3D MnO$_2$/Graphene composites with large areal capacitance for high-performance asymmetric supercapacitors

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Introduction

Due to the intrinsic poor conductivity of MnO$_2$ (10$^{-5}$–10$^{-6}$ S/cm), many works about the MnO$_2$/graphene or CNT composites for supercapacitors have been reported these years. However, the presence of MnO$_2$ in most of these composites reported is still low (usually less than 0.5 mg/cm$^2$), resulting in a low area-normalized capacitance, which is not meaningful for energy storage at device level. Until recently, the MnO$_2$/Carbon nanotube/textile and graphene/MnO$_2$ composites with high mass loading of MnO$_2$ have been reported, respectively. Noted that these reported MnO$_2$ composites with high mass loading only can achieve large areal capacitance at a very low scan rate (0.05 mV/s) and still have a low rate capability, such as MnO$_2$-CNT-textile composite (about 9.5% retention, 3.8 mg/cm$^2$, 10 mV/s to 200 mV/s), and graphene/MnO$_2$ composite (about 8.5% retention, 4.9 mg/cm$^2$, 10 mV/s to 200 mV/s). The realization of high-performance MnO$_2$ composites with high mass loading is still meaningful and challenging. In this paper, we reported an effective and simple strategy to prepare MnO$_2$/Graphene composites with large areal mass loading of MnO$_2$ and better rate capability for asymmetrical supercapacitors (ASCs).

Experimental

Graphene oxide (GO) was prepared by the oxidation of natural graphite powder according to a modified Hummers’ method. Typically, Ni foam (NF, 2 cm × 1 cm × 0.1 cm, mass per unit area 25.5 mg cm$^{-2}$) were immersed in a 10mL GO suspension(5 mg mL$^{-1}$) in a 15mL Teflon-lined stainless steel autoclave. The sealed autoclave was heated in an electric oven at 180 °C for 12 h to get G-gel/NF. The MnO$_2$ was electrodeposited on the G-gel/NF via Amperometric i-t curve technique under +1V for 30~120s in a conventional three-electrode cell. The ASC was assembled by MnO$_2$/G-gel/NF and G-gel/NF electrodes with a separator (Absorbent cellulose membrane) sandwiched in it. The absorbent cellulose membrane was dipped in 0.5 M Na$_2$SO$_4$ solution for 10 min and subsequently was assembled with electrodes in an small plastic bag (1.7 cm × 1.2 cm).

Results and Discussion

Figure 1. (a) SEM images of G-gel/NF. Insets are magnified SEM image and the photos of pristine Ni foams (NF) and G-gel/NF. (b) HRTEM image of MnO$_2$/G-gel/NF.

GO nanosheets were reduced into G-gel and coated on Ni foam. The color of Ni foam became dark after hydrothermal reaction (insert in Fig. 1a). Scanning electron microscopy (SEM) images (Fig. 1a) clearly show that the G-gel has been successfully grown on the NF. Fig. 1b shows a high-resolution TEM (HRTEM) image and its selected area electron diffraction (SAED) pattern, indicating that the MnO$_2$ was uniformly coated on the G-gel/NF surface.

The electrochemical performance of the MnO$_2$/G-gel/NF composites was shown in Figure 2. a. Significantly, the MnO$_2$/G-gel/NF electrode achieves a much higher capacitive current density than pristine G-gel/NF and MnO$_2$/NF, indicating the superior electrochemical performance of MnO$_2$/G-gel/NF and demonstrating the G-gel/NF is a good support for MnO$_2$. Furthermore, the electrochemical performance of MnO$_2$/G-gel/NF with different areal mass densities for MnO$_2$ was also studied (Figure 2b). The MnO$_2$/G-gel/NF with MnO$_2$ mass of 6.11 mg/cm$^2$ achieves the highest areal capacitance of 1.5 F/cm$^2$ (245 F/g) at a scan rate of 10 mV/s, which is substantially higher than other MnO$_2$ nanostructure in the literature. With respect to high mass loading (> 1 mg/cm$^2$), a 17% capacity retention of initial capacitance when scan rate varies from 10 mV/s to 200 mV/s has been obtained by MnO$_2$/G-gel/NF with 6.11 mg/cm$^2$ MnO$_2$ mass. This is an outstanding rate capability compared with ever reported values. Moreover, a high performance ASC device with the MnO$_2$/G-gel/NF (MnO$_2$ mass: 6.11 mg/cm$^2$) cathode and G-gel/NF anode has also been demonstrated (Figure 2 c and d). The excellent capacitive performance even at high mass loading can be attributed to the highly conductive and 3D porous structure of G-gel/NF supports that enables efficient charges transport and accessible diffusion of the electrolyte.

Acknowledgment

Y.X. Tong acknowledge the support of this work by the Natural Science Foundations of China (21273290). Strategic emerging industries in Guangdong Province (2011A010802004).

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