

Graphene-wrapped electroconductive hybrid spheres

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Keywords: grapheme, hybrid spheres, electroconductivity, ionic interaction

Abstract

We present a simple approach for the fabrication of electro-conductive spheres. Assembly of graphene sheets containing anion with cationic polymer spheres was performed by simply mixing them. Deposition of graphene on polymer sphere resulted in thin layers of graphene on spheres to thickness of about 5 nm, and good electroconductivity..

1 Introduction

As well known, graphene, two-dimensional graphite, exhibits remarkable, electronic properties that quantify it for applications in future optoelectronic devices.^{[1]-[4]} To date, most of researches concerning the applications of graphene have been poured into the evaluation of natural properties of graphene itself, mass production of well crystalline graphene nanosheets or the two-dimensional device applications, such as transparent conductive films. Recently, our group found that the simple modification of graphene surface without loss of the conductivity can be adapted to fabricate three-dimensional functional materials such as conductive micro/nanospheres, which have been highly requested due to the environmental problems induced by highly toxic chemicals during the metal-plating process.

Herein, we present a simple approach for the fabrication of monodisperse nanospheres with outstanding electro-conductivity, as an alternative to the conventional metal-plated conductive particles.

2 Results and Discussion

In order to obtain conductive nanospheres, assembly of graphene sheets of anion charge with cationic polymer spheres was performed by simply mixing them together in water medium, as illustrated in Figure 1.

We found a spontaneous change of dispersion from respective colloidal states of graphene and polymer spheres to irreversible agglomerates, indicating the formation of graphene-polymer sphere assembly accompanied by spontaneous anion-cation coupling reaction.

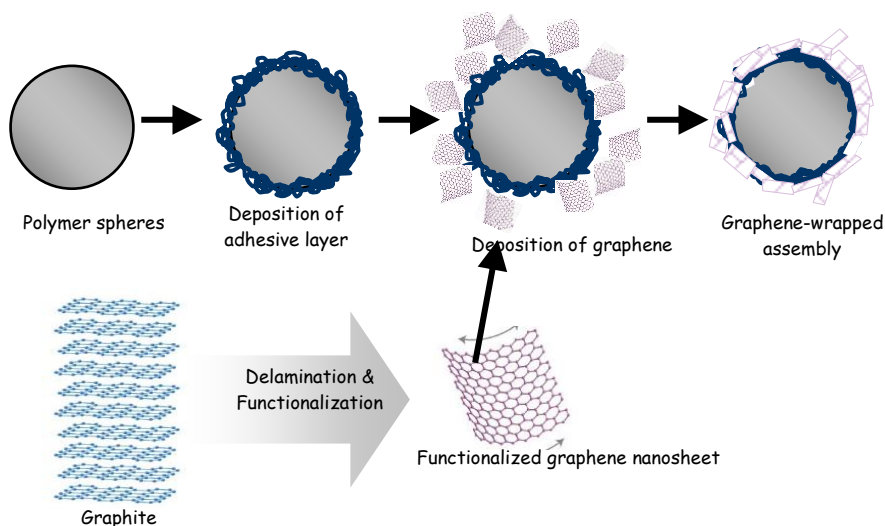


Figure 1. Schematic illustration of preparation of graphene-wrapped hybrid spheres.

As shown in Figure 2, SEM images obviously show that the polymer spheres were successfully decorated by graphene nanosheet patch. In this system, the ionic interaction drove the graphene sheet to anchor on the polymer surface. Although the repulsive force among anionic graphene sheets should suppress the formation of multilayered adsorption of graphene on the surface of cationic polymer spheres, it was found that deposition of anionic graphene sheets on the cationic surface of polymer spheres seems to occur rapidly to form graphene-polymer hybrid spheres without any void surface. Deposition of graphene sheets on polymer sphere is supported by TEM examination, showing that thin layer of graphene sheet was well deposited on the surface of polymer spheres to thickness of about 10 nm.

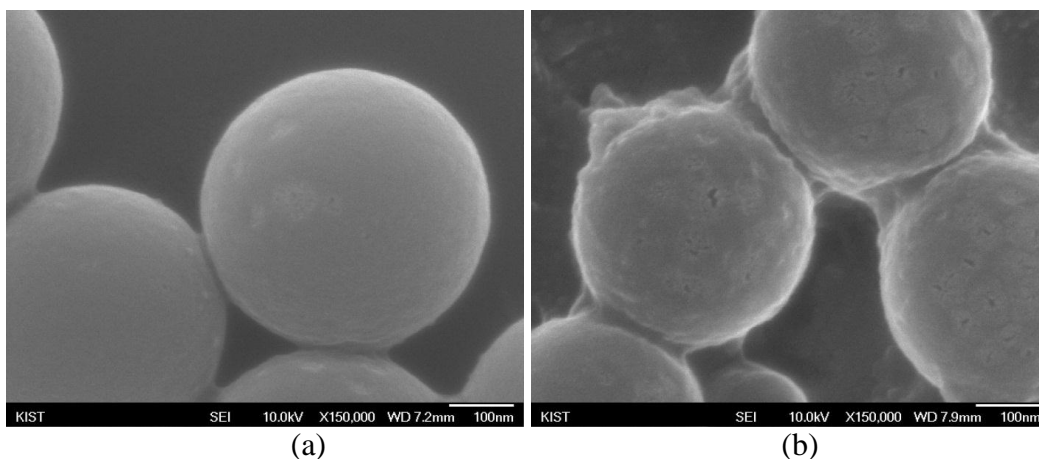


Figure 2. Scanning electron microphotographs of (a) PS spheres and (b) graphene-wrapped hybrid spheres.

In order to assess the electrical conductivity of graphene-wrapped hybrid spheres, the suspension of hybrid spheres in ethanol medium was deposited on a fresh slide glass pre-heated at 150 °C to form a translucent film, which exhibited an electrical conductivity of 2.51 S/m under four-probe method. Also, electron flow between hybrid spheres was successfully accomplished through ohmic contact of the graphene layers deposited on PS surfaces, as found in Figure 3.

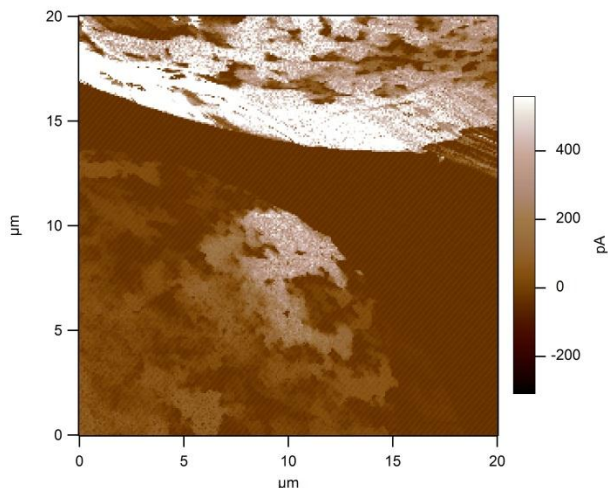


Figure 3. AFM microphotographs of graphene-wrapped hybrid spheres under the conductive mode, showing electron flow.

While the electrical conductivity of the cells made with graphene-wrapped hybrid spheres would not be enough, possibly due to the partial lack of ohmic contact between each hybrid sphere, it can be told that the electron transfer behavior found in graphene sheets is preserved through simple formation of hybrid with insulating polymer spheres.

3 Materials and Characterizations

Negatively charged graphene sheets: negatively charged graphene sheets were prepared through chemical oxidation of expandable graphite flake (Graftech) using a modified Hummer's method, followed by reduction using hydrazine hydrate as noted in refs [5] and [7]. First of all, the ground graphite flake (~ 0.85 g) was stirred in 98% H_2SO_4 (23 mL) for 8 h, and KMnO_4 (3 g) was gradually added to the dispersion. Next, the mixture was diluted with distilled water and heated at 100°C for 30 min. The reaction was terminated by addition of distilled water (140 mL) and 30% H_2O_2 solution (10 mL). The mixture was washed by repeated centrifugation at 8000 rpm for 30 min, first with 5% HCl aqueous solution, and then distilled water. The resulted graphite oxide was suspended in water to give a brown-colored dispersion, which was subjected to dialysis to completely remove residual salts and acids.

Exfoliation of the obtained graphite oxide to graphene oxide (GO) was achieved by ultrasonication of the dispersion. The obtained brown dispersion was then subjected to 30 min of centrifugation at 3000 rpm to remove any unexfoliated graphite oxide. Finally to obtain negatively charged graphene sheets, homogeneous dispersion (100 mL) of the synthesized graphene oxide was mixed with 250 mL of distilled water, 10 mL of hydrazine solution and $700\ \mu\text{L}$ of ammonia solution. Under intensive stirring, the dispersion was put in an oil bath controlled at 95°C for 1 h. Excess hydrazine in the resulting dispersion was extensively removed by repeated dialysis against ammonia solution once the reduction is complete.

Positively charged polystyrene spheres: cationic polystyrene spheres were prepared by emulsifier-free emulsion copolymerization, as noted in ref [6].

Assembly: cationic PS spheres (0.08 g) and anionic graphene sheets (0.05 g), respectively dispersed in deionized water, were mixed on sonicator for 30 min and then were vigorously shaken for 12 h at room temperature on vortex shaker. Subsequently, the coagulates were collected by centrifugation of 5000 rpm and dispersion in water at least three times, and finally dried on freeze-dryer for 24 h.

The morphology of cationic PS spheres and hybrid spheres was characterized by field emission-scanning electron microscope (JSM-6701F, JEOL) working on accelerating voltages of 5 to 15 kV. The specimens were platinum-coated prior to examination. TEM images were acquired using a JEOL 3000F transmission electron microscope. The accelerating voltage was 300 kV. Atomic force microscopy (AFM) imaging was performed on Nanoscope III (Asylum). Electrical conductivity measurement was performed by the four-probe method using Keithley 6512 digital multimeter equipped with a YEW2553DC voltage current standard at room temperature.

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