

Tightly Connected MnO₂-Graphene with Tunable Energy Density and Power Density for Supercapacitor Applications

Chih-Yao Chen¹, Chen-Yen Fan¹, Ming-Tsung Lee¹, Jeng-Kuei Chang^{1,2,3*}

¹ Institute of Materials Science and Engineering,

² Department of Chemical and Materials Engineering,

³ Department of Mechanical Engineering,

National Central University, Taoyuan, Taiwan

E-mail: jkchang@ncu.edu.tw; Fax: +886-3-2805034

Materials synthesis and characterization

All chemicals used in this study are of analytical grade, and used without further purification. Natural graphite powder (Alfa Aesar; with a particle size of ~70 μm and a purity of 99.999 %) was oxidized using a modified Staudenmaier method to produce graphite oxide (GO). Briefly, the graphite (5 g) was continuously stirred in a mixed solution of sulfuric acid (88 mL), nitric acid (45 mL), and potassium chlorate (55 g) for approximately 100 hours. Afterwards, the resulting GO was rinsed with 5% HCl aqueous solution and then repeatedly washed with deionized water until the pH of the filtrate was neutral. The product was dried and pulverized. Finally, GO was rapidly heated (~30 °C/min.) to 1050 °C in an inert Ar atmosphere and cooled in the furnace. After the thermal exfoliation and reduction, graphene was produced.

MnO₂/graphene nanocomposites were synthesized using an ethanol-assisted graphene-sacrifice reduction method. KMnO₄ was used as the precursor, which was

reduced by graphene and ethanol to form MnO_2 . In one pot, 0.1 M KMnO_4 was dissolved in 0.2 M KOH aqueous solution (20 mL). In the other pot, graphene was dispersed (with ultrasonication) in ethanol and water mixed solution (20 mL/10 mL). After combination of the two pots, a vigorously stir continued for 3 h to ensure the completeness of the reduction reaction. The resulting precipitates were separated by centrifugation followed by thoroughly washing with deionized water. All the samples were dried overnight at 80 °C prior to analyses. A plain MnO_2 sample (without graphene incorporation) was also prepared for comparison.

Microstructure of the samples was examined using scanning electron microscopy (SEM, JEOL JSM-7000F) and transmission electron microscopy (TEM, FEI Tecnai F20 G2). The crystallinity was determined with an X-ray diffractometer (XRD, Rigaku MiniFlex II) with a Cu target.

Electrochemical characterizations were performed using cyclic voltammetry (CV) and chronopotentiometry (CP) in 3 M KCl aqueous solution at 25 °C. The applied potential and current were regulated with a potentiostat (Autolab, 302N). The synthesized powder was mixed with isopropyl alcohol and Nafion and then pasted on a glassy carbon disc to prepare the working electrode. A platinum wire and an Ag/AgCl (in 3 M KCl solution) electrode were used as the reference and counter electrodes, respectively.

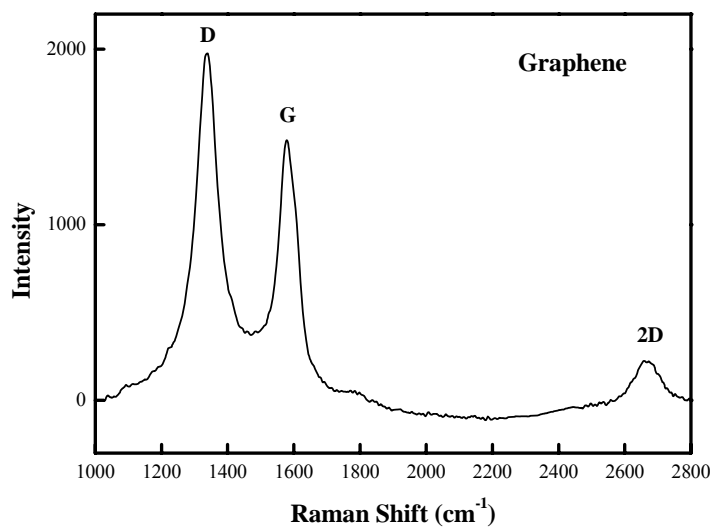


Fig. SI1. Raman spectrum of the graphene prepared.

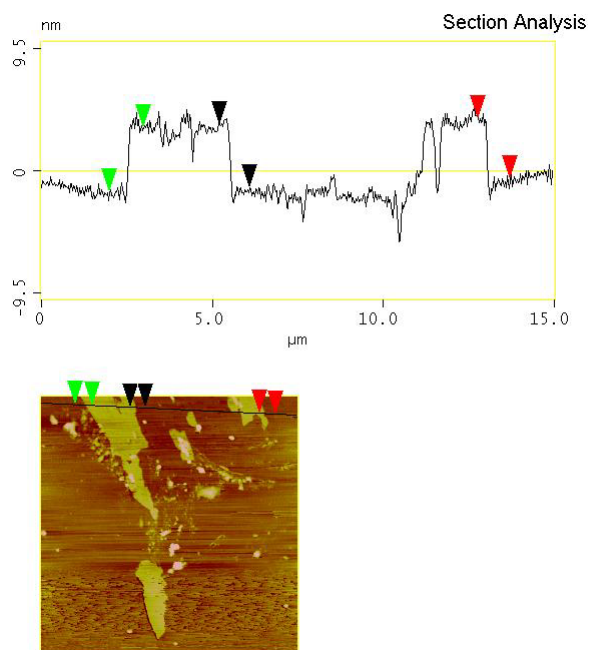


Fig. SI2. AFM analysis of the graphene prepared.

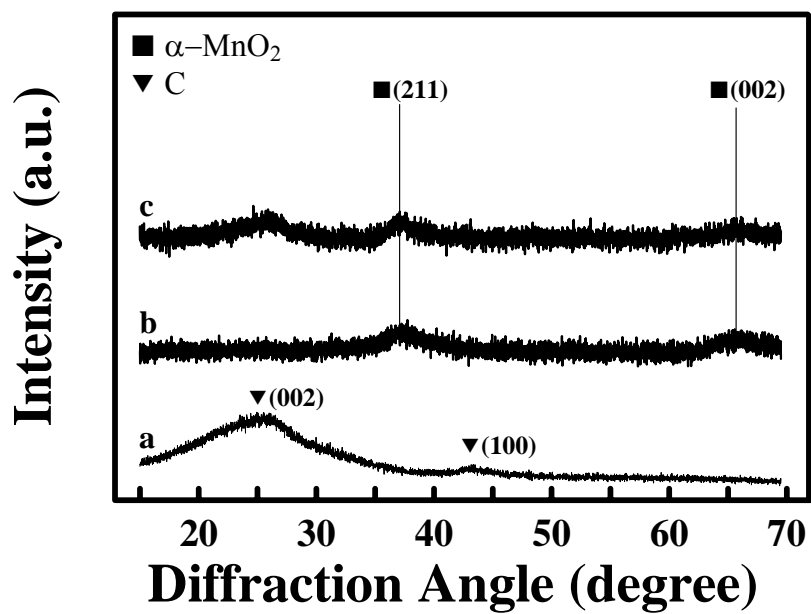


Fig. SI3. X-ray diffraction patterns of pristine graphene (curve a), plain MnO₂ (curve b), and the MnO₂/GNS-90/10 nanocomposite (curve c).

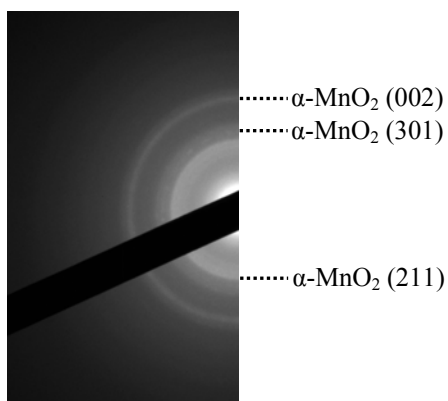


Fig. SI4. Electron diffraction pattern of the MnO₂/GNS-90/10 nanocomposite.

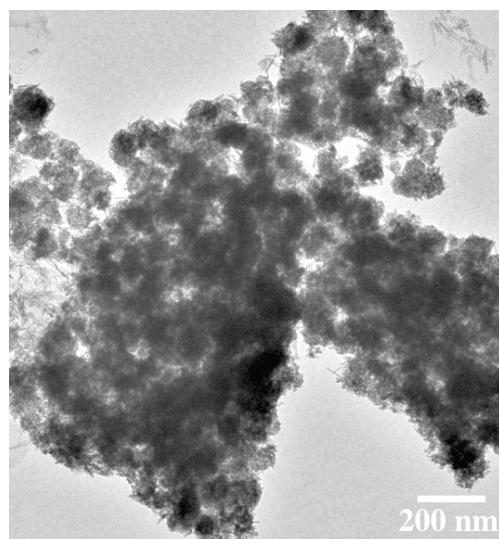


Fig. SI5. TEM image of the MnO₂/GNS-90/10 nanocomposite.

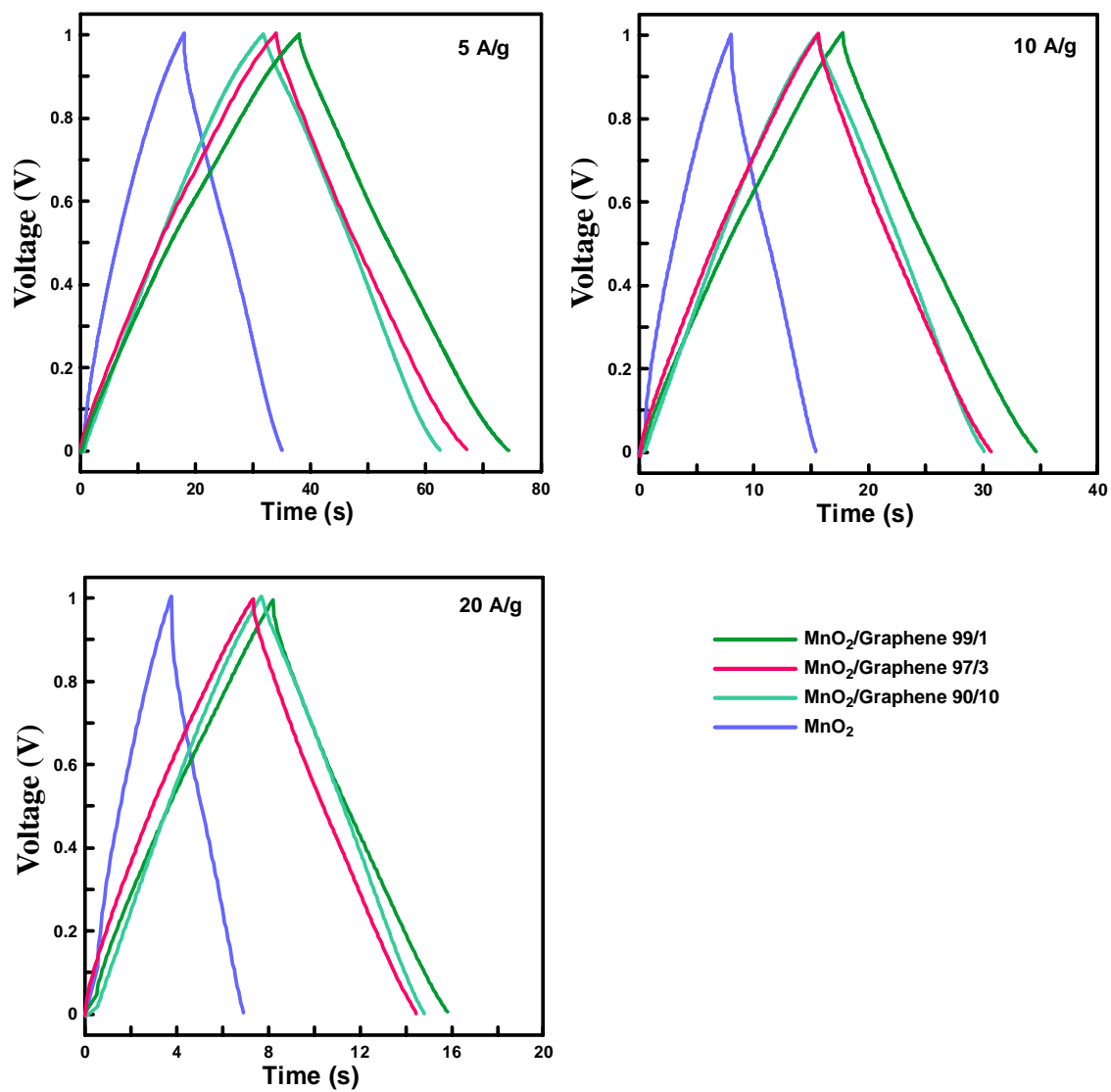


Fig. SI6. Galvanic charge/discharge curves measured on a two-electrode configuration at various applied current densities.