Design and synthesis of porous TiO₂@C nanotube bundles with enhanced supercapacitive performance

Jingru Wang,^a Wenyao Li*,^a Yuanyu Ge,^c Jia Shen,^b Yanhong Zhao,^a Yan Zhang,^a Jianhui Yuan^a

^a*School of material engineering, Shanghai University of Engineering Science, Shanghai 201620, China.*

^b*Sanford Burnham Prebys Medical Discovery Institute, 10901 North Torrey Pines Road, La Jolla, California, 92037, USA.*

^c*College of Chemistry, Donghua University, Shanghai 201620, China*

E-mail: liwenyao314@gmail.com

Abstract

Porous TiO₂@C nanotube bundles (NTBs) are synthesized by a simple hydrothermal treatment with subsequent carbonization, which exhibited an enhanced specific capacitance of 274.2 F g⁻¹ at 0.5 A g⁻¹ with high rate capability (81% retention of its initial capacitance when current density increased 10 times) and excellent long-term cycling stability (102% of its original capacitance after 5000 cycles) compared with bare TiO₂ electrode. Thus it can be considered as a perspective material for high-performance supercapacitors.

Keywords

TiO₂@C; Nanotube bundles; Nanocomposites; Supercapacitor

Introduction

Supercapacitors as an energy storage device have attracted growing interest in recent years[1]. According to the charge storage mechanism [2], supercapacitor electrode materials can be classified as: electrical double layer capacitors (EDLCs) made of carbon materials and pseudocapacitors using redox-active materials such as transition metal oxides (MnO_2 [3], RuO_2 [4], NiO [5], etc.) and conducting polymers[6]. For EDLCs, carbon-based materials generally display a low specific capacitance, even though they have outstanding long-term chemical and electrochemical stability and high electrical conductivity[7, 8]. On the contrary, the pseudocapacitor electrode materials have high specific capacitance but generally suffer from the poor electrical conductivity and the irreversibility of Faradaic reactions on electrode surface. To achieve high specific capacitance and good electrochemical stability of the pseudocapacitor electrode materials, it generally increases the electrical conductivity by mixing them with conductive substances to solve this problem. [9] In addition, it is noteworthy that pseudocapacitors store charge only in the first few nanometers on the surface of the electrode material [10], the lack of porous channels in the active materials is also the main weakness that limits their rate and capacity for supercapacitors. [11,12] Therefore, to maximize utilization of the composite electrode materials, one important strategy is to construct more porous channels.

Among the various pseudocapacitor electrode materials, TiO_2 has been considered to be a promising electrode material for supercapacitors [13]. Especially, TiO_2 nanotubes with large surface area and high porosity hold wide interest as supercapacitor electrode materials[14]. However, the specific capacitances of TiO_2 -based electrode materials are significantly small which was attributed to the

poor electrochemical activity and electrical conductivity. Inspired by the above strategy, there are some conductive materials incorporated into TiO_2 to address these limitations and improve the specific capacitance, such as carbon loaded TiO_2 [15], $\text{Co}(\text{OH})_2/\text{TiO}_2$ nanotubes[16] and $\text{RuO}_2 \cdot x\text{H}_2\text{O}-\text{TiO}_2$ [17]. Nevertheless, the result is not good as expected. In fact, the intrinsic features of nanomaterials, for instance the effective contact areas and transport channel, have a significant influence on pseudocapacitive performance. Based on the above discussion, it will be meaningful and also a great challenge to further develop TiO_2 -based electrode materials with high conductive combined with more porous channels for supercapacitor by offering large interfacial areas, reduced ionic diffusion distances and facilitate charge and transport.

Herein, the ultra-long TiO_2 nanotube bundles was first synthesized by a simple hydrothermal process. Then a very thin carbon layer with high electronic conductivity uniformly cover on the surfaces. Moreover, it is very interesting that it full of pores distributed on the surfaces of carbon coated nanotube bundles after carbonization. The composite porous $\text{TiO}_2@\text{C}$ nanotube bundles combined the ultra-long nanotubes and high electronic conductivity carbon layer with porous channels can greatly enhance specific capacitance and stability of the TiO_2 electrode materials.

Experiment part

Preparing of TiO_2 nanotubes bundles: In a typical process, 0.5g of the anatase and rutile two-phase mixture nanopowder (prepared by hydrolyzing titanium tetrachloride[19]) and 10M NaOH (40 ml) were first mixed in a 50 mL Teflon-lined stainless-steel autoclave with a magnetic rotor. The autoclave was put inside a methyl silicone oil bath on a heating magnetic stirrers at 120 °C for 48 h. The mechanical disturbance condition can be controlled by the stirring rate at 1000 rpm/min. After reaction, the autoclave was taken out and naturally cooled to room temperature. The

product was collected by centrifugation, washed with de-ionized water for several times to reach a PH value of 9. After that, the wet centrifuged sodium titanate materials were subjected to a hydrogen ion exchange process in a diluted HNO_3 (0.1 M) solution for several times. Finally, the suspension was centrifuged again, washed with deionized water for several times until a PH value of 7 was reached, generating the products and then dried in vacuum oven at $60\text{ }^\circ\text{C}$ for 4 h.

Preparing of Porous $\text{TiO}_2\text{@C}$: As-synthesized samples were heated in a tube furnace under N_2 atmosphere which flow through an Erlenmeyer flask filled with ethyl alcohol. The carbonization temperature was set at $400\text{ }^\circ\text{C}$ for 10 h. At the same time, to provide a mildly changed environment, the heating rate was set at $10\text{ }^\circ\text{C}/\text{min}$ in the carbonization process. The ethyl alcohol molecular brought by the N_2 flow was filled in the samples, and then carbonized in high temperature to achieve the product.

Materials characterizations

The samples were characterized using an XRD instrument (PA-Nalytical X'Pert PRO, Japan). The morphology and phase of the samples was examined using a scanning electron microscope (SEM; S-4800) and a transmission electron microscope (TEM; JEM-2100F), respectively. N_2 adsorption/desorption isotherms were measured on an automated nitrogen adsorption analyzer (ASAP 2460, Micromeritics, America) at 77K. The sample was outgassed at $100\text{ }^\circ\text{C}$ for 4 h under vacuum before measurement. The mass of electrode materials was weighed on an XS analytical balance (Mettler Toledo; $\delta = 0.01\text{ mg}$).

Electrochemical characterizations

Electrochemical performances of the as-obtained products were performed on an Autolab (PGSTAT302N potentiostat) using a three-electrode mode in a $0.5\text{ M Na}_2\text{SO}_4$ solution. Working electrodes were prepared by mixing the as-synthesized $\text{TiO}_2\text{@C}$ or

TiO₂ products (80 wt%) with acetylene black (15 wt%), and poly(tetrafluoroethylene) (5 wt%). A small amount of N-methylpyrrolidinone was then added to the mixture. The mixture was then dropped onto graphite paper (coating area: 1 cm²) and dried at 80 °C overnight to remove the solvent. The reference electrode and counter electrode were saturated calomel electrode (SCE) and platinum (Pt), respectively. Standard current-voltage (C-V) and galvanostatic charge-discharge curves were measured between 0 and 0.8 V. EIS measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz. All electrochemical experiments were carried out at 25±2°C. The specific capacitance is calculated from the discharge curves using the following formula, $C = I \cdot \Delta t / (\Delta V \cdot m)$, where I (A), Δt (s), m (g), and ΔV (V) are the discharge current, discharge time consumed in the potential range of ΔV , mass of the active materials, and the potential windows, respectively.

Result and discussion

Fig. 1 shows the XRD pattern of the obtained products, all of the diffraction peaks can be assigned to anatase phase TiO₂ (JCPDS Card No. 001-0562) and Carbon (marked with blue blocks). It implies that a calcined process under the N₂ atmosphere which carry the ethyl alcohol molecule is effective to make a carbon layer cover on the TiO₂ completely.

Fig. 1 XRD pattern of the TiO₂@C.

The SEM image of Fig. 2a and b shows that the products are composed of many TiO₂@C nanotube bundles (pure TiO₂ is in Fig. S1) which are made up of intertwined nanotubes. The length was up to several micrometres and easily assembled to a network. The TEM investigation is shown in Fig. 2d, the inner diameter of nanotubes was ~8 nm. Enlarged TEM images taken from the red boxed area (in Fig. 2d) is shown in Fig. 2c. Interestingly, lots of pores can be found on the surfaces of nanotubes (marked with red cycles). **This phenomenon could be explained that the residual bound moisture in the nanotube walls were escaped out in hydrothermal process at high temperature.** Therefore, there are a lot of porous channels could enable effective electrolyte transport and active site accessibility. The HRTEM image of a single nanotube is shown in Fig. 2e (taken from the blue boxed area in Fig. 2d). It is found that there is a very thin carbon layer ~ 4 nm cover on the nanotubes, which could enhance the conductivity of the TiO₂ nanotubes. The corresponding FFT pattern (top-right inset) confirms its single crystal character. The lattice fringes with an interplanar spacing of ~ 0.35 nm corresponding to the (101) planes of TiO₂.

Fig. 2 Microstructure of $\text{TiO}_2\text{@C}$ nanotube bundles (a) low and (b) high magnification SEM images, (d) TEM images, (c) enlarged TEM images taken from the red boxed area, and (e) HRTEM images taken from the blue boxed area, inset showing the corresponding FFT pattern and interplanar spacing.

In order to obtain more detailed information for the porous $\text{TiO}_2\text{@C}$ nanotube bundles, the N_2 adsorption-desorption isotherms for the $\text{TiO}_2\text{@C}$ and their corresponding pore size distribution are shown in Fig. 3. The shapes of hysteresis loops have often been identified with specific pore structures. The H3 loop, which does not exhibit any limiting adsorption at high p/p_0 , is observed because of the aggregates of nanotube bundles giving rise to slit-shaped pores. At the same time, there are lots of non-rigid mesoporous on the nanotube surface. Therefore, the pressure hysteresis extends to the low attainable pressures, which is thought to be associated with the swelling of non-rigid porous structure on the nanotube surface. The BET specific surface area is calculated to be $172.5 \text{ m}^2/\text{g}$. The high BET surface area of the $\text{TiO}_2\text{@C}$ NTBs could provide more active sites and the possibility of efficient transport for electrons and ions in the electrode, hence may lead to enhanced electrochemical capacity. Form the

pore size distribution, the pore radius is mostly centered at ~ 4 nm, which is match well with the inner diameter of hollow nanotubes and some small pores on the surfaces of nanotube bundles. The small peak intensity in the lower range (~ 3 nm) could due to the relatively smaller pores of the nanotubes. The pore radius centered at ~ 13 nm could be assigned to interstice formed by the self-assemble of nanotube bundles.

Fig.3. Nitrogen adsorption-desorption isotherms of the TiO₂@C NTs. The inset shows the BJH pore size distribution.

The electrochemical behavior of the TiO₂@C NTBs was evaluated with cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) measurements in three-electrode configurations in 0.5 M Na₂SO₄. For comparison, the pure TiO₂ were also investigated. The CV curves of the TiO₂@C and TiO₂ electrodes at 50 mV s⁻¹ are shown in Fig. 4a. It can be seen that the two curves are close to a rectangular and symmetric shape, indicating an ideal pseudocapacitive nature of fast charge-discharge processes, and the TiO₂@C possesses the bigger loop area than TiO₂ electrode. We then explored the further CV investigation under different scan rates for TiO₂@C electrode, Fig. 4b. Along with the scan rates rising from 1 to 50 mV s⁻¹, the CV

curves' shape nearly remains unchanged and still keep rectangular approximately, indicating the excellent electrochemical reversibility and high-rate property. The similar phenomena were also found in pure TiO₂ electrode (Fig. S2a).

Galvanostatic CD measurements were also carried out on the electrodes at different current densities. Fig. 4c shows the charge-discharge curves of the TiO₂@C and TiO₂ electrodes at 0.5 A g⁻¹. It can be seen that the charge curves are symmetric to their corresponding discharge counterparts. It is noted that the specific capacitance of TiO₂@C electrode can reach 274.2 F g⁻¹, which is significantly higher than that of the TiO₂ electrode (77.2 F g⁻¹). This could be mostly ascribed to the carbon layer on the nanotubes surface which provide good electrical conductivity to make more electrochemically active sites on the surface took part in the process of energy storage. To further evaluate the capacitive performance of the TiO₂@C electrode, the galvanostatic CD curves measured at different current densities are shown in Fig. 4d. A high symmetric nature is observed in all the charging-discharging curves, indicating the ideal electrochemical capacitive characteristics and a superior reversible redox reaction in the entire potential region. The specific capacitance for the porous TiO₂@C NTBs electrode was also considerably higher than that of recently reported TiO₂-based electrodes (Table 1).

Rate capability is a critical factor for supercapacitors in high power applications. The specific capacitances obtained at various current densities are shown in Fig. 4e. It is noted that with the current density increasing from 0.5 to 5 A g⁻¹, the TiO₂@C electrode exhibit 81% retention of its initial capacitance (274.2 dropped to 222.2 F g⁻¹), which is higher than that of the TiO₂ electrode (67.5% retention, 77.2 dropped to 52.1 F g⁻¹, Fig. S2b). The superior rate capability can be attributed to the network fabricated by the self-assembling TiO₂@C nanotubes bundles providing nearly perfect

substrate for electron movement. The pores provide large electrochemically active surface areas for charge transfer and reduce the ion-diffusion distance. Meanwhile, the carbon layer directly attached to the nanotube surfaces offers fast electron transport and fast surface electrosorption of Na^+ as well as the fast and reversible faradic process.

Cycling performance are of great importance for supercapacitors. In this study, the long-term cycle stability of the electrodes was evaluated by repeating the CV test at 50 mV s^{-1} , Fig. 4f. As can be seen, after 5000 cycles of CV testing, the $\text{TiO}_2@\text{C}$ electrode did not show any loss instead of increasing to 102% of the initial value. This may be ascribed to an activation process that occurs at the beginning of the CV cycling test. With the electrolyte gradually penetrating into the electrodes, more and more active points of the electrode materials become activated, thus contributing to the increase of the specific capacitance. Thus, the $\text{TiO}_2@\text{C}$ electrode exhibited an excellent electrochemical stability.

Fig. 4 (a) CV curves of the $\text{TiO}_2@\text{C}$ and TiO_2 at 50 mV s^{-1} , (b) CV curves of the $\text{TiO}_2@\text{C}$ at different scan rates, (c) Galvanostatic charge-discharge curves for the $\text{TiO}_2@\text{C}$ and TiO_2 at 0.5 A g^{-1} , (d) Galvanostatic charge-discharge curves for the $\text{TiO}_2@\text{C}$ at different current densities, (e) Specific capacitance as a function of the current densities of the $\text{TiO}_2@\text{C}$ and TiO_2 electrodes. (f) Cycling performance of the $\text{TiO}_2@\text{C}$ at 50 mV s^{-1} .

Table 1 Comparison of electrochemical performance

Descriptions	Specific capacitance	Reference
TiO ₂ /AC	92 F g ⁻¹	[20]
rGO-TiO ₂ nanobelts	169 F g ⁻¹	[21]
Thorny TiO ₂ nanofibers	17.05 F g ⁻¹	[22]
TiO ₂ /graphene	97.5 F g ⁻¹	[23]
TiO ₂ /CNT	137 F g ⁻¹	[23]
TiO ₂ /graphene	84 F g ⁻¹	[24]
TiO ₂ nanofibers	65.84 F g ⁻¹	[25]
TiO ₂ -graphene hydrogel	175 F g ⁻¹	[26]
Porous TiO ₂ @C nanotube bundles	274.2 F g ⁻¹	This work

Electrochemical impedance spectroscopy (EIS) measurement was also employed to characterize the electrodes, and the Nyquist plots are exhibited in Fig. 5a. The equivalent fitting circuit is shown in Fig. 5b based on their corresponding fitting curves (Fig. S3). The equivalent series resistance (ESR) (R_s) value of the TiO₂@C and TiO₂ are 1.7 and 2.68 Ω , respectively. Moreover, the TiO₂@C have a smaller charge transfer resistance (R_{ct}) value (24.6 Ω) than TiO₂ (92.5 Ω), indicating a superior conductivity of the TiO₂@C microstructure due to the carbon layers, thus providing an ideal pathway for ion and electron transport without kinetic limitations.

Fig. 5 (a) Nyquist plots of the $\text{TiO}_2\text{@C}$ and TiO_2 electrodes. (b) the equivalent fitting circuit of as-formed electrodes.

Conclusion

In summary, porous $\text{TiO}_2\text{@C}$ nanotube bundles were synthesized by a simple process of hydrothermal treatment with subsequent carbonization. The $\text{TiO}_2\text{@C}$ NTBs electrode exhibited an enhanced specific capacitance of 274.2 F g^{-1} at 0.5 A g^{-1} with high rate capability (81% retention of its initial capacitance when current density increased 10 times) and excellent cycling stability (102% of its original capacitance after 5000 long-term cycles). These findings showed that the $\text{TiO}_2\text{@C}$ NTBs was a promising electrode material for high-performance supercapacitors.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant Nos. 51602192, 51602193, 51301192), the Foundation of Shanghai University of Engineering Science (2015-05), the Project of Shanghai University Young Teacher Training Scheme (ZZGCD15037), and the Shanghai “YangFan” Project (14YF1409500).

References

- [1] J.R. Miller, P. Simon, Science 321(5889) (2008) 651-652.

- [2] A. González, E. Goikolea, J.A. Barrena, R. Mysyk, *Renew. Sust. Energ. Rev.* 58 (2016) 1189-1206.
- [3] J. Shao, X. Zhou, Q. Liu, R. Zou, W. Li, J. Yang, J. Hu, *J. Mater. Chem. A* 3(11) (2015) 6168-6176.
- [4] C. C. Hu, K.-H. Chang, M.-C. Lin, and Yung-Tai Wu, *Nano Lett* 6(12) (2006) 2690-2695.
- [5] L. An, K. Xu, W. Li, Q. Liu, B. Li, R. Zou, Z. Chen, J. Hu, *J. Mater. Chem. A* 2(32) (2014) 12799-12804.
- [6] C. Zhou, Y. Zhang, Y. Li, J. Liu, *Nano Lett* 13(5) (2013) 2078-2085.
- [7] Z. Wang, Z. Wu, G. Di Benedetto, J.L. Zunino, S. Mitra, *Carbon* 91 (2015) 103-113.
- [8] K.S. Yang, B.-H. Kim, *Electrochim. Acta* 186 (2015) 337-344.
- [9] X. Lu, G. Wang, T. Zhai, M. Yu, J. Gan, Y. Tong, Y. Li, *Nano Lett* 12(3) (2012) 1690-1696.
- [10] P. Simon and Y. Gogotsi, *Nat. Mater.*, 7 (2008) 845-854.
- [11] J. H. Liu, J. S. Chen, X. F. Wei, X. W. Lou and X. W. Liu, *Adv. Mater.*, 23 (2011), 998-1002.
- [12] Y. W. Li, J. J. Shao, Q. Liu, X. J. Liu, X. Y. Zhou, J. Q. Hu, *Electrochem. Acta*, 151 (2015), 108-144.
- [13] Z. Zheng, J. Chen, R. Yoshida, X. Gao, K. Tarr, Y.H. Ikuhara, W. Zhou, *Nanotechnology* 25(43) (2014) 435406.
- [14] H. Zhang, Z. Chen, Y. Song, M. Yin, D. Li, X. Zhu, et al., *Electrochem. Commun* 68 (2016) 23-27.
- [15] H. Tang, M. Xiong, D. Qu, D. Liu, Z. Zhang, Z. Xie, et al., *Nano Energy* 15 (2015) 75-82.
- [16] F. Tao, Y. Shen, Y. Liang, H. Li, *J. Solid State Electrochem.* 11(6) (2006) 853-858.
- [17] C.-C. Hu, H.-Y. Guo, K.-H. Chang, C.-C. Huang, *Electrochem. Commun.* 11(8) (2009) 1631-1634.
- [18] Y. Tang, Y. Zhang, J. Deng, J. Wei, H. Le Tam, B.K. Chandran, et al., *Adv Mater* 26(35) (2014) 6111-6118.
- [19] S. Novaconi, N. Vaszilcsin, *Mater. Lett* 95 (2013) 59-62.
- [20] M. Selvakumar, D.K. Bhat, *Applied Surface Science* 263 (2012) 236-241.
- [21] C.C. Xiang, M. Li, M.J. Zhi, *A. J Mater Chem* 22 (2012) 19161-19167.
- [22] J. Wang, G. Yang, W. Lyu, W. Yan, *Journal of Alloys and Compounds* 659 (2016) 138-145.
- [23] X. Sun, M. Xie, J. J. Travis, G. Wang, H. Sun, J. Lian and S. M. George, *J. Phys. Chem. C*

117(2013) 22497-22508

[24] X. Sun, M. Xie, J J. Travis, G Wang, H. Sun, J. Lian and S M. George, J. Electrochem. Soc. 159(2013) A364-369.

[25] X. He, C.P. Yang, G.L. Zhang, D.W. Shi, Q.A. Huang, H.B. Xiao, Y. Liu, R. Xiong, Materials & Design 106 (2016) 74-80.

[26] J. Kim, W.-H. Khoh, B.-H. Wee, J.-D. Hong, RSC Adv. 5 (2015) 9904-9911.