) CNT/MC/MnO₂-20; (c) CNT/MC/MnO₂-30.

allows for easy accessibility of ions to the electrode/electrolyte interface and charging the capacitors. The energy density of CNT/MC/MnO₂-20 can be estimated to be 25.5 Wh kg⁻¹ at a power density of 1.1 kW kg⁻¹ (Figure 4(c)) which is much higher than not only the CNT/MC electrode (15.6 Wh kg⁻¹) [6], but also most of carbonaceous and MnO₂-based electrodes, such as CNTs (<10 Wh kg⁻¹), graphene (3.15 Wh kg⁻¹), and MnO₂ nanoparticles (<20 Wh kg⁻¹) [17–19]. More significantly, the energy density is still as high as 16.3 Wh kg⁻¹ for CNT/MC/MnO₂-20 even at a high power density of 17 kW kg⁻¹. The long-term cycle stability of the CNT/MC/MnO₂-20 was also investigated. Figure 4(d) demonstrates the specific capacitance as a function of cycle number at a current density of 5 A g⁻¹, in galvanostatic charge-discharge measurements for up to 1000 cycles.

After the cycling test, there are about 86% of its initial capacities that are maintained, due to the loss of adhesion of MnO₂ with the current collector or the dissolution of MnO₂ nanoparticles into the solution [20]. This cycling performance is also superior to most of other MnO₂ nanoparticles based supercapacitors. The present results have shown that the as-designed CNT/MC/MnO₂ hybrid network exhibits an excellent electrochemical performance, even for high-rate charge/discharge operations.

Based on the above discussions, the specific capacitance of CNT/MC/MnO₂ hybrid network is not only better than the reported carbonaceous electrodes, such as CNTs (180 F g⁻¹), graphene nanosheets (175 F g⁻¹) [21, 22], and CNT/MC networks (210 F g⁻¹), but also superior to most of other carbon/MnO₂ composites, such as MnO₂/carbon aerogel

FIGURE 4: (a) charge-discharge curves of CNT/MC and CNT/MC/MnO₂ hybrid networks at 1 A g⁻¹; (b) relationship of the specific capacitance with charge/discharge current density of CNT/MC/MnO₂ hybrid networks; (c) Ragone plots of CNT/MC/MnO₂-20; (d) variation of specific capacitance with cycle number at a current density of 1 A g⁻¹ of CNT/MC/MnO₂-20.

(219 F g⁻¹) and grapheme/MnO₂ (310 F g⁻¹) [23, 24]. Pure MnO₂ always exhibits high specific capacitance; however, the poor conductivity of MnO₂ results in low rate capability for high power performance. Xu et al. reported the synthesis of mesoporous MnO₂ nanowire array, which exhibited a specific capacitance as high as 493 F g⁻¹ [25]. However, at a high current density of 12 A g⁻¹, only 84 F g⁻¹ was observed. The sustainable specific capacitance of our materials is mainly due to its ability to have short paths ion diffusion with the CNT/MC networks and effective utilization of active material due to its uniform structures.

4. Conclusions

In summary, functional carbon nanotube/mesoporous carbon/manganese dioxide (CNT/MC/MnO₂) hybrid networks have been designed and fabricated via a facile route for

electrochemical energy storage. The obtained structures combined the advantages of large surface area and excellent electron-transport capabilities of MnO₂ with the good conductivity of carbon nanotube/mesoporous carbon networks and short transportation pathway of unique 3D-network configuration. The CNT/MC/MnO₂ hybrid networks exhibit greatly increased specific capacitance (351 F g⁻¹ at 1 A g⁻¹) compared with CNT/MC networks as supercapacitor electrode in 1 M NaSO₄ aqueous electrolyte. The energy density of CNT/MC/MnO₂-20 can be estimated to be 25.5 Wh kg⁻¹ at a power density of 1.1 kW kg⁻¹, and the energy density is still as high as 16.3 Wh kg⁻¹ even at a high power density of 17 kW kg⁻¹, indicating excellent electrochemical performance. It is reckoned that the present work also sheds light on the design of carbon and transition metal oxides 3D-networks for other applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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