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COMMUNICATION

Facile fabrication of freestanding three-dimensional composites for supercapacitors[†]

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A facile and highly efficient method for the fabrication of freestanding three-dimensional (3D) composites with different morphologies was designed by the combination of electrospinning method and hydrothermal reaction. The controlled hierarchical nanoarrays showed excellent electrochemical performance for potential use as supercapacitor electrode.

The rapid development of flexible electronic equipment such as stretchable displays, dispersed sensors and wearable multimedia gadgets poses new challenges for the fabrication of compatible wearable energy storage devices such as supercapacitors. However, the main bottleneck of the supercapacitor is its large size, heavy weight and low capacity. It is still a big challenge to fabricate highly efficient miniaturized energy-storage devices that are compatible with the flexible/wearable electronics.

Different forms of flexible electrodes were obtained based on various flexible substrates such as metal-based substrate, plasticbased substrate, paper-based substrate and fiber-based substrate in previous research¹⁻³. Among these, fiber-based materials could be directly used as wearable and embedded devices based on their intrinsic flexiblity and three-dimensional architexture. Electrospinning as an ideal method to prepare nanofibres directly and continuously, has become one of the most powerful tools for fabricating free-standing nanofibers with small and uniform diameters, high surface area, and continuous porous structure⁴⁻⁶. However, up to now, the brittle mechanical property of carbon nanofibers is still a shortcoming for practical applications, even though much research has been done to improve elastic property by creating porosity using methods such as utilizing pore generating agents or post activation methods^{5,7,8}. Therefore, developing highly flexible binder-free electrode materials, in which active materials are self-supported onto three dimensional (3D) porous backbone with

very crucial to enhance the whole capacitive performance of electrodes9-11. Zinc oxide (ZnO) is a suitable candidate for supercapacitor applications because of its low cost, biocompatible and environmental friendliness, good electrochemical activity. More importantly, ZnO nanorods can be grown easily on fibers at low temperatures (less than 100°C) providing three-dimensional (3D) hetero architectures with large specific surface area, which is necessary to fabricate high-efficiency supercapacitors¹²⁻¹⁴. Here, we used a combination of electrospinning and hydrothermal method as a convenient procedure to overcome the low rate capability and poor reusability of ZnO materials by eliminating defects through hydrothermal crystallization. In addition, the synergistic effect from the faradaic capacitance of ZnO nanorods and the double layer capacitance of the flexible carbon nanofibers was utilized here for improving the energy/power capabilities. However, an uniform seed layer of ZnO needs to be incorporated in the carbon nanofibers before the growth of ZnO nanorods on the carbon fiber surfaces. This is a challenge as it is not only difficult to ensure homogeneous dispersion of ZnO seeds but it is also time-consuming¹⁵⁻¹⁷. Therefore, we developed an innovative, convenient and fast method to achieve uniform dispersion of ZnO seeds by incorporating Zn acetate as a seed precursor in the spinning solution prior to extrusion. In this communication, we report for the first time about building flexible three dimensional electrodes based on electrospinning and hydrothermal growth process of ZnO nanorod arrays with different morphologies on carbon nanofibers. Zinc acetate was selected as a precursor for ZnO nanocrystals, terephthalic acid (PTA) was explored as the sublimating agent to generate macropores inside electrospun carbon nanofibers during carbonization resulting in selfsustained carbon film¹⁸, and acid-treated multiwalled carbon nanotubes (MCNTs) were added to enhance the whole conductivity and specific surface area. The as-fabricated 3D composites showed good performance as supercapacitor electrode. The present research achievements are hoped to provide a simple method to implement three-dimensional flexible electrodes for the development of energy storage materials for wearable devices.

short electronic pathways and reduced ion diffusion resistance is

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COMMUNICATION



Fig. 1. SEM images of the nanocomposite fibers of TP-CNFs and ZTP- CNFs before (a, b) and after (c, d) carbonization, respectively. TEM images of TP-CNFs (e) and ZTP-CNFs (f). The insets in 'f' show higher magnification of the edge of ZTP-CNFs and digital photographs of ZTP-CNFs being folded into multiple layers and the recovery of folded carbon films demonstrating their high flexibility.

The preparation of the electrodes and the electrochemical tests are illustrated in the Electronic Supplementary Information (ESI) section. Morphologies by SEM images of as-synthesized composite nanofibers of TP-CNFs and ZTP- CNFs are shown in Fig. 1a and 1b, respectively. Both these composites exhibit random distribution of long and continuous carbon nanofibers of cylindrical morphology. The addition of zinc acetate did not affect the morphology of the nanofibers (Fig. 1b) compared to the fibers without zinc acetate addition (Fig. 1a). As expected, a slight decrease in the average diameter of both types of the above nanofibers occurred after carbonization (Fig. 1c and 1d) compared to the as-prepared nanofibers (Fig. 1a and 1b). In addition, there is an observable difference between the surfaces of the carbon nanofibers of TP-CNFs and ZTP-CNFs as they have two different formulations. The addition of zinc acetate apparently leads to a more porous structure in the case of ZTP-CNFs (Fig. 1d) compared with TP-CNFs in Fig. 1c. The higher porosity of the former is due to the decomposition of Zn(CH₃COOH)₂ during carbonization apart from the sublimation of PTA and the evaporation of DMF, as can be seen from the following equation (1):

$$Zn(CH_{2}COO)_{2}+2O_{2}=ZnO+2CO_{2}+3H_{2}O$$
 (1)

This decomposition is confirmed by the homogeneous deposition of ZnO nanocrystals on the individual nanofibers as can be seen in Fig. 1f. Zinc acetate loaded as spinning precursor not only helps with the more uniform distribution of ZnO seed but also guides the growth of ZnO nanorods along the carbon fiber axis, as supported by the morphological study of hierarchically structured ZnO nanorods on carbon nanofibers after hydrothermal reaction (vide infra). In addition, the use of zinc acetate and PTA created Journal Name

Page 2 of 4

additional pores to increase the specific surface area and further improve the flexibility of the self-sustained carbon film. The formation of flexible carbon fiber matrix is mainly due to a substantial number of macropores created within the carbon nanofibers when PTA sublimed from inside of nanofibers. The macroporous structure of the carbon nanofibers prevents crack propagation and therefore, prevents breakage of fibers. Porosity, thus attenuates the folding stresses¹⁸. As displayed in the inset of Fig. 1f, the as-obtained ZTP-CNFs could be folded into multiple layers and recovered without any cracks because of their excellent flexibility. In order to further determine the effect of PTA and zinc acetate on the porous structure of the carbon nanofibers, N2 adsorption isotherms of the as-prepared nanofibers are shown in Fig. S1. The CNFs in the absence of PTA and zinc acetate show type I isotherm suggesting micropores with high nitrogen uptake at relatively low pressure. However, the TP-CNFs containing PTA during electrospinning show somewhat of a type IV isotherm with hysteresis loop at higher relative pressure, which indicates the presence of macroporosity. The higher nitrogen uptake of ZTP-CNFs confirms that the addition of zinc acetate further improved the pore volume and specific surface area of the nanofibers. The surface areas are 590.3, 466.5, 603.3 m^2/g for CNFs, TP-CNFs, ZTP-CNFs, respectively and the incorporation of zinc acetate in the latter clearly increased the surface area. Even though the surface area of TP-CNFs is less than that of CNFs, the increased pore volume of TP-CNFs (0.26 cc/g) when compared to CNFs (0.16 cc/g) reduced stresses by arresting crack growth when the fibers were bent, thus enhancing the flexibility of the fibers. The PAN carbon nanofibers are not only a substrate but also a template for ZnO nanoparticles and prevent the agglomeration of ZnO during carbonization process. Moreover, some turbostratic carbon structures with nanosized graphite domains and abundant edge defects along the main surface of ribbon-shaped carbon fibers can be exhibited from the high magnification image as inserted in Fig. 1f. This type of oriented growth of graphite crystals and defect-rich carbon materials could further improve the whole electrical conductivity significantly¹⁹. These results also suggest that electrospinning is ideally suited to prepare a relatively homogeneous ZnO seed layer (Fig. 1f) on highly flexible and conductive nanofibers.

The morphologies of the hierarchically structured ZnO nanorods on carbon nanofibers after hydrothermal reaction are depicted in Fig. 2. Hexagonal-shaped ZnO nanorod arrays with sharp and slender tips were deposited on the surface of the CNFs (Fig. 2a and 2d). Nanofiber growth is ascribed to the rapid growth of ZnO along the c-axis direction. By increasing the growth time to 5h, dense, well-oriented and highly uniform ZnO nanorod arrays, which cover the substrate more completely could be observed (Fig. 2b and 2g). The ZnO nanorod diameters range from 100 to 200 nm. However, not all ZnO nanorods grew vertically on the carbon nanofiber surface because of steric hindrance by the surrounding nanorods. By contrast, a random distribution of ZnO nanorods resulted from the absence of ZnO seed in TP-CNFs as shown in Fig. 2c. This confirms that ZnO nanowires cannot grow along the carbon fibers without ZnO seed, i.e., the ZnO seed could guide the growth of ZnO nanorods along the carbon fiber axis. The energy dispersive X-ray (EDX) spectra in Fig. 2e and Fig. 2h reveal the presence of more amount of Zn in ZTP-CNFs/ZnO-2 than in ZTP-CNFs/ZnO-1

Journal Name



Fig. 2. SEM image of ZTP- CNFs/ZnO-1 after hydrothermal growth of ZnO for 3h at low (a) and high magnification (d). SEM image of ZTP-CNFs/ZnO-2 after hydrothermal growth of ZnO for 5h at low (b) and high magnification (g). SEM image of TP-CNFs/ZnO after hydrothermal growth of ZnO for 5h (c). The EDX spectrum of the ZTP- CNFs/ZnO-1(e) and ZTP- CNFs/ZnO-2 (h). Elemental mapping by EDX spectroscopy of the ZTP-CNTs/ZnO-1(f). XRD patterns of the nanocomposites (i).

because of more dense coverage with nanorods after longer hydrothermal treatment. In order to understand the atomic composition of hydrothermal powder and trace the location of ZnO nanorods, elemental mapping by EDX spectroscopy of the ZTP-CNTs/ZnO-1 sample was carried out and the result is shown in Fig. 2f. C and N are homogenously distributed over the entire image of the nanofibers while Zn and O (Fig. 2f) are present at the locations where ZnO rods are shown as in the SEM images. Elemental mapping by EDX spectroscopy confirms the alignment of ZnO nanorods along the axis of carbon nanofibers, which suggests that the nanofibers with zinc oxide loading can guide and control the epitaxial growth of ZnO nanorods on the ZnO seeds.

According to the above experimental results, a plausible growth mechanism for the ZnO nanostructures with different morphologies is proposed (Fig. 3). Initially, ZnO seeds with polycrystalline nature were formed during carbonization (Fig. 1f), which acted as crystal nuclei for further growth of ZnO. Unlike the dip-or spin-coated substrate where ZnO seeds stack compactly, the sample prepared by electrospinning process revealed a loose and uniform arrangement of ZnO (Fig. 1f), which allows the polycrystalline nanoparticles to grow along the surface of the substrate. During the hydrothermal anisotropic growth process, zinc ions were probably transformed to Zn(OH)₂ in alkaline solution and then Zn(OH)₂ was converted into ZnO nanoparticles on ZnO seeds leading to the growth of ZnO nanowires (Fig. 2a and 2d). The ZnO nanowires can grow gradually and result in the formation of hexahedral ZnO nanorod arrays (Fig. 2b and 2g). Finally the more oriented and thick ZnO nanorods continually grow along the c-axis to form self-sustained threedimensional structure, which is the most thermo-dynamically stable form owing to the natural tendency to minimize polar surface and reduce the whole surface energy. The XRD patterns of as-prepared nanocomposites with different morphologies are shown in Fig. 2i. Except for TP-CNFs, all of the nanomaterials show the diffraction peaks at 31.8° (100), 34.5° (002), 36.3° (101), 47.6° (102), 56.5° (110)



COMMUNICATION

Fig. 3. Schematic formation process of the nanocomposites

and 62.9° (103), which can be perfectly indexed to the typical hexagonal wurt-zite structure of ZnO (JCPDS 36-1451). The full widths at half-maximum of the ZTP-CNTs/ZnO-1 and ZTP-CNTs/ZnO-2 peaks are smaller compared to those of ZTP-CNFs (Fig. 2d), which indicates that the hydrothermally grown ZnO nanorods are highly crystalline. Moreover, the strongest intensity of (002) diffraction peak of ZTP-CNTs/ZnO-2 (Fig. 2d) indicates preferential orientation of ZnO nanorods in the c-axis direction. Thus the XRD results corroborate the orientation of ZnO nanorods by SEM observation. It is also worth noting that no diffraction peaks corresponding to phases other than ZnO were observed, which indicates the high purity of the products synthesized.

Fig. 4a presents the cyclic voltammetry (CV) curves of different nanocomposite electrodes at a scan rate of 5 mV/s. The specific capacitance of ZTP-CNTs is higher than that of TP-CNTs owing to the synergistic effect between the double layer capacitance and the redox type capacitance resulting from the large number of active sites of ZnO in the composite electrodes. All of the curves of nanocomposites except TP-CNFs display a quasi-rectangular shape with slight distortion, in which a pair of faradaic redox peaks appeared as a result of the intercalation and deintercalation of Na⁺ from the electrolyte into ZnO: ZnO+Na⁺+e⁻ \leftrightarrow ZnONa. The integrated area of ZTP-CNFs/ZnO-2 is higher than that for other electrode materials, which suggests that the ZTP-CNFs/ZnO-2 has the highest specific capacitance. The CV curve is almost rectangular without distinct redox indicating that the electrodes are charged and discharged at a pseudo-constant rate over the entire potential range. The large capacitance exhibited by these systems is demonstrated to arise from a combination of the double-layer capacitance and pseudo-capacitance associated with surface redox-type reactions. The specific capacitance as a function of the scan rate is plotted in Fig. 4b and the inset shows the CV curves of ZTP-CNFs/ZnO-2 by varying the scan rate from 5 to 100 mV/s. The CV curves almost retain their rectangular shape with little variance even at a fast scan rate of 100 mV/s, indicating a fast, reversible reaction and excellent high-rate discharge capacity. A decrease of specific capacitance is observed by increasing the scan rate, which can be ascribed to the reduced diffusion time for insertion/extraction of protons or Na⁺ cations into ZTP-CNFs/ZnO-2 at high scan rate. The galvanostatic charge/discharge curves of the as-prepared ZTP-CNFs/ZnO-2 nanocomposites at different current densities are illustrated in Fig. 4c. The potentials of the charge/discharge lines are nearly proportional to the charge/discharge time in the Na₂SO₄ electrolyte, confirming the excellent electrochemical reversibility. The specific capacitance obtained from the discharge curves is calculated to be 169 F/g at a low current density of 1 A/g, which is comparable with the results of the CV measurements. About 59.2% of capacitance was retained as

COMMUNICATION

the current density was increased to 10 A/g, which can be attributed to the low resistance for charge diffusion and a short pathway for ion transportation offered by three-dimensional electrodes, resulting in fast and reversible electrochemical adsorption-desorption and redox reaction. The ragone plot derived from the discharge curves is shown in Fig. 4d. As the current density increased from 1 A/g to 10 A/g, the power density increased from 0.48 kW/kg to 4.25 kW/kg while energy density decreased from 21.30 Wh/kg to 9.23 Wh/kg. Significantly, the CV curves in Fig. 4e collected from the ZTP-CNFs/ZnO-2 under different conditions suggest that the flexible electrode can be bent and even twisted without affecting the device performance much, demonstrating its excellent mechanical stability for potential use in flexible energy storage device. Stability testing was performed on the electrodes under the constant charge/discharge at 2A/g for 3000 cycles and the results are depicted in Fig. 4f. The electrode showed 79.5% capacitance retention after 3000 cycles, along with the very stable charge/discharge curves for the last 10 cycles (see inset in Fig. 4f) indicating its excellent capacitance retention. SEM image of ZTP-CNFs/ZnO-2 after 3000 cycles showed little or no change in the ZnO nanorod morphology (see the inset in Fig. 4f). The improved electrochemical performances further verify the synergistic effect between the



Fig. 4. CV curves of the hybrid electrodes at a scan rate of 5 mV/s (a). Specific capacitance of ZTP-CNFs/ZnO-2 electrodes as a function of a various scan rates. The inset is the CV curves of ZTP-CNFs/ZnO-2 at various scan rates (b). Charge/discharge curves of ZTP-CNFs/ZnO-2 nanocomposite electrode at various current densities (c). Ragon plot of ZTP-CNFs/ZnO-2 electrode (d). Cyclic voltammograms of ZTP-CNFs/ZnO-2 at a scan rate of 50mV/s under flat, and twisted conditions (e). Cycling performance of the nanocomposite electrodes. The inset showed the galvanostatic charge/discharge curve for the last 10 cycles and the SEM image of the surface of the Zn(20)-ACNF electrode after 3000 cycles (f).

Journal Name

double-layer capacitance arising from the large surface area and excellent conductivity and the pseudocapacitance of the numerous electrochemically active sites of ZnO in ZTP-CNFs/ZnO-2.

In summary, We have successfully fabricated free-standing ZTP-CNFs/ZnO nanocomposites with different morphologies by the combination of electrospinning method and hydrothermal reaction. Zinc acetate loaded as spinning precursor can not only guide ZnO nanorods grow along fiber axis but also create additional pores to increase the specific surface area and improve the flexibility. Terephthalic acid (PTA) can further ensure the carbon film to be self-sustained as numerous macropores were generated inside electrospun carbon nanofibers during its sublimation, and the addition of acid-treated multiwalled carbon nanotubes (MCNTs) enhanced the whole conductivity and specific surface area. The asfabricated 3D composites showed excellent electrochemical performance as supercapacitor electrode. Integration of the faradaic capacitance of ZnO and the double layer capacitance of the flexible carbon nanofibers in a controlled hierarchical manner is hoped to provide a simple method to fabricate a three-dimensional flexible electrode leading to the potential development of wearable energy storage devices.

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4 | J. Name., 2012, 00, 1-3

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