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Synthesis of single-layer graphene oxide/alumina nanocomposite from commercially grade graphite flakes

Omid Jawhid[1], Gholam Hossein Zohuri[1,2,*]

[1]Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran.
[2]Environmental Chemistry Research Centre. Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran.
**Correspondence e-mail: zohuri@um.ac.ir*

Abstract

Reduced graphene oxide/alumina (rGO/Al_2O_3) nanocomposite powders have been prepared successfully via mixing of synthesized graphene oxide (GO) and aluminum nitrate using a two-step process: synthesis of GO/Al_2O_3 composite through ultrasonication treatment and chemically reduction of the synthesized composite via refluxing in presence of hydrazine hydrate. The thickness of synthesized GO sheets and morphology of the prepared composite were characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. According to the AFM analysis, the synthesized GO can be considered as a monolayer. The Fourier transform-infrared (FT-IR) spectrum index bands of prepared GO and rGO/Al_2O_3 were appeared at about 1725 and 1160 cm^{-1}, respectively.

***Keywords**: commercially grade graphite flakes, graphene oxide, Al_2O_3/rGO, thermally conductive electrically insulating.*

* *Corresponding author Email: zohuri@um.ac.ir*

1. Introduction

The intrinsic thermal and electrical conductivity of polymers is typically low [1]. Highly thermal conductive and electrical insulating polymer composites are thirstily anticipated for various applications like electronic packaging and thermal management [2]. Introducing of ceramic fillers, such as boron nitride (BN), aluminum nitride (AlN), aluminum oxide (Al_2O_3), zinc oxide (ZnO), silicon carbide (SiC) and graphene oxide (GO), into a polymer matrix have attracted more attention in order to improve their thermal conductivity and electrical insulation properties [3]. In general, nitrides, may provide much better desired attributes in comparison with oxides, however, they are also more expensive than oxides.

Unfortunately, utilizing of carbon-based materials like graphite, graphene and carbon nanotubes (CNTs) leads to an increase in the electrical conductivity of polymer composites. Coating of electrical insulating layers onto carbon-based materials has been widely developed to solve this problem, for example Al_2O_3@rGO, SiO_2@rGO, SiC@GO and BN@MWCNTs [4-7].

In this study, GO was synthesized from commercially grade graphite flakes and then, reduced graphene oxide/alumina nanocomposite (rGO/Al_2O_3) was prepared. The synthesized GO can be used for catalytic applications, as an additive to improve mechanical and thermal properties of polymers, adsorption of heavy metals presents in petrochemical industry, etc. The synthesized graphene based nanocomposite could be applied to applications in the development of super capacitor devices, devices for drug delivery, biosensors and electrochemical sensors.

2. Materials and Methods

2.1. Materials

Hydrochloric acid (37%) was purchased from Panreac Quimica S.A.U. Sulfuric acid (95-97%), phosphoric acid (85%), potassium permanganate, tetraethyl orthosilicate (TEOS) and hydrogen peroxide (30%) were purchased from Merck Company (Germany). Hydrazine hydrate (N_2H_4, 80%) obtained from Sigma Aldrich (Germany). Aluminum nitrate ($(AlNO_3)_3.9H_2O$) was bought from BDH Chemicals Ltd Poole (England). Deionized water was used in the whole work.

2.2. Methods

2.2.1. Preparation of GO

Industrial grade graphite flakes (30 g) was dispersed in a mixture of phosphoric acid (50 ml) and sulfuric acid (450 ml) using continuous stirring at room temperature (for 3 h). The reaction mixture was cooled down (to 0 ℃ in an ice bath) and potassium

permanganate (90 g) was very slowly added, so that the temperature does not rise further than 10 ℃, followed by mechanical stirring (at lower than 20 ℃ for 2 h). The reaction container transferred into an oil bath and stirred (for 12 h at 50 ℃). Ice water (450 ml) containing hydrogen peroxide (50 ml) was added dropwise into the reaction mixture. The brown colored product filtrated and washed with HCl (10%) and water (3 times) and was then freeze dried (at -50 ℃ for 24 h).

2.2.2. Preparation of rGO/alumina nanocomposite

Aluminum nitrate (40 g) was dissolved in ethanol (115 ml) under continuous stirring (for 20 min). Aqueous solution of GO (500 ml, 40 g/L) was prepared (under sonicating and stirring for 30 min) and slowly added in the prepared alumina solution followed by stirring and sonicating for further 40 min.

The reaction mixture was refluxed in the presence of hydrazine hydrate (at 80 ℃ for 7 h). The obtained precipitate was dried (at 70 ℃ for 24 h) and followed by oxidizing (at 350 ℃ for 1 h) in an air atmosphere.

3. Results and Discussion

Topography of the synthesized GO layer is shown in Figure 1. As the line scan (blue line) the thickness of the sheets is about 0.3 nm could be considered as a monolayer [8].

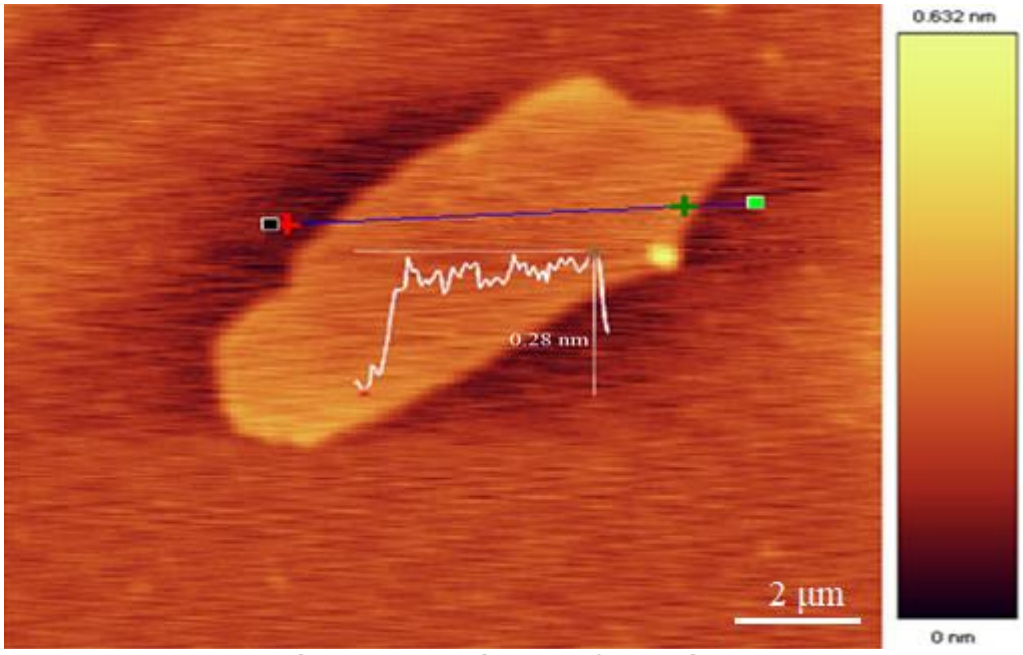

Figure 1. AFM image of monolayer GO.

The pristine graphite, synthesized GO and the reduced GO/alumina composite powders characterized by using FT-IR spectra (Figure 2). The index band of prepared GO was appeared at about 1725 cm^{-1}. Two characteristic peaks of the nanocomposite

powder are observed at around 1380 and 1100 cm^{-1}. One is C-C stretching at 1384 cm^{-1}; another peak, at around 1119 cm^{-1}, corresponds to Al-O-C bonding [9]. This bonding implies that our process induces the formation of chemical bonding between reduced GO sheets and the alumina matrix.

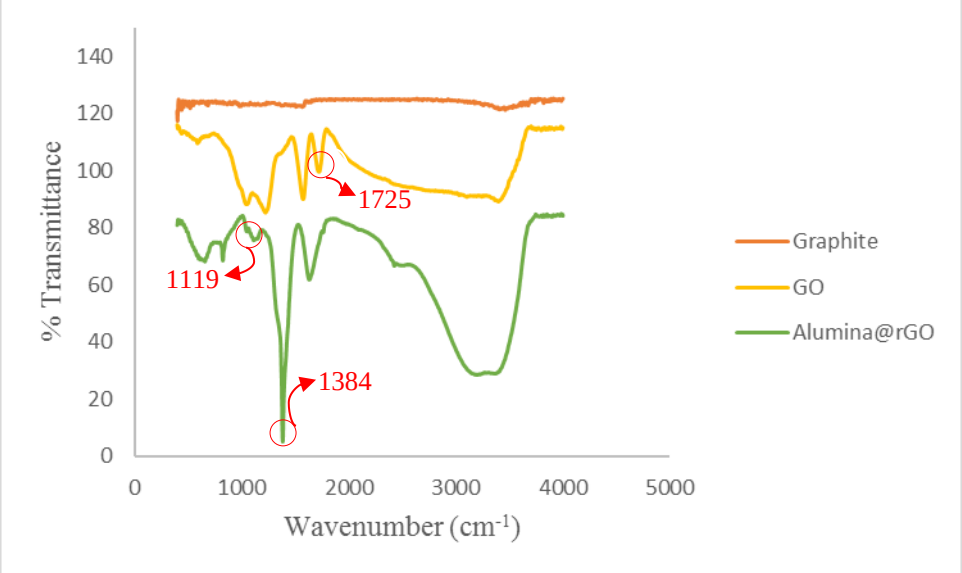

Figure 2. FTIR analysis of the graphite, GO and rGO/Al_2O_3 nanocomposite.

Structure and morphology of the synthesized product surface was investigated using SEM images (Figure 3). It is clear that how the graphite sheets are placed on each other (Figure 3a). Figure 3b shows that the graphene oxide sheets are exfoliated.

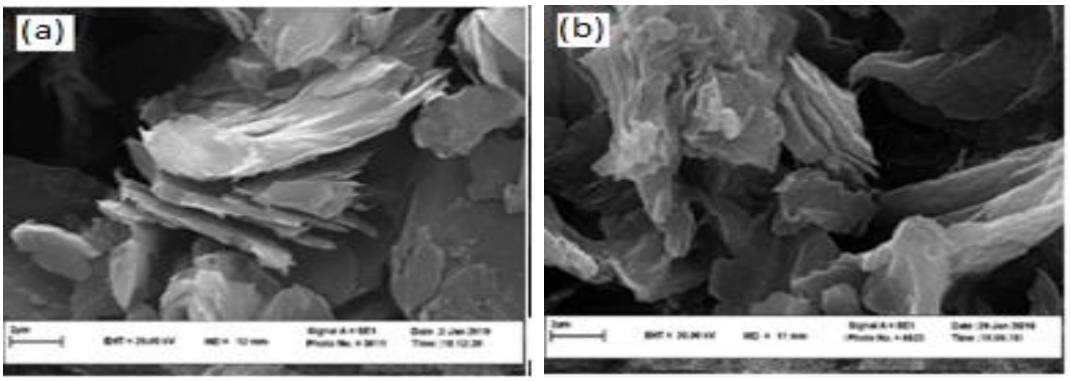

Figure 3. SEM images of (a) graphite flakes, (b) GO.

SEM and EDS analysis shows, however, the alumina particles are embedded on the rGO surface (Figure 4).

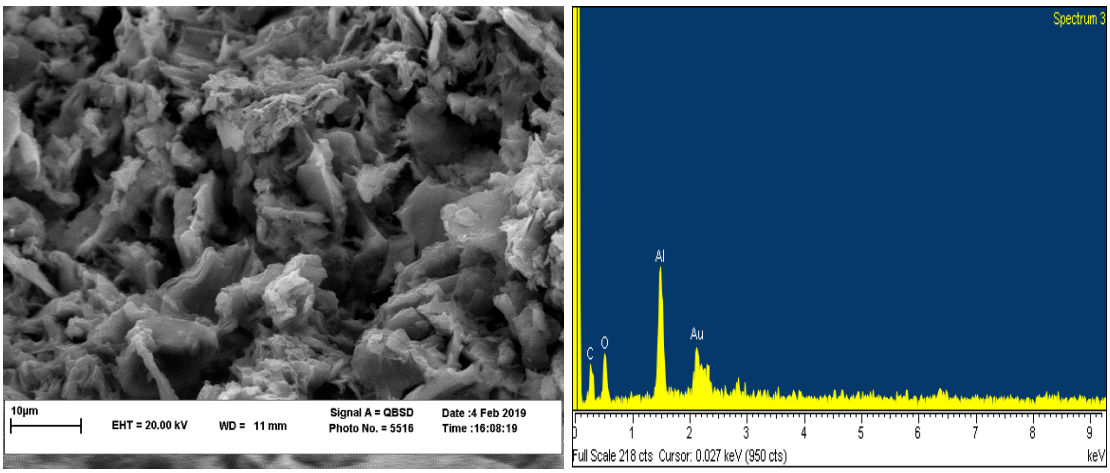

Figure 4. SEM and EDS analysis of the synthesized rGO/alumina nanocomposite.

4. Conclusion

A novel method for fabricating reduced GO/alumina nanocomposites, with an industrial perspective, has been proposed. Most interestingly, bond of Al-O-C was observed using FT-IR analysis and the ultra-thin GO nanosheets was detected using AFM patterns.

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References

[1] Yeongseon K, Minjae K, Hong-Gyu S, Ji Young J, Sung-Hyeon B, Sang Eun S. Roles of silica-coated layer on graphite for thermal conductivity, heat dissipation, thermal stability, and electrical resistivity of polymer composites. *Polymer*. 2018; 148: 295-302.

[2] Dae Ho L, Nakyung L, Hoyyul P. Role of silica nanoparticle in multi-component epoxy composites for electrical insulation with high thermal conductivity. *Journal of the American Ceramic Society*. 2017; 101: 2450-2458.

[3] Xingyi H, Chunyi Z. Polymer Nanocomposites: Electrical and Thermal Properties. Switzerland: Springer, Cham. 2016: 281-315.

[4] Naresh Muthu R, Rajashabala S, Kannan R. Hexagonal boron nitride (h-BN) nanoparticles decorated multi-walled carbon nanotubes (MWCNT) for hydrogen storage. *Renewable Energy, Elsevier*. 2016; 85: 387-394.

[5] Agnieszka Maria J, Joanna J, Joanna K, Antoni K, Wanda Z, Andrzej O. Controlled synthesis of graphene oxide/alumina nanocomposites using a new dry sol–gel method of synthesis. *Chem. Pap.* 2017; 71: 579–595.

[6] Subhash S, Keerti R, Kaushik P. Synthesis, characterization of graphene oxide wrapped silicon carbide for excellent mechanical and damping performance for aerospace application. *Journal of Alloys and Compounds*. 2018; 740: 436-445.

[7] Shalaby A. S. A, Staneva A. D, Aleksandrov L. I, Iordanova R. S, Dimitrie Y. B. Preparation, characterization and thermal stability of reduced graphene oxide/ silicate nanocomposite. *Bulgarian Chemical Communications*. 2016; 48: 38 – 42.

[8] Zhang S, Thuy Hang N, Zhang Z, Yue H, Yang W. Preparation of g-C_3N_4/graphene composite for detecting NO_2 at room temperature. *Nanomaterials*. 2017; 7(1): 12.
[9] Lee B, Young Koo M, Hwan Jin S, Tae Kim K, H. Hong S. Simultaneous strengthening and toughening of reduced graphene oxide/alumina composites fabricated by molecular-level mixing process. *Carbon*. 2014; 78: 212-219.