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Three-dimensional nano MnO_2/CB composite and its application for electrochemical capacitor

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ABSTRACT

A three-dimensional nanostructure composed of birnessite MnO_2 and carbon black (CB) was built via a quite simple co-precipitation method at room temperature. The natural porous construction of conductive CB granules provided enough sites for MnO_2 deposition. The as-prepared composite showed that dispersive MnO_2 nanowires were directly crystallized on the surface of CB matrix, which was believed to be beneficial to its electrochemical performance. The further investigation of cyclic voltammetry (CV) in 1 M Na_2SO_4 confirmed the inference, which showed good symmetrical rectangular shape, and the specific capacitance was calculated about 186 F/g at a scan rate of 2 mV/s. After 1000 cycles of CV at 10 mV/s, the initial capacitance was maintained at about 91%, indicating that the designed structure had benefit to high electrochemical stability.

1. Introduction

Manganese dioxide (MnO_2), with high theoretical specific capacitance of 1370 F/g [1], has been considered as promising active material for energy storage, such as electrochemical capacitors (ECs) [1,2] and batteries [3], because of natural abundance and environmental friendliness. However, due to poor electronic conductivity (10^{-5}–10^{-6} S/cm) [4] and low surface area, the practical specific capacitance of bulk MnO_2 without conductive agent is far below the theoretical figure (ca. 1 F/g) [5], indicating that only a limited fraction of the bulk is electrochemically active. To deal with this problem, many efforts have been done, among which an idea of preparation of composite seems fascinating. Peng et al. have reported that MnO_2/carbon nanocomposites prepared by self-limiting growth between carbon substrates and permanganate had excellent electrochemical performance [6]. Long et al. have reported that favorable electrochemical performance could be obtained by depositing MnO_2 on carbon nanofoam [7]. They both use conductive material with large surface area as matrix, and load highly-dispersed MnO_2 on its surface to build a three-dimensional (3D) structure. The matrix serves as connected inner tunnels for electron transportation, and highly-dispersed MnO_2 would tremendously improve the utilization of active material. Carbon-based skeletons, graphene [8] or carbon nanotubes [9] for instance, were often chosen as matrixes. But stacking by C_6 in large scale, these two pristine carbon structures are relatively flawless without modification, making them less active to react to oxidants. Besides they often have to be prepared in sophisticated ways and are hard for large production. As for carbon black (CB) whose outer surface is stacked by tiny graphene layers, they have defects distributed all over the surface at the joint of layers, which leads to favorable chemical activity. Furthermore, CB has large surface area and 3D porous structure, also cheap and available in the market.

Based on the above, dispersed MnO_2 nanowires were loaded on the surface of CB to obtain a 3D architecture in this study. The structure of the composite synthesized was illustrated in detail, and the structural advantage of the composite was further confirmed by its good capacitive performances conducted in ECs.

2. Experimental

Commercial CB (Vxc-72, 256 m^2/g Carbot) was purified by dilute nitric acid. 0.145 g treated CB was dispersed in deionized water and 2 mmol $KMnO_4$ solution was added into the mixture and kept stirring for 3 h. 3 mmol $MnCl_2$ solution was then dropped slowly into the solution for an hour, and kept stirring for 3 h until the reaction was fulfilled. Dark brown precipitate was centrifuged and washed several times, and dried at 100 °C overnight.

The X-ray diffraction (XRD) patterns were determined by a Rigaku D/max 2500 v/PC system using CuKα radiation ($\lambda = 1.5406$ Å). Structures and morphologies were characterized by high-resolution transmission electron microscope (HRTEM, Philips Tecnai G2 F20) and field emission scanning electron microscope (FESEM, Nano430).

Electrodes for electrochemical measurements were prepared as follows. 95 wt.% of MnO_2/CB was dispersed in absolute ethanol with 5 wt.% polytetrafluoroethylene to get a mixed slurry. Then the slurry was spread onto a stainless steel mesh followed by uniaxial pressing. CV and electrochemical impedance spectroscopy (EIS) studies were

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conducted in a three-electrode configuration in 1 M Na_2SO_4 with saturated Hg/Hg_2SO_4 as the reference, using a PARSTAT 2273 system (Princeton applied research).

3. Results and discussion

The XRD patterns of acid treated CB and MnO_2/CB were shown in Fig. 1a. The pattern of MnO_2/CB could be indexed as birnessite phase (JCPDS no. 80–1098), which composed of 2D edge-shared MnO_6 octahedra layers [10]. The two peaks around $2\theta = 12°$ and 25°, both broad and weak, corresponded to (001) and (002) basal reflections respectively, suggesting that the *c*-axis orientation was not perfect. The diffraction peaks between $2\theta = 35°$ and 70° interpreting the stacking sequences, such as 2H and 3R, could be hardly seen, indicating that the stacking state of the *ab* plane might not be highly ordered [11]. La calculated from (100) peak of CB was about 4.07 nm.

The morphologies of CB and the composite characterized by HRTEM were shown in Fig. 1b. CB was piled up by small connected granules about 40 nm, constructing a 3D architecture also providing certain mesopores and macropores. With the length of La, it could be calculated that the whole surface of a CB granule consisted of about 300 graphene pieces, thus there would be plenty joints of graphene layers. From Fig. 1c, we could tell that the composite of CB and MnO_2 was successfully synthesized. Porous MnO_2 nanowires were dispersively coated on the surface of CB. In high magnification image of Fig. 1d, MnO_2 whiskers were directly developed on the surface of CB granules and showed good connection. The diameters of whiskers were less than 5 nm, indicating that the *c*-axis orientation was not perfectly developed.

The mechanism of whole procedure was illustrated in Fig. 1e. Pristine CB was first treated by dilute nitro acid to remove metal residues and other impurities to get clean surface, which consisted of graphene layers. Carbon atoms of graphene were connected through sp^2 hybrid orbital, and left π electrons to form big active electron clouds, which could be delocalized to complex protons from water to provide hydrophilic sites to increase the hydrophilicity [12]. Due to space stacking preference, there would be exposed carbon atoms and defects distributed at the joints of graphene layers. Since exposed carbon atoms were more vulnerable to react with $KMnO_4$, certain amount of MnO_2 nanocrystals would precipitate directly on the surface after $KMnO_4$ was added. As time went on, certain crystal would grow on the existing nanocrystals because some microelectrochemical cell reactions would happen at defective sites, where electrons were driven to reduct $KMnO_4$ to MnO_2 [13]. As $MnCl_2$ solution was dropped into the mixture, new products would take the previous MnO_2 nanocrystals as nucleation sites and the nanowire morphology could probably due to birnessite-type MnO_2, which preferred to grow along the *ab* plane [10].

The electrochemical stability of electrode was investigated by CV. Fig. 2a showed CV curves conducted at different scan rates. Symmetrical rectangular shapes of all curves indicated their ideal pseudo-capacitive nature. The specific capacitance calculated at 2 mV/s was 186 F/g. The long-term operation stability was investigated at 10 mV/s. As shown in Fig. 2b, after a thousand cycles, anodic and cathodic waves centered at about 0.25 and −0.05 V vs. Hg/Hg_2SO_4 can be seen clearly compared with the first cycle. This difference is probably due to further crystallization of birnessite MnO_2 during cycles [14], which sometimes had redox peaks on CV because of ion intercalation and deintercalation from 2D-layer structure [15]. The shape of the 1000th cycle distorted at the switching point of scan direction, which could be explained that MnO_2 might exfoliate from the CB matrix during cycles and lead to enlargement of contact resistance, because soluble manganese would be produced due to polarization [11]. The capacitive retention properties of composite were shown in Fig. 2c. It was 91% after 1000 cycles, which proved that the designed 3D architecture of the composite paid off.

FESEM photos of electrode before and after 1000 cycles were shown in Fig. 3. Fig. 3a showed that the granules were closely connected after uniaxial pressing, which would benefit electron transportation. After 1000 cycles shown in Fig. 3b, the granules seemed to grow bigger, which might be due to the further crystallization described before. Some holes appeared among the granules, and the connection was not as perfect as before, which might attribute to the exfoliation of MnO_2.

To further investigate the change of electrode after cycles, EIS tests were carried out after 1st cycle and 1000th cycle. The spectra after 1st

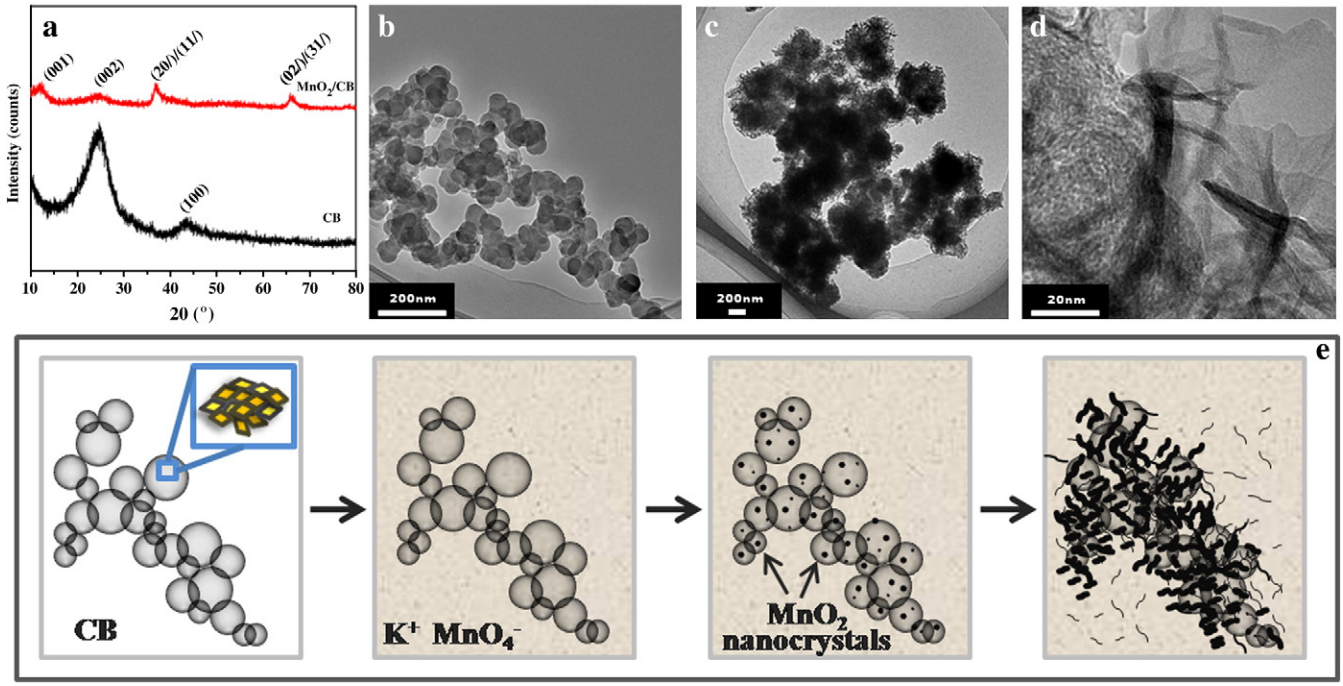

Fig. 1. a). XRD patterns of CB and as-synthesized composites; b) and c). HRTEM photos of CB and MnO_2/CB respectively; d). HRTEM photo of high magnification of the composite; e). Schematic illustration of preparation of MnO_2/CB composite.