

Boosting energy storage performance of commercial Fe₃O₄ Nanoparticles by facile anchoring on rGO Nanosheets

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Graphene with its extraordinary electrical conductivity and theoretically large surface area (2630 m² g⁻¹) has sparked increasingly attention as an electrode material or complementary component in energy storage applications.¹ Accordingly, graphene/metal oxide nanocomposites have been extensively synthesized and investigated as promising electrode materials for supercapacitors.² In this fashion, metal oxide particles serve as high capacitance faradaic species as well as spacers that prevent restacking of graphene layers. Eventually, combination of electrochemical double layer capacitance (EDLC) originated from graphene and faradaic capacitance coming from the metal oxide along with synergistic effects will result in improved performance, superior to the single components. Among all metal oxides, Fe₃O₄ is considered as a propitious negative electrode material due to its broad potential window, high theoretical capacitance, low cost, and benignity.^{3,4} However, like other metal oxides it suffers from relative poor electrical conductivity which can be mitigated by hybridizing with carbonaceous materials (e.g. graphene). However, only few works studied the effect of graphene hybridization with Fe₃O₄ for supercapacitor applications.^{5,6}

Herein, we report a cheap method to anchor commercially available Fe₃O₄ nanoparticles (10-20 nm) on graphene oxide (GO) nanosheets via facile electrostatic co-precipitation. Their evaluation as negative electrode materials for aqueous asymmetric supercapacitors (ASCs) is also reported. Various nanocomposites with different component ratios (Fe₃O₄:rGO = 1:0.5; 1:1; 1:2; 1:3; 1:4; and 1:5) have been prepared to explore the optimized condition for the highest energy storage performance. Structural, compositional, and morphological characteristics of the prepared samples were achieved by X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). **Figure 1a** shows TEM image of Fe₃O₄-rGO [1:1] nanocomposite, revealing homogeneously dispersed iron oxide nanoparticles on thin layers of rGO. Furthermore, N₂ adsorption/desorption measurements were conducted to investigate textural properties of the prepared samples, showing significant increased specific surface area upon introducing rGO into the samples (i.e. 143 m² g⁻¹ for Fe₃O₄-rGO [1:1] sample against 93 m² g⁻¹ for the pure Fe₃O₄ nanoparticles). The electrochemical behavior of the samples as supercapacitor electrode materials was investigated through different techniques including cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) in 3 M KOH solution. Interestingly, all nanocomposites showed better electrochemical storage properties than pure Fe₃O₄ nanoparticles and rGO nanosheets (**Figure 1b**), suggesting superior performance due to synergistic effects. As it is seen, Fe₃O₄-rGO [1:1] nanocomposite exhibited the highest capacitance (446 F g⁻¹ at a scan rate of 5 mV s⁻¹) and best rate capability in comparison with the rest of composites. To further evaluate the applicability of Fe₃O₄-rGO nanocomposite, asymmetric supercapacitors (ASC) based on Fe₃O₄-rGO [1:1] nanocomposite as negative electrode and commercial MnO₂ as positive electrode were assembled and examined by various electrochemical techniques. Fe₃O₄-rGO//MnO₂ ASC demonstrated a maximum specific energy of 8.1 Wh kg⁻¹ and a maximum specific power of 4.5 kW kg⁻¹, with excellent rate capability and cycling stability over 2000 cycles.

References:

- [1] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K. M. Kohlhaas, E.J.Zimney, E. A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, *Nature*, **442** (2006), 282.
- [2] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A.C. Ferrari, R.S. Ruoff, V. Pellegrini, *Science*, **347** (2015), 1246501.
- [3] Q. Qu, S. Yang, X. Feng, *Advanced Materials*, **23** (2011), 5574.
- [4] Y. Chen, H. Xia, L. Lu, J. Xue, *Journal of Materials Chemistry*, **22** (2012), 5006.

[5] T. Qi, J. Jiang, H. Chen, H. Wan, L. Miao, L. Zhang, *Electrochimica Acta*, **114** (2013), 674.

[6] K. Wasinski, M. Walkowiak, P. Polrolniczak, G. Lota, *Journal of Power Sources*, **293** (2015), 42.

Figures:

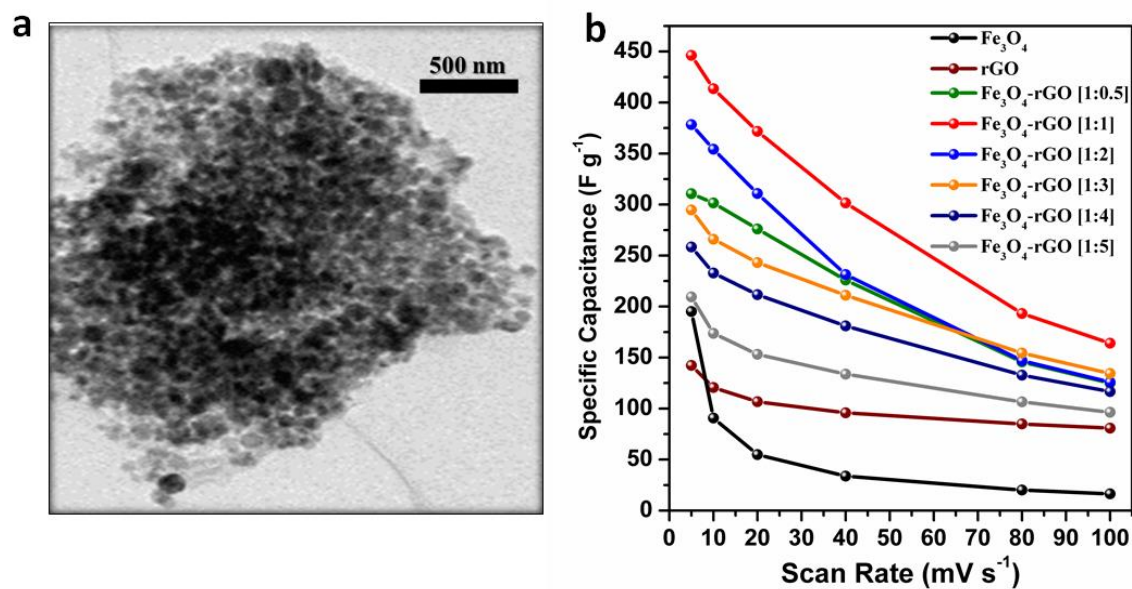


Figure 1. (a) TEM image of Fe₃O₄-rGO [1:1] nanocomposite, showing well dispersed nanoparticles on rGO layers (b) Rate capability of the samples at various scan rates.