ELECTROCHEMICAL CHARACTERIZATION OF GRAPHENE BASED MATERIALS FOR SUPERCAPACITOR APPLICATIONS

Seong-Min Bak, Sang-Bok Ma, and Kwang-Bum Kim*

National Research Laboratory of Energy Conversion and
Storage Materials, Dept. of Material Science and Engineering,
Yonsei University,
134 Shinchon-dong, Seodaemoon-gu, Seoul, 129-749,
Republic of Korea
*kbkim@yonsei.ac.kr

Introduction

Supercapacitors have attracted a great deal of interest as an intermediate energy storage device between secondary batteries and conventional dielectric capacitors [1]. Manganese oxides have received considerable attention for supercapacitors due to their electrochemical behavior, low cost and environmental compatibility [2]. However, their poor electrical conductivity limits their applications as electrode materials for high-power supercapacitors. Recently, several studies on the synthesis of MnO_2/carbon nano-hybrid materials have been reported to improve the high rate capability of MnO_2 [3,4]

Graphene or graphene nanosheets (GNS) have received rapidly growing interest due to their superb characteristics of chemical stability, high electrical conductivity, and large surface area [5]. These merits support the application of GNS as an excellent template material for the preparation of nano-hybrid materials with metal oxides for supercapacitor applications. In this study, we report on the synthesis of manganese oxide/graphene (MnO_2/GNS) nano-hybrid materials and their electrochemical properties for supercapacitor applications.

Experimental

Graphite oxide (GO) was synthesized from purified natural graphite powder by a modified Hummers method, which has been described previously [6]. GNS was produced by chemical reduction of GO at 90 °C for 24 h, using hydrazine hydrate. Elemental analysis showed the C/O atomic ratio 10.6 for the GNS. MnO_2 was spontaneously deposited onto the GNS template by a direct redox reaction between GNS and MnO_4^-. The morphology and microstructure of the as-prepared metal oxide/GNS nano-hybrids were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical properties were determined using a three-electrode electrochemical cell in which the MnO_2/GNS electrode was used as the working electrode, a platinum mesh as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

Results and Discussion

Fig. 1a-b shows SEM images of the GNS and 45 wt.% of MnO_2 loaded GNS nano-hybrid materials. As shown in Fig. 1a, GNS consisted of randomly agglomerated, thin, crumpled sheets closely associated with each other. After MnO_2 deposition (Fig. 1b), the GNS agglomerates appeared slightly thicker, implying that the graphene acted as a 2D template for the selective, heterogeneous precipitation of MnO_2. Fig. 1c shows the XRD patterns of the as-prepared 45 wt.% MnO_2/GNS, and birnessite-type MnO_2 (JCPDS 42-1317). There are four characteristic 2θ peaks at around 12.2°, 24.7°, 36.6°, and 65.8° for MnO_2/GNS. These peaks were indexed to birnessite-type MnO_2 and the peak at 12.2° was ascribed to the (001) plane of the layered structure of birnessite MnO_2. No evidence of diffraction peaks for graphene appeared in the diffraction pattern and the use of GNS as a template did not influence the structure of MnO_2.
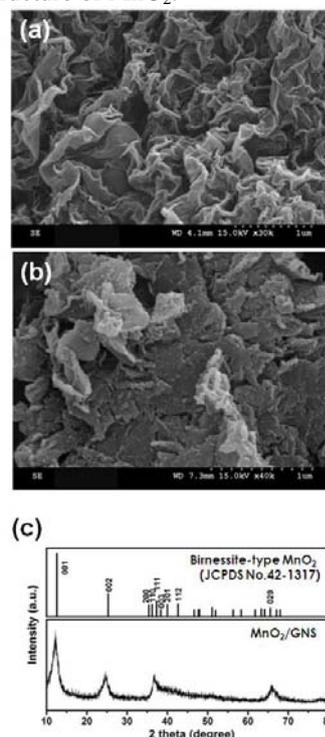

Fig. 1. SEM images of (a) GNS, (b) 45wt% MnO_2/GNS and (c) XRD patterns of 45wt% MnO_2/GNS and birnessite-type MnO_2 (JCPDS No.42-1317)

A typical TEM image of MnO_2/GNS nano-hybrid is shown in Fig. 2. It clearly shows that the entire surface of graphene is covered with birnessite MnO_2 at the nanometer scale. It should be noted that metal oxides were coated onto the surface of GNS with little trace of the homogeneous nucleation and growth of MnO_2 away from the GNS. This suggests that the GNS acted as a 2D template for the selective, heterogeneous precipitation of MnO_2. GNS might act as a reducing agent of permanganate ions as well as a 2D template for the selective heterogeneous nucleation of MnO_2.
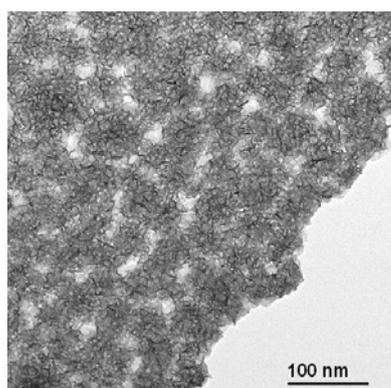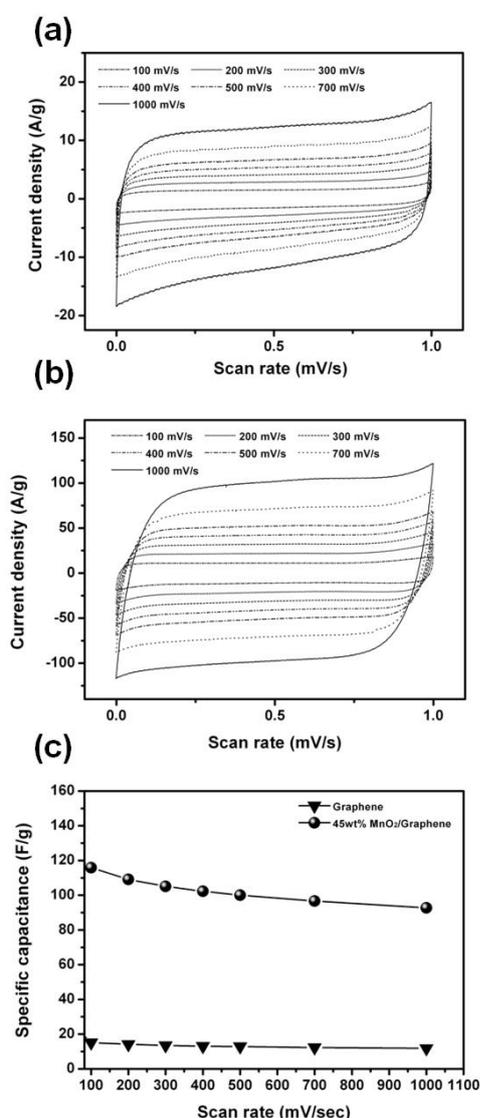
Fig. 2. TEM image of MnO$_2$/GNS

(a)

(b)

(c)

Fig. 3. Cyclic voltammograms (CVs) of (a) GNS, (b) 45wt% MnO2/GNS, and (c) specific capacitance of MnO$_2$/GNS as a function of potential scan rate.

Fig. 3 a-b shows the cyclic voltammograms (CVs) of the GNS and 45 wt.% MnO$_2$/GNS nano-hybrid electrodes as a function of the potential scan rate within a potential window of 0 to 1 V$_{SCE}$ in 1M Na$_2$SO$_4$ aqueous solution. The potential scan rate was varied from 100 to 1000 mV/s in order to evaluate the high rate capability of the electrodes. The current value in the CVs was normalized with respect to the mass of GNS and MnO$_2$/GNS. The CVs of the MnO$_2$/GNS nano-hybrid electrode were rectangular and symmetric with respect to zero current on the x-axis and their current response increased with increasing MnO$_2$ content in the hybrid.

The total specific capacitance (C$_s$) of the GNS and MnO$_2$/GNS nano-hybrid electrode is plotted as a function of the potential scan rate in Fig. 3c. The specific capacitance of the GNS electrode was calculated to be 23, 15 and 12 F/g at 10, 100 and 1000 mV/s, respectively, in 1 M Na$_2$SO$_4$ solution. For 45 wt% MnO$_2$/GNS, the C$_s$ was calculated to 137, 116 and 93 F/g corresponding to the potential scan rate of 10, 100, 1000 mV/sec, respectively. Excellent high rate capability could be achieved for the 45wt% MnO$_2$/GNS and pure GNS electrodes. The specific capacitance of 45 wt% MnO$_2$/GNS decreased by ~20 % from 116 to 93 F/g as the scan rate was increased from 100 to 1000 mV/s.

Conclusions

MnO$_2$/GNS nano-hybrid materials were successfully synthesized by a direct redox reaction between GNS and MnO$_4^-$ using GNS as a 2D template for the selective heterogeneous nucleation of MnO$_2$. CVs of MnO$_2$/GNS in 1M Na$_2$SO$_4$ solution exhibited a typical pseudo-capacitive behavior even at a very high scan rate of 1000mV/s. Our results suggest that GNS in the nano-hybrid not only provided a 2-D template of a high specific surface area for the deposition of metal oxides at the nanometer scale, but also served as a highly conductive support.

References
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