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Using silicon nanoparticles to modify the surface of graphene nanosheets

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ABSTRACT

In this work, the synthesis and properties of the graphene/silicon nanocomposites as a function of volumetric ratio of Si nanoparticles and graphene nanosheets suspensions has been investigated experimentally. Firstly the silicon nanoparticles and graphene nanosheets suspensions were synthesized by pulsed laser ablation method with Q-switched Nd:YAG laser. Then the mixture samples with different volumetric ratio of the graphene and Si suspensions were irradiated with UV radiation. UV–Vis–NIR spectroscopy, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Raman spectrum, potential and dynamic light scattering, and photoluminescence spectra were used to characterize the ablation products and graphene/silicon nanocomposites produced by UV irradiation. Results confirmed the successful production of silicon nanoparticles and graphene nanosheets, and also formation of graphene/silicon nanocomposites. According to the results, with increasing the concentration of graphene nanosheets in the suspensions the surface morphology of the graphene/silicon nanocomposites was exfoliated. Zeta potential implies that the suspension of samples with higher concentration of graphene nanosheets is more stable.

1. Introduction

Recent years have seen a rapid growth of interest by the scientific and engineering communities in the nanostructured materials [1–3]. The graphene based composites have interested a lot of attention due to the fact that inclusion of graphene helps to make better device performance. Graphene composites can be used for a wide range of applications in photonics and optics [4,5].

Over the past several years, the interest in nanocomposites of Si nanoparticles (NPs) and graphene nanosheets (GNSs) components has been exponentially enhanced due to their high electrical conductivity and small volume changes on lithiation in the lithium-ion batteries, which are extensively considered as the most promising portable power source for electric vehicles and electronic devices such as cell phones, digital cameras, laptops, etc [6–8]. In fact, because of the abundance in nature, reasonable price and high theoretical capacity, silicon has become an amazing option for anode in lithium-ion batteries [7,9] and graphene has been demonstrated to have significant physical and chemical properties like high carrier mobility at room temperature, large surface area, good optical transparency and superior electrical and thermal conductivity in comparison with other carbon nanostructures like graphite, carbon nanotubes and fullerenes [10].

Graphene/Silicon Schottky junction has shown potential applications in solar cells. In 2012, a graphene film and a pillar-array patterned silicon substrate were used to construct a graphene/silicon Schottky junction solar cell [11]. Miao et. al, has shown improved light harvesting in chemically doped graphene/n-Si Schottky junction solar devices [12]. Also graphene/Si heterostructure can be used for a variety of tunable optoelectronic devices with high responsivities over a broad spectral bandwidth in the visible region [13]. In general we can say that one of the important applications of graphene/silicon nanocomposites is in the rechargeable power sources for electronic devices. The achievement of high charge/discharge stability is the key to fabricating materials used in lithium-ion batteries. The merit of the prepared graphene/silicon nanocomposites is that the graphene may serve as an excellent carbon source for preparing carbon/Si hybrid anodes with respect to its high mechanical strength, high chemical and thermal stability, and high electrical conductivity [9].

Owning to these unique characteristics, many researchers have widely used graphene and graphene nanosheets as a flexible carbonaceous coating to develop variety of Si-based materials by different methods [8]. In these materials, GNSs were usually produced by the mechanical peeling-off of graphite, chemical vapor deposition, and chemical or thermal reduction of graphite oxide [7–9,14–16]. The method of production usually affects the properties of nanoparticles and graphene nanosheets. Since the commercial Si nanoparticles for lithium-ion batteries applications are still suffering from their high cost [17], we used the pulsed laser ablation (PLA) method to producing

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silicon nanoparticles and graphene nanosheets. Among all these several techniques, using pulsed laser ablation of solids in liquid medium has fundamental superiorities compared to the other methods and provides an impressive procedure for preparing various nanoscale materials. Overall this technique will not generate any poisonous byproduct and the nature of produced nanomaterials could be controlled by the ablation environment characteristics and also by adjusting different features of the used laser, such as its pulse width, wavelength and spot size [18–29].

There are also several physical and chemical methods to compose nanostructures. One is ablating one material in the solution of another one [18]. Another is irradiating the mixture of nanostructures solution by laser pulse [23]. In this case at least one of nanostructures should have a wide absorption peak around the laser wavelength. In the case of graphene or semiconductors we may use suitable UV sources to irradiate the nanostructures and compose them, since they have wide absorption band in the UV region. In some other cases we used ultrasonic waves to compose nanostructures [10].

Due to its remarkable applications, many researchers have prepared graphene/silicon nanocomposites through different methods including spray drying and subsequent annealing [6], chemical vapor deposition [7,14], ball milling and P-milling [8], chemical reduction of graphene oxide solution containing nano silicon [15,30], in-situ growth and magnesium thermal reduction [31], etc. Despite the widespread use of these preparation methods, the produced graphene/silicon composites do not exhibit desirable performances always. For example, in the case of physical mixing or solution-based methods, Si nanoparticles are rarely distributed uniformly on the graphene layer [6]. Thus, in contrast to the rather complicated mentioned chemical synthesis, UV radiation processes for preparing nanocomposites have attracted more attention and many researchers have implemented this novel method to produce variety of nanocomposities. According to Bastani et. al, UV-curable nanostructural composites have the advantages of both UV-curable systems and composite materials. As a result, they have been considered extensively in industries of coatings, inks, adhesives and printing. In UV-curable systems the photon absorption of UV–visible electromagnetic radiation initiates the curing reactions [32]. Kim et. al, investigated the preparation and properties of unsaturated polyester UP/montmorillonite nanocomposite by UV radiation [33] and Xia Li et. al, prepared polynailine/CuCl nanocomposites by UV rays irradiation method. In this method, photons in the UV rays and Cu^{2+} ions replaced conventional oxidant such as ammonium persulfate to promote polymerization of aniline monomer [34]. Han Xie and his co-worker also reported using UV radiation method along with sol–gel process to produce the polymer/SiO_2 nanocomposites [35].

In this experimental research, Si NPs and graphene nanosheets were produced through laser ablation method and then one-step synthesis of graphene/silicon nanocomposites was achieved by UV radiation for the first time. We have focused our study on the effects of volumetric ratios on the structure and morphology of graphene/silicon nanocomposites.

2. Experimental setup

2.1. Synthesis of graphene nanosheets and silicon nanoparticles

Graphene nanosheets were produced by pulsed laser ablation of a graphite plate (99.9%) in distilled water environment. Height of distilled water on the target was 0.8 cm. Graphite target was ablated with the fundamental wavelength (1064 nm) of a pulsed Nd:YAG laser operated at 7 ns pulse width and 5 Hz repetition rate. 6000 laser pulses were used to produce graphene nanosheets. The fluence of laser beam was 0.7 J/cm^2 with 6 mm diameter. Output of laser was focused on the surface of graphite target using a 100 mm focal length convex lens. Silicon nanoparticles were produced using the same system. Both targets and containers were cleaned ultrasonically in alcohol, acetone and deionized water before the experiments respectively.

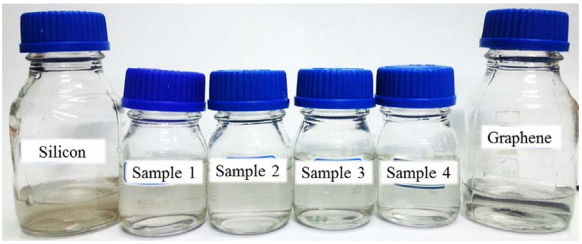

Fig. 1. Si nanoparticles and graphene nanosheets suspensions produced by laser ablation and mixture of Si nanoparticles and graphene nanosheets.

2.2. Synthesis of graphene/silicon composites

In the second step, the produced Si nanoparticles and graphene nanosheets suspensions were mixed in the different volumetric ratio. The samples were irradiated with UV radiation at room temperature and air atmosphere by using PHILIPS- TUV- 8 W - G8 T5- Ultraviolet Lamp, which emits strong lines at wavelength of 254 nm. The exposure time of the samples irradiated was 40 h. We mixed graphene nanosheets and Si nanoparticles suspensions at the volume ratio of 1/2 (sample 1), 1/1 (sample 2), 3/2 (sample 3), and 2/1 (sample 4), in other words 25, 37, 45, and 50 ml of graphene nanosheets suspension was mixes with 50, 37, 30, and 25 ml of Si nanoparticles suspension respectively. To indicate the weight of silicon and graphene in the suspensions dried targets were weighted before and after the ablation process. Ablated mass of silicon was 10^{-4} gr/ml and ablated mass of graphite was 2.5×10^{-5} gr/ml. Regarding these magnitudes the mas ratio of graphene nanosheets to silicon nanoparticles in samples were 0.125, 0.25, 0.375 and 0.5 gr/ml from sample 1–4 respectively.

Pictures of Si nanoparticles, graphene nanosheets and graphene/silicon nanocomposites suspensions are presented in Fig. 1. It was observed that after ablation the color of Si nanoparticles suspension was turbid and the color of graphene nanosheets suspension was colorless. The lack of color in the solution in this sample is due to the larger concentration of graphene nanosheets in comparison with carbon nanoparticles. With increasing the concentration of graphene nanosheets suspension the color of graphene/silicon nanocomposites suspensions was changed from turbid to colorless.

2.3. Characterization

A variety of analytical techniques were applied for the characterization of products. The optical properties of the graphene nanosheets, Si nanoparticles suspensions and graphene/silicon nanocomposites were examined at room temperature by Varian Cary-500 spectrophotometer. The crystalline structure of samples was analyzed by X-ray diffraction (XRD) with Cu-Kα radiation (λ = 1.54060 Å), using an STOE–XRD diffractometer. Zeiss EM10C transmission electron microscope was employed to investigate the size and form of samples. Transmission electron microscopy (TEM) was done by depositing a drop of the concentrated suspension on a carbon-coated copper grid. Scanning electron microscopy (SEM) micrographs were taken using KYKY-EM3200 systems. By using Zetasizer device (Malvern, Nano ZS (red badge) ZEN 3600), potential and Dynamic Light Scattering (DLS) of samples were measured. Raman spectroscope (light source: 532 nm diode laser from Avantes company, holder: model CVH100 cuvette holder from ThorLab company, spectrometer: Avaspec 3648 from Avantes company, light transfer: FCUVIR 400-1 fiber optics from Avantes company) was utilized to determine the structure, quality and amount of graphene in suspension. The luminescence properties of the samples were measured at room temperature by photoluminescence (PL) spectrophotometer (Cary Eclips) using a Xe lamp as the light source. The ablated mass was determined by weighing the substrate before and after the ablation process (using KERN 770 scale), with an