Preparation and Characterization of Conductive Polymer/Reduced Graphite Oxide (RGO) Composite via Miniemulsion Polymerization

Amany Gaffer[1] Delvin Aman[2]
1. Additives department - Petroleum Application Division, Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El Zomour St., Nasr city, PO Box 11727, Cairo, Egypt
2. Catalysis department - Petroleum Refining Division, Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El Zomour St., Nasr city, PO Box 11727, Cairo, Egypt

Abstract

Polymer/reduced graphite oxide (rGO) composite nanoparticles were prepared via miniemulsion polymerization. The rGO was modified with a reactive surfactant, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). The AMPS-modified rGO was emulsified in the presence of styrene (St) and Methyl meth acrylate (MMA) monomers, and the stable miniemulsion was polymerized to form poly (St-co-MMA)/rGO composite latex nanoparticles. The structure and morphology of the composite were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and particle size distribution of prepared composite by zeta seizer (ZS). The electrical conductivity of the reduced graphene polymer composite has been measured to be approximatel 2.5 S cm^{-1}

Keywords: Polymer/graphite composite, Miniemulsion, polymerization.

1. Introduction

Graphene, which is defined as a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice [1], has attracted significant interests in recent years due to its potential applications in many different areas [2-8]. One possible route to harness the remarkable properties of graphene sheets for applications would be to incorporate graphene sheets in composite materials. Manufacturing such composites requires not only that graphene sheets be produced on a sufficient scale but used in recent decades to prepare conducting polymer composites. Polymer-based materials with conductivity are highly desirable in practical applications, such as electronic devices, sensors, and electromagnetic shielding [1,7]. Because most polymers are insulating, a variety of materials may be used as conducting filler, such as metal nanoparticles [8], metal nanowires [9], and metal oxide particles [10]. Among these conducting fillers, graphite, which is naturally abundant, has been used in recent decades to prepare conducting polymer composites. The polymer composites containing the rGO filler displayed an outstanding electrical conductivity, suggesting their utility as electrode materials for use in lithium ion batteries and electronic circuits. The simple and effective technique reported here offers a new route to the large-scale environmentally friendly production of highly conductive polymer composites for practical applications.

Several methods have been used for fabricating polymer/graphite composites, including mechanical mixing [11], melt mixing [12], and in-situ controlled radical polymerization [13]. Among these techniques, miniemulsion polymerization is a useful method for preparing nanoscale latex particles, including the graphite filler [2,14,15]. Miniemulsion polymerization offers several advantages over other dispersion polymerization methods, such as the preparation of nano-sized latex particles with finely controlled shapes.

In this paper we synthesized reduced graphite oxide/poly (styrene-co-methyl meth acrylate composite with a high electrical conductivity using the miniemulsion polymerization technique.

2. Experimental section

2.1. Materials

Natural graphite, styrene (St) (99%) and methyl meth acrylate (MMA, 99%) were purchased from Sigmae-Aldrich and were used as received. Sodium dodecyl sulfonate (SDS) (85%, Samchun Chemical) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (99%, Aldrich) were used as received. Potassium persulfate (KPS) (99%) was obtained from Samchun Chemical and was purified by recrystallization from methanol. Potassium permanganate $KMnO_4$ (99%), sodium nitrate $NaNO_3$ (99%), sulfuric acid H_2SO_4 (98%), and hydrogen peroxide H_2O_2 (30%) were used to oxidize the pristine graphite.

2.2. Preparation of AMPS-treated rGO

The GO was synthesized from graphite powder by using Hummer method [16]. In this method, 1 g graphite powder and 1 g $NaNO_3$ were added to 46 mL H_2SO_4 solution in an ice bath. Prepared mixture was ultrasonicated for 10 min. Further, 5 g $KMnO_4$ was slowly added to the resulting mixture and then it was ultrasonicated for 30 min at 35 °C. To the formed solution, 100 mL DI water was slowly added and again ultrasonicated for 5 min, after which 8 mL H_2O_2 was added. Further the solution was filtered, washed with 150 mL HCl solution (10 wt. %) and 100 mL DI water. The GO was separated by centrifugation at 4000 rpm. Synthesized 0.1 g graphite oxide was added to 400 mL DI water and this mixture was further ultrasonicated for 30 min. GO layers were expected to be exfoliated through this ultrasonication process. The specification and details of an ultrasonicator and its processing parameters used during the experiments are as follows: ultrasonic processor: UP200S (Make Hielscher Ultrasonics GmbH, Germany), working frequency: 24 kHz, nominal output power: 200 W, diameter of stainless steel tip of horn: 13 mm. The temperature used for the reduction of GO was 1000° C. The treatments were performed in a horizontal tube furnace using a ceramic boat with a graphite cover to prevent the blowing of the material. 0.3 g of GO was introduced into the furnace and heated at 5 °C min under a N_2 atmosphere (100 mL min-1) to 1000° C and kept for 1 h [17].

Then 0.2 g rGO was introduced into a 1 L flask containing 300 ml DI water. The mixtures were stirred at room temperature for 30 min at 1000 rpm and then were sonicated for a further 30 min to achieve complete dispersion of the rGO nanosheets in water. The 0.16 g AMPS was added to the mixture to a concentration of 80 wt% relative to the rGO. The mixture was then stirred for a further 24 h at 800 rpm at room temperature. The AMPS-treated rGO was filtered and dried.

2.3. Synthesis of poly (St-co-MMA)/rGO composites by miniemulsion polymerization

AMPS-treated rGO (modified with 80 wt% AMPS relative to the rGO) was added to the monomer mixture of 9 g St and 1 g MMA, and the mixture was stirred for 1 h to allow effective solvation of the rGO with the monomers. The mixture was introduced into a 250 mL flask containing the DI water stirred at 1500 rpm, and 2 wt% (relative to the monomer) 0.2 g SDS, a surfactant, was immediately added to the flask The mixture containing the AMPS-treated rGO and SDS was stirred for 30 min and sonicated for 10 min to obtain the miniemulsion latex. 0.15 g KPS was added and the contents of the flask were purged with nitrogen for 30 min before increasing the temperature to 70° C to initiate polymerization. The reaction proceeded for 4 h under a nitrogen atmosphere, and the polymerization reaction was stopped by cooling to room temperature [18].

3. Characterization

X-ray diffraction Analysis (XRD) was carried out using Shimadzu XD-1 diffractometer in 2θ range between 4 and 80^o. The morphology of the samples was characterized by scanning electron microscopy (SEM) (Hitachi S-4200) using an accelerating voltage of 8 kV and high-resolution transmission electron microscopy (HR-TEM) (JEOL 2100F). Size distribution of prepared composite was analyzed by zeta seizer ZS (Malvern,UK). The composite sheet were used to measure the electrical conductivity using a benchtop Hanna conductivity meter kept at 25 °C with circulating water from a controlled temperature stabilizer.

4. Results and discussion

The microstructure of graphite implies numerous graphene nanolayers and graphite nanosheets (2-8 nm thick) which are composed of graphene nanoplatelets that can be as thin as one carbon atom layer [12]. Thus, the thickness of the solvated graphite and sheets in fully exfoliated may be hassling to the thickness of a single carbon layer. Although the difficulties associated with separating graphene nanoplatelets but it has good electrical and mechanical properties [19-21]. Hummer's method may be the best method for preparing exfoliated by oxidizing natural graphite powders to GO [18]. rGO was prepared by reducing the GO using high temperature [17]. Fig. 1 illustrates the oxidation and the reduction procedures of the natural graphite and the GO, respectively, for obtaining the rGO.

XRD patterns of graphite, graphene oxide, and high temperature reduced graphene are showed in Fig. 2. As can be seen, a sharp 2 θ reflection at 26.05^o in the natural graphene originated from interlayer spacing and there is a clear peak at $2\theta = 8.6°$ corresponding to the inter-layer spacing of 0.83 nm in the XRD pattern of graphene oxide due to the introduction of oxygen-containing groups and the intercalation of moisture. Moreover, high temperature reduced graphene shows a broad peak at $2\theta = 23–26°$ which is in a good agreement with other reports [22]. High transparency of graphene to the electron beam has been investigated using transmission electron microscopy (TEM) image shown in Fig. 3. Fig. 4 shows SEM images of the pristine graphite, which consisted of well-stacked thin nanosheets. The stable and most transparent locations are likely to be monolayer graphene; whereas the darker area indicated multilayer of graphene. In addition, wrinkled and sheet-like shape of graphene is shown in this figure. It can be concluded that graphene is probably partially exfoliated into individual nanosheets by high temperature reduction and ultrasonic treatment. From SEM and TEM images of the rGO, it can be concluded that the rGO were exfoliated during the oxidation and reduction and ultrasonic treatment of the natural graphite and that the rGO sheets were distributed from tens-of-nanometer to hundreds-of-nanometer in size [23].

It is known that graphene oxide is electrically insulated while reduced graphene nanosheets have good electrical conductivity [24]. And the prepared poly(St-co-MAA) without rGO was not electrically conductive but when rGO introduced, it was showed electrical properties. We can explain that, the oxidation and reduction of graphite expanded the inter-sheet distances due to the addition of oxygen-containing functional groups resulting from reactive surfactants such as 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). The use of the AMPS surfactant as an rGO modifier plays a major role for exfoliating and dispersing rGO in the composites. The sulfate and amido groups of AMPS form hydrogen bonds with polar groups, such as hydroxyl and carboxylic groups, on a GO surface .These results revealed that the dispersion of rGO in monomer solution may be become easier due to the expansion of the inter-sheet distance by (AMPS) which facilitated monomer intercalation. As shown in Fig.5 SEM of poly(St-co-MAA)/rGO composites synthesized via miniemulsion. Composite nanoparticles formed from the 2 wt% rGO were 70 nm in diameter and the size distribution was fairly uniform. The morphological properties of the poly (St-co-MAA)/rGO composite nanoparticles were characterized by analyzing the particle size distributions as shown in Fig.6. These results suggest that the monomers and rGO droplet became less stable, disturbing the uniform growth of the droplet in emulsion state. The result can be explained by the inhomogeneous size-distribution of the rGO sheets from tens-of-nanometer to hundreds-of-nanometer in size [18].The composite particles were assumed to have a spherical shape with average diameter about 40-70nm.

The electrical conductivity of reduced graphene polymer composite has been measured using the standard four-probe method at room temperature and it has been found that its electrical conductivity is approximately 2.5 S cm^{-1} which is in good agreements with reported results [25, 26].

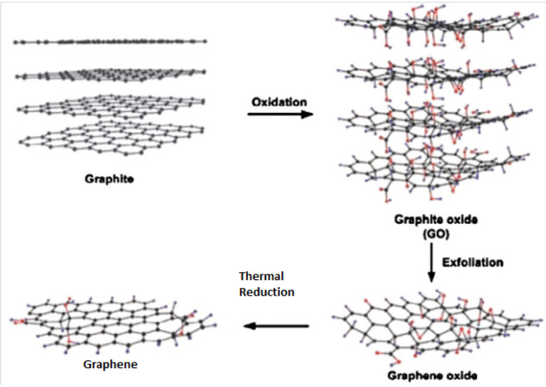

Fig. 1. Procedures for obtaining GO and rGO from graphite.

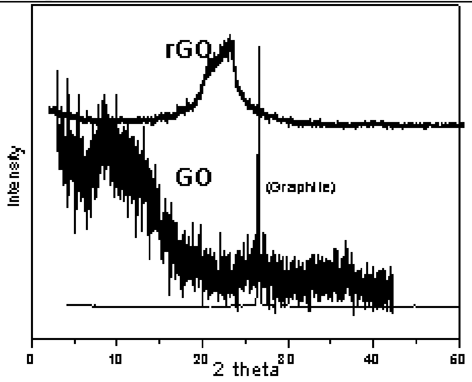

Fig. 2. X-ray diffraction graphite, GO and rGO.

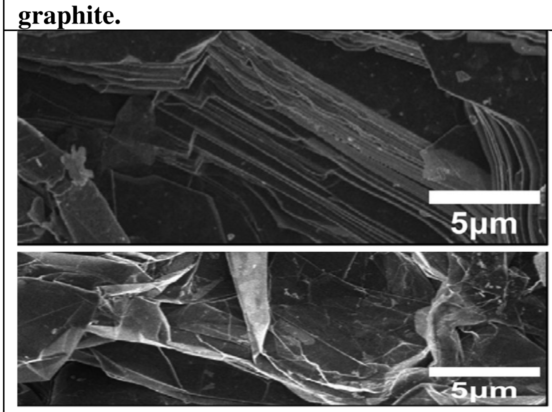

Fig. 3. SEM images of the pristine graphite (upper) and rGO (down).

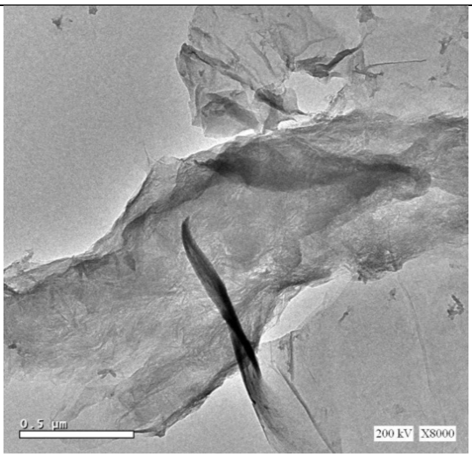

Fig. 4. TEM image of the rGO.

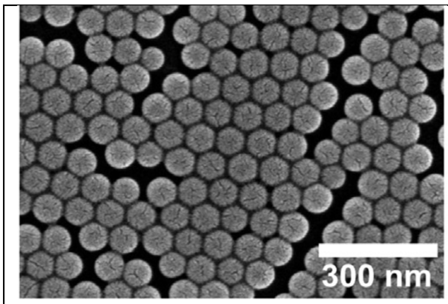

Fig. 5. SEM image of poly (St-co-MAA)/rGO composite nanoparticles.

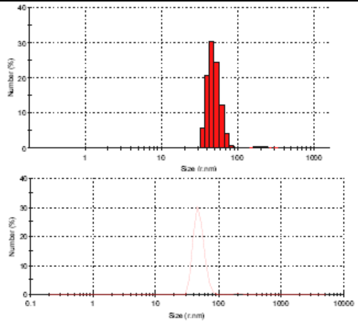

Fig. 6. Size distribution of the poly(St-co-MAA)/rGO composite nanoparticles

5. Conclusion

Poly (St-co-MMA)/rGO composite nanoparticles were synthesized via miniemulsion polymerization method. This procedure offers a promising route to the production of conductive composite materials based on graphite. The modification of rGO with AMPS enlarged the inter-sheet distance between the graphene layers and facilitated the intercalation of monomers into the rGO nanoscale and this providing a driving force for stably dispersing the rGO in the St and MMA monomer solution. The miniemulsion promoted the polymerization of the poly (St-co-MMA)/rGO composite to form nano latex particles characterized by a narrow size distribution. The poly (St-co-MMA)/rGO composite nanoparticles prepared with 2 wt% rGO displayed an average diameter of 40-70 nm. The electrical conductivity of reduced graphene polymer composite has been approximately 2.5 S cm $^{-1}$

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