The Supercapacitive Behavior of MnO$_2$/graphene Composite Prepared by Electrostatic Self-assembly Process

Honghong Cheng$^1$, Lu Long$^1$, Jinqing Wu$^1$, Dong Shu$^1$, Zongxuan Kang$^1$, Xianping Zou$^1$

$^1$School of Chemistry and Environment, South China Normal University.

$^2$Key Laboratory of Electrochemical Technology on Energy Storage and Power Generation of Guangdong Higher Education Institutes, South China Normal University.

*Corresponding author E-mail: dshu@scnu.edu.cn (Dong Shu).

Address: South China Normal University, Guangzhou 510006, PR China.

Abstract: MnO$_2$/graphene (MnO$_2$-G) composite was successfully synthesized by an electrostatic self-assembly process as shown in Fig.1. First, positively charged colloidal MnO$_2$ nanosheets and negatively charged colloidal graphene nanosheets were uniformly mixed; then graphene nanosheets were assembled on MnO$_2$ nanosheets via electrostatic attraction. The structure and morphology of the obtained materials were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results shown the mass ratio of graphene was about 4.3% in MnO$_2$-G material.

![Fig. 1](image1)

The capacitive properties of the samples were characterized by means of cyclic voltammetry (CV), galvanostatic charge-discharge (Fig.2(a)), and cycle life test (Fig.2(b)) in 1M Na$_2$SO$_4$ aqueous solution. The specific capacitance of MnO$_2$-G composite was found to be 280Fg$^{-1}$ at a current density of 0.2Ag$^{-1}$. Remarkably, its specific capacitance sharply increased during the initial 1000 cycles and then slowly increased to its maximum value at about the 3000th cycle, indicating that an electrochemical activation process occurred during the initial thousands of cycles. During initial electrochemical cycles, the small interlayer spacing of the MnO$_2$-G hinder Na$^+$ ions from electrolyte intercalate into the interlayer, resulting in a low specific capacitance value. Along with the cycling, the electrolyte gradually intercalated into the bulk of the electrode and the interlayer spacing of MnO$_2$-G was full of Na$^+$, which was further facilitated the ion exchange between interlayer and electrolyte. Therefore, the electrode exhibited higher specific capacitance after 3000 cycles. Additionally, over 96.8% of maximum capacitance was retained after 10000 cycles, exhibiting its excellent cycle stability. The enhanced specific capacitance and excellent cycle performance of MnO$_2$-G composite compared to pure MnO$_2$ were attributed to the synergic effect of highly specific capacitance of MnO$_2$ and excellent conductivity of graphene. Our experimental results demonstrated that MnO$_2$-G composite is a promising candidate as an electrode material for supercapacitors.

Key words: MnO$_2$/graphene composite; electrostatic self-assembly; supercapacitor; cycle stability