Supporting Information

Conformational Changes of Graphene and Induced by Metal: Melting Metal can Spin a Graphene's Cocoon to Encapsulate its Own

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1. Experimental Section

Preparation of graphene-encapsulated metal microspheres: The GNSs were fabricated in our previous work.[1] The graphene-encapsulated Cu (Cu@G) microspheres were prepared by *co-pyrolysis* of GNSs and Cu(NO₃)₂·5H₂O. Typically, the GNSs (20 mg) and Cu(NO₃)₂·5H₂O (100 mg) were dispersed in 20 ml ethanol and tip-sonicated for 30 min with a Misonix 3000 probe sonicator at 100 W. Then, after removing ethanol at 80 °C under vigorous stirring, the Cu@G microspheres were obtained by annealing the mixture of GNSs and Cu(NO₃)₂ at 800 °C for 3 hours in nitrogen gas atmosphere. For investigating the formation process of Cu@G microspheres, intermediate products were also prepared by annealing the mixture of GNSs and Cu(NO₃)₂ at 800 °C for 0 and 1 h, respectively.

Fe@G microspheres and Co@G microspheres can also be prepared by using similar procedures. The Fe@G microspheres were obtained by heating the mixture of GNSs and Fe(NO₃)₃ at 1000 °C for 3 hours in nitrogen gas atmosphere. For investigating the formation process of Fe@G microspheres, intermediate products were also prepared between 800 to 1000 °C. The Co@G microspheres were obtained by heating GNSs and Co(NO₃)₂ at 1000 °C for 3 hours

Characterization: Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) measurements were carried out with a JEOL JEM-3010 F microscope operating at 200 kV. The measurements on the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images, energy dispersive X-ray spectrum (EDX) elemental mapping, and corresponding HRTEM images were carried out using Tecnai G2 F20 U-TWIN electron microscope with an accelerating voltage of 200 kV. The samples for TEM and HRTEM observations were prepared by dispersing the products in ethanol with an ultrasonic bath for 15 min and then a few drops of the resulting suspension were placed on a nickel grid.

Scanning electron microscope (SEM) observation was conducted on a Hitachi S-4700 field emission scanning

electron microscope.

X-ray diffraction (XRD) measurements were performed with a Rigaku D/max-2500B2+/PCX system using Cu K α radiation (λ =1.5406 Å) over the range of 5-90° (2 θ) at room temperature.

The Raman spectra were recorded from 1000 to 2000 cm⁻¹ at room temperature using a HR 800 Raman spectrometer (produced by HORIBA Jobin Yvon company) with an excitation line of 532 nm and using an Olympus microscope and a 50×microscopy objective to focus the laser beam onto a spot of 1 μ m².

X-ray photoelectron energy spectra (XPS) spectra were recorded using monochromatic AlK(1486.6 eV) X-ray sources with 30 eV pass energy in 0.5 eV step over an area of 650 μ m × 650 μ m to the sample. Before XPS measurement, the sample is degassed under a high-vacuum condition (< 10⁻⁷ Pa) to remove the adsorbed water and oxygen. Atomic concentrations were calculated using peak areas of elemental lines after Shirley background subtraction and taking account of the sensitivity factors, the asymmetry parameters as well as the measured analyzer transmission function.

[1] Guo P, Song H, Chen X. Electrochemical performance of graphene nanosheets as anode material for lithium-ion batteries. *Electrochemistry Communications*, **2009**, 11, 1320–4.



2. Supporting Data

Figure S1 EDX spectrum of the Cu@G microsphere shown in the Figure 1 c-f, which was obtained from HAADF-STEM elemental mapping measurement, and (inset) its elemental composition. Ni signal come from the nickel grid.



Figure S2. XRD patterns of Cu@G microspheres.



Figure S3. SEM and model images of a Cu@G microsphere obtained at 1000 °C for 2 h, which should reveal the curl information of GNSs.



Figure S4 XRD pattern of Fe@G microspheres.



Figure S5 SEM images of (a) Fe@G microspheres, and (b) a typical Fe@G microsphere obtained at 1000 °C for 3 h.



Figure S6. EDX spectrum and elemental composition of Fe@G microsphere inserted in the spectrum.



Figure S7. SEM image of a Fe@G microsphere, in which it can be seen that a GNSs is curled.



Figure S8 SEM images Fe/GNSs intermidiate products obtained at 800 °C for 0 h (a), 1000 °C for 0 h (b), (c,d) SEM and model images of microspheres obtained at 1000 °C for 1 h, and (d) conceptional model of curl of GNSs driven by metal.

Discussion: Formation of Fe@G microspheres is similar to that of Cu@M microspheres. At 800 °C for 0 h, Fe nanoparticles are well-dispersed on the graphene layer (Fig. S8a). After annealing in further, an "pomegranate-like" structure of graphene-coated many Fe nanoparticles (Fig. S8b) is formed, which is very similar to that for Cu shown in Fig. 3b. This indicates that the "pomegranate-like" structure is a necessary stage for formation of M@G microsphere. At 1000 °C for 2 h, Fe particles in the GNSs coats can aggregate in further into the larger spheres (Fig. S8 c, d). However, compared with surface of microspheres obtain at 1000 °C for 3 h (Fig. S5), surface of Fe@G microspheres obtained at 1000 °C for 1 h is rougher. Interestingly, some inner particles are exposed outside the GNSs coats. And imperfect M@G microsphere as shown in Fig. S7c and d, can also be found in Cu/GNSs system (Fig. S3). In addition, a Fe@G microsphere, in which a graphene sheet is inserted, is also observed. These results could reveal that, when they aggregate into bigger particles, melting metal nanoparticles can drive GNSs curling from their boundary to center and then form a coat to encapsulate many metal particles (Fig. S8e, and Scheme 1).



Figure S9. SEM images of (a) Co@G microspheres, and (b) a typical Co@G microspheres microsphere.



Figure S10. XRD pattern of Co@G microspheres.



Figure S11. (a) TEM image of Cu/GNSs composites and (b) HRTEM images of a typical Cu nanoparticle connected tightly with GNSs obtained at 800 °C for 0 h.



Figure S12. Raman spectra of (a) Cu nanoparticles/GNS composite nanosheets obtained at 800 °C for 0 h and (b) Cu@G microspheres obtained at 800 °C for 3 h.



Figure S13. XPS spectra: (a) C1s and (b) O1s spectra of GNS. (c) C1s, (d) Cu2p3/2, and (e) O1s spectra of Cu nanoparticles/GNS composite nanosheets obtained at 800 °C for 0 h. (f) C1s, (g) Cu2p3/2, and (h) O1s of Cu@G microspheres obtained at 800 °C for 3 h.