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Short Communication

Ultrasound assisted synthesis of Sn nanoparticles-stabilized reduced graphene oxide nanodiscs

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ABSTRACT

Sn nanoparticles-stabilized reduced graphene oxide (RGO) nanodiscs were synthesized by a sonochemical method using $SnCl_2$ and graphene oxide (GO) nanosheets as precursors in a polyol medium. TEM and XPS were used to characterize the Sn-stabilized RGO nanodiscs.

1. Introduction

The isolation of graphene oxide nanosheets by the Scotch tape method in 2004 [1] has led to an extraordinary amount of interest among researchers across virtually all scientific disciplines. This is mainly due to the presence of covalently bound oxygen-containing functional groups in graphene nanosheets providing remarkable structural, mechanical and electronic properties. In such graphene nanosheets, carbon allotropes are arranged in a hexagonal lattice by strong sp^2 hybridized bonds in a two dimensional structure. In addition, GO nanosheets show a very high surface area ($2630\ m^2\ g^{-1}$) and a high electrical conductivity ($10^{-6}\ \Omega\ cm$) [2–4]. However, there is a limitation in electronic and optoelectronic applications [1,5] since GO nanosheet is a zero band-gap semiconductor. Research is focused on tuning the band-gap by modifying GO nanosheets into nanoribbons, quantum dots, hybrid materials, hollow spheres, etc. The high performance of modified GO sheets is due to quantum confinement and edge effects [6–10]. Significant effort has been devoted to develop such self assembled nanocomposites using various methods including solution-based synthesis, solvothermal methods, electro-beam lithography and ultrasonic spray pyrolysis; however it is difficult to control the size distribution by these methods [1,7]. The development of new methods to generate uniform size distribution under mild reduction conditions using minimal external reagents is a key challenge. Guo et al. [6] reported the synthesis of hollow GO spheres using an emulsification process. Song et al. [9] synthesized mesoporous RGO spheres using a combined method of spray pyrolysis and self-aggregation. Sonochemical method has been recently applied for the reduction of GO to RGO nanosheets to obtain a homogeneous dispersion of exfoliated graphene sheets with simultaneous loading of metal nanoparticles [11,12]. The shear forces generated by acoustic cavitation are enough to overcome the van der Waals forces between the graphene sheets resulting in the exfoliation of the graphene sheets. We have recently reported the ultrasonic synthesis of Pt/Sn bimetallic nanoparticles loaded RGO using simultaneous reduction of Pt/Sn ions and GO for electrochemical applications [13].

The aim of the current study was to synthesize RGO nanodiscs stabilized by Sn nanoparticles by an integrated reduction method where GO sheets were used to generate RGO nanodiscs with a simultaneous deposition of sonochemically generated Sn nanoparticles on the edges of the nanodiscs. The sonochemical procedure established in this study utilizes the physical and chemical effects generated during acoustic cavitation.

2. Experimental details

All chemicals were of the highest purity available and were used as received without further purification. About 100 mg of

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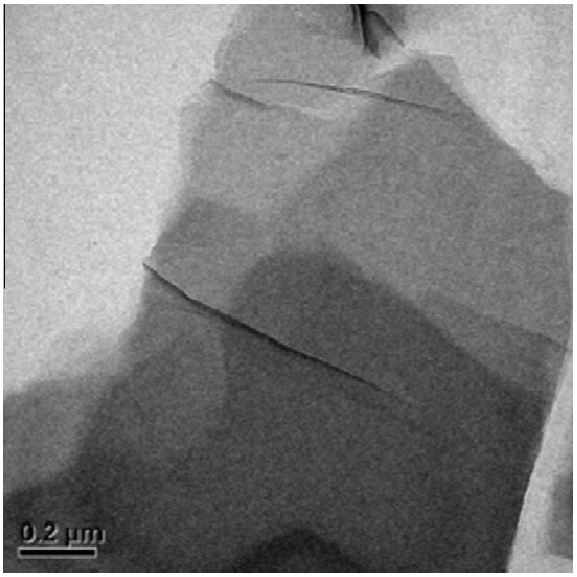

Fig. 1. TEM image of sonochemically prepared reduced graphene oxide nanosheets.

GO nanosheets with 100 mg $SnCl_2$ was dispersed in 40 ml of ethylene glycol in a sonication vessel sonicated for about 3 h under argon atmosphere. Generally, GO nanosheets used in the experiments were typically about 1 μm in length. A horn type 20 kHz Branson sonifier (40 W cm^{-2}) with a tip diameter of 1 cm was used. Following sonication, solid product was separated from the supernatant by centrifugation at a speed of 10,000 rpm for 10 min and subsequently washed five times with absolute ethanol in order to remove any contaminant. Finally, the product (yield 120 mg) was dried under vacuum at room temperature. For comparison, similar experiments were performed with only 100 mg of GO nanosheets dispersed in 40 ml of ethylene glycol in a sonication vessel in the absence of $SnCl_2$ (yield 70 mg).

Material phase analysis of the prepared nanostructures was carried out by X-ray photoelectron spectroscopy, XPS (measured using Physical Electronics PHI 5600 XPS spectrophotometer with monochromatic Al-K (1486.6 eV) excitation source), and the morphology of the samples was analyzed using High Resolution Transmission electron microscopy (HRTEM; recorded using TECHNAI G^2 model). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo IS-5 FT-IR spectrophotometer equipped with an attenuated total reflectance (ATR) accessory. Atomic force microscopic (AFM) studies were carried out in XE100-Park systems. All of the images were obtained using a tapping mode with silicon cantilevers. ICP-OES experiments were carried out in Teledyne Leeman Labs, Prodigy High Dispersion ICP-OES instrument.

3. Results and discussion

TEM images of the products obtained after sonication treatment are shown in Figs. 1–3. A very interesting observation is the difference in RGO morphology in the absence and presence of $SnCl_2$ in the reaction medium. It can be seen from Fig. 1 that sonication of pure GO in EG led to the formation of RGO nanosheets. These sheets are a few micrometers in size with slightly scrolled on edges, which indicates that the adopted ultrasonic procedure effectively exfoliated the GO as reported in earlier studies [12]. Sonication led to mostly single layered (>70%, topographic height 2.0 nm) sheets with a lateral width of 21 nm as determined by AFM analysis (data not shown). However, when $SnCl_2$ was present in the solution, RGO nanodiscs were formed (Fig. 2a and b). The particle size distribution of GO nanodiscs is about 80–100 nm in diameter.

First, let us consider the reason for the formation of disc shaped RGO in the presence of $SnCl_2$. It is probable that conversion of acid (–COOH) functional groups to ester (–COOR) occurred in the presence of $SnCl_2$, a Lewis acid catalyst and ethylene glycol (R) [14]. The shear forces that are generated by acoustic cavitation may break the nanosheets into nanodiscs that may possess a lower surface energy [6,11,15–17]. Such conversion process may also be aided by the presence of Sn ions which upon sonication produces Sn(0) nanoparticles. It is well known that the secondary reducing radicals generated during acoustic cavitation can reduce metal ions to form metal particles. The Sn nanoparticles seem to aggregate on the edges that provide stability to the discs that otherwise may lead to folded/scrolled edges. TEM images clearly show the presence of Sn particles predominantly on the edges of the nanodiscs. From the high resolution TEM image (Fig. 3a), Sn nanoparticle lattice fringes are clearly visible. The observed amorphous pattern with rings in selected area electron diffraction (SAED) also provides further evidence to the formation of Sn nanoparticles. No other impurity is seen in the EDX (Fig. 3b and c), which indicates that the formed Sn and RGO discs are 100% pure. The Sn nanoparticles are generally spherical in shape with a size distribution of about 2–6 nm in diameter. In addition, FT-IR analysis were performed to provide evidence for the conversion of acid (–COOH) functional group to ester on the nanodisc. The FT-IR spectrum of

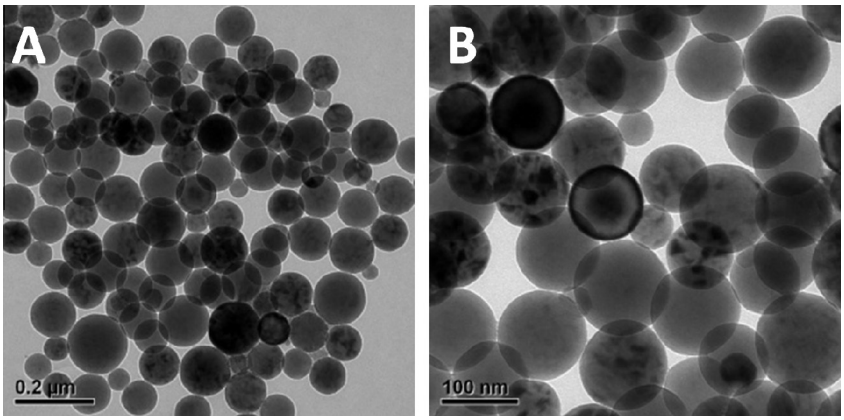

Fig. 2. TEM image of sonochemically prepared Sn nanoparticles intersected reduced graphene spheres.