SPION-Graphene Nanocomposites for Electrochemical Energy Storage and Conversion Devices

Vishwas N. Joshi[1], Anuja-Ria Joshi[2].

[1.] Anvesha Labs Incorporated, Setauket, NY, USA.
[2.] Stony Brook University, Stony Brook, NY, USA.

Superparamagnetic iron oxide nanoparticle (SPION) nanostructures by themselves suffer from aggregation after reaction, poor capacity retention and low electronic conductivity [1]. Graphene, a 2D material wherein carbon atoms are in a hexagonal arrangement, has high surface area, high conductivity, excellent chemical and thermodynamic stability, unique light-weight characteristic and superior optical, thermal and mechanical properties [2]. Aggregation or restacking of graphene reduces specific surface area of electrodes and negatively affects electrode and device performance [2], whereas, SPION-graphene nanocomposites (SPION-GNCs) minimize graphene aggregation and restacking and exhibit synergistic effects, and enhanced electrode and device performance [3].

Herein, we report preparation of SPION-GNCs by thermal treatment of SPIONs stabilized with methoxy-polyethylene glycol-carboxylic acids (mPEG-COOHs). mPEG-OHs (0.5-5 kDa) were oxidized to mPEG-COOHs [4] by following methods: i) sulfuric acid/chromium trioxide; ii) Copper (I) Chloride and 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) under ambient/aerobic conditions; iii) aerobic oxidation with TEMPO and ceric ammonium nitrate; and iv) TEMPO and oxygen (O_2) under very high pressure at 20 to 40 °C. TEMPO/O_2 at >10 atmospheres and room temperature produced clean mPEG-COOHs after 48 to 72 h without any detectable degradation products. TEMPO can be removed by washing the final product with saturated sodium thiosulfate solution acidified with hydrochloric acid. This method is suitable for large-scale production of mPEG-COOHs; however, an expensive high-pressure reactor and appropriate engineering controls for safe O_2 venting are required.

mPEG-COOH stabilized SPIONs were prepared by heating a mixture of Fe(III)-organometallic complex and mPEG-COOH in 2-pyrrolidone at 200-300 °C for 1.5 to 5 h. The average size of the SPIONs can be manipulated (4 to 10 nm diameter) by adjusting Fe(III)-complex-to-mPEG-COOH molar ratio and mPEG-COOH molecular weight.

SPION-GNCs were prepared by heating mPEG-COOH stabilized SPIONs at 125°C to 175°C for 2h – 72h. **Fig**. **1** shows STEM and HRTEM of SPION-GNC that was prepared by heating mPEG-2k-COOH stabilized SPIONs at 135 °C for 4h {The mPEG-2k-COOH stabilized SPIONs were prepared heating a mixture of mPEG-2k-COOH and Fe(III)- organometallic complex (1:4 molar ratio) at 200 °C for 0.5 h, followed by heating at 300 °C for 4h; all the results presented here are for this SPION-GNC sample}. The SPION particle sizes range from 2 to 20 nm with an average size of ~10 nm (**Fig**. **1A**) and have a crystalline structure (**Fig 1**. **B-D**). HRTEM also shows the presence of graphene nanoparticles (GNPs) as judged from contrast and lattice parameters (**Fig 1B**). The STEM-EDS shows that the SPIONs are dispersed in graphene; the copper signal in EDS is from the grid and silicon signal is likely from glassware used for synthesis (data not shown).

The saturation magnetization (Ms = 1.99 x 10^{-4} emu), remanent magnetization (Mr = 1.39 x 10^{-5} emu), and squareness (Ms/ Mr = 0.07) values (295.15 K; thin film) indicate that superparamagnetism of the SPIONs is retained following SPION-GNC synthesis (**Fig**. **2A**). XPS data further confirms that the

hybrid nature of SPION-graphene composite (**Fig**. **2B**). SEM/EDX analysis shows higher composition of carbon than iron suggesting that the SPIONs are dispersed in graphene matrix (data not shown). The current-voltage curves for SPION-GNC are not linear suggesting their non-conducting/semiconducting nature at room temperature, while thermogravimetric analysis indicates ~37.4% graphene/organic contents. Further, the specific capacity of SPION-GNC drops from ~935 mA h g^{-1} for the first cycle to ~320 mA h g^{-1} for the 50th cycle at 100 mA g^{-1} charge/discharge rate (data not shown).

Efforts are underway to produce SPION-GNCs with improved performance for electrochemical energy storage and conversion devices, e.g., electrodes for rechargeable lithium ion batteries and supercapacitors for portable electronic devices and hybrid electric vehicles.

References:

[1] G. Huang, et al, ACS Appl. Mater. Interfaces, 6 (2014) 7236.
[2] D. Chen, et al, Chem. Rev., 112 (2012) 6027.
[3] L. Li, et al, Carbon, 67 (2014) 500.
[4] M. Hudlicky, "Oxidations in Organic Chemistry" (ACS, Washington DC).
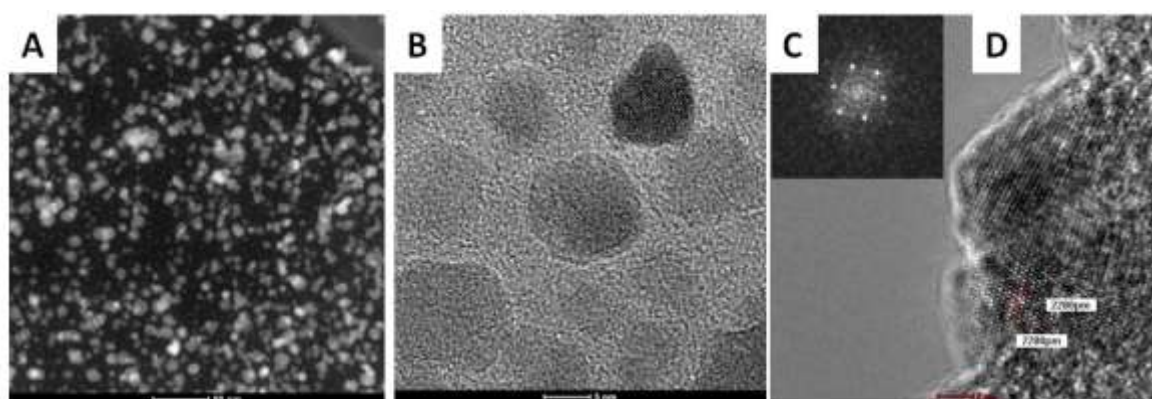
Figure 1. STEM (**A**) and HRTEM (**B**) of SPION-graphene hybrid particles. The diffractogram (**C**) and lattice parameters (**D**) suggest crystalline structure.
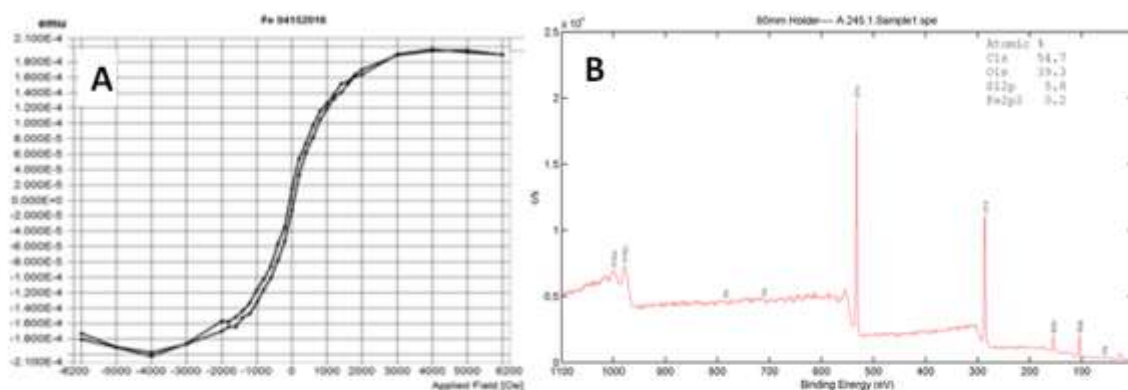
Figure 2. Magnatization curve (A; thin film) and XPS (B; dried) of SPION-graphene composite particles prepared from mPEG-2k-stabilized SPIONs.