Heavily aluminated graphene nanoplatelets as an efficient flame-retardant

In-Yup Jeon, Sun-Hee Shin, Hyun-Jung Choi, Soo-Young Yu, Sun-Min Jung, Jong-Beom Baek*

School of Energy and Chemical Engineering, Center for Dimension-Controllable Covalent Organic Frameworks, Ulsan National Institute of Science and Technology (UNIST), 50, UNIST, Ulsan, 44919, South Korea

A B S T R A C T

Substantial amounts of aluminum (Al), which is one of the most abundant elements and period III post-transition metals, can be incorporated into graphene nanoplatelets (GnPs) by ball-milling graphite in the presence of solid Al beads. After thoroughly etching away any unreacted Al residues, the structure and properties of the resultant aluminated GnPs (AlGnPs) were characterized using various analytical techniques including transmission electron microscopy (TEM) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). The results indicate that AlGnPs contain a considerable amount of Al (30.9 wt%, by TEM energy dispersive X-ray spectrum) and display good dispersibility in various solvents, including water. Next, composite films from aqueous AlGnP/poly(vinyl alcohol) (1/4, wt/wt) solutions were cast and tested for flame retardation. The results indicate that AlGnPs could serve as an outstanding flame retardant that operates by both chemical (condensation) and physical (cooling and blocking) mechanisms. This suggests that AlGnPs may provide a promising option for a new, cost-effective, eco-friendly, yet efficient flame retardant.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The extensive use of plastics in everyday life is driven by a remarkable combination of properties such as light weight, cost-effectiveness, easy-processing, and high versatility. However, plastics consist mainly of non-metallic elements such as carbon, hydrogen, oxygen, nitrogen, and halogens. They are macromolecules of organic fuels, and thus most plastics are highly flammable. Although some plastics, specifically halogenated plastics (*e.g.*, poly(vinyl chloride), PVC), are known to possess flame resistance, they generate corrosive (*e.g.*, hydrochloric acid, HCl) and/or toxic gases (*e.g.*, chlorinated dioxins) upon catching fire [1–3]. Hence, for safety, it is necessary to add flame retardants to flammable plastics. The major flame retardants are inorganic halogenated and phosphorus compounds [4–6]. Other minor flame retardants are boric acid, ammonium phosphates and borates, ammonium sulfate and chlorides, zinc chloride and borate, antimony oxide, sodium borate and dicyandiamide [3,7,8]. Due to their low-cost and high-

efficiency, halogenated flame retardants have been the most widely used [9,10]. However, like halogenated plastics (*e.g.*, PVC), such retardants are associated with critical disadvantages. The burning of these compounds produces smoke that contains halogenated dioxins, which become the main threat to human life and health rather than the flame itself [11]. Thus, the use of halogen-containing flame retardants has been gradually reduced or even banned in some jurisdictions [12–14]. Inorganic metal hydroxides have been considered as major commercial alternatives to halogenated flame retardants due to their thermal dehydration [15–17]. However, their drawbacks are the need for high loading amounts due to poor efficiency and inherent incompatibility with organic polymers. These properties, when metal hydroxides are used, lead to serious loss of the mechanical properties of plastics [18]. Among the metal hydroxides, organic phosphorus compounds in particular, are used as additives to oxygen and/or nitrogen containing plastics. However, they are associated with the formation of organic phosphates, which plasticize and lead to diminishing mechanical properties [19,20]. Given this situation, there are a wide range of opinions about how to proceed with urgent development of new flame retardants. There are many issues that must be resolved, related to manufacturing cost, mechanical properties, loading

levels, health, and environment.

As compared with existing flame retardants, graphene derivatives have recently drawn attention as eco-friendly, efficient flame retardants, because they have demonstrated many exceptional properties, such as outstanding thermal conductivity, large surface area (covering large area of fuel surface), excellent physical strength, and superior structural stability [21–24]. Aluminum hydroxide is one of the most frequently used plastic additives as non-toxic flame retardants. It condenses at approximately 180 °C, absorbing a considerable amount of heat (endothermic cooling) and generating water (cooling and diluting fuel) for suppressing flammability [25,26]. Hence, developing graphene and aluminum hybrid system is one of the important challenges in new, cost-effective, eco-friendly, yet efficient flame retardants. However, for commercial viability, the issues associated with compatibility with plastics and cost-effective production must be resolved. Recently, we developed a simple, but efficient method that can produce various edge-selectively functionalized graphene nanoplatelets (EFGnPs) by a mechanochemical reaction [27–30]. Based on well-optimized reaction conditions, we were able to design and synthesize for the first time, aluminated graphene nanoplatelets (AlGnPs). Aluminum (Al) is the third most abundant element with non-toxicity. Combination of thermally stable graphitic frameworks and Al moiety can be expected to show synergistic enhancement in flame retardation. When tested as a flame retardant, they displayed very effective flame retardation for poly(vinyl alcohol) (PVA). Their outstanding flame retardation could be attributed to both chemical and physical mechanisms. The non-flammable molecules (e.g., H_2O and CO_2), generated by endothermic reaction (condensation) of oxygenated groups in AlGnPs and PVA, dilute the combustible gases and the formation of a protective graphitic network blocks the contact between fuel (PVA) and oxygen. Therefore, considering their competitive price and efficient flame retardation, AlGnPs will provide a promising option for a new class of flame retardants.

2. Experimental

2.1. Materials

Graphite was obtained from Alfa Aesar (Product #: 14735, Natural, 100 mesh, 99.9995% metals basis) and used as received. Aluminum (Al) was purchased from Aldrich Chemical Inc. (Product #: 266523, beads, 5–15 mm, 99.9% trace metals basis) and used as received. All other solvents were supplied by Aldrich Chemical Inc. and used without further purification, unless otherwise specified.

2.2. Syntheses of AlGnPs

AlGnPs were prepared simply by the mechanochemical reaction between graphite powder and Al beads. Graphite (5.0 g) and aluminum (Al, 5.0 g) with stainless steel balls (500 g, diameter 5 mm) were placed into a stainless steel container. After the container was sealed, five cycles of charge (5 bar, Argon gas)/discharge (0.05 mmHg) were applied to completely remove air to prevent the side reaction. The container was fixed in the planetary ball-mill machine, and pivoted with 500 rpm. After 48 h, the resultant product was collected and then repetitively washed with concentrated HCl (~37%) to remove unreacted aluminum with carbon and other metallic impurities, if any. Final product was exchanged with distilled water and freeze-dried at −120 °C under a reduced pressure (0.05 mmHg) for 48 h to yield a dark black powder (AlGnPs: 7.73 g, of which Al is at least 2.73 g).

2.3. Preparation of AlGnP/PVA and PVA film

AlGnP (0.4 g) was dispersed into distilled water (50 mL) by using a sonicator and poly (vinyl alcohol) (PVA, 1.6 g) (Product #: 341584, Aldrich, MW 89,000–98,000) was completely dissolved in AlGnP/water solution at 100 °C. This solution was poured in petri dish (diameter = 10 cm) and then water was slowly removed at 70 °C to form AlGnP/PVA film for 12 h. Finally, round AlGnP/PVA film (diameter = 10 cm) was dried off completely at 100 °C under reduced pressure (0.05 mmHg). The PVA film (2.0 g, diameter = 10 cm) was also cast for comparison using the same procedure for AlGnP/PVA film.

2.4. Instrumentation

The field emission scanning electron microscopy (FE-SEM) was performed on FEI Nanonova 230. The TEM specimen were prepared by dipping carbon micro-grids (Ted Pella Inc., 200 Mesh Copper Grid) into well-dispersed samples in ethanol. The high-resolution transmission electron microscopy (HR-TEM) was performed on a JEOL JEM-2100F microscope and atomic resolution transmission electron microscopy (AR-TEM) was carried out on a Titan Cubed G2 60-300 microscope. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was carried out with a TOF-SIMS V instrument (ION-TOF GmbH, Germany) using a 10 keV Bi^+ primary ion beam source. Thermogravimetric analysis (TGA) was conducted on a TA Q200 (TA Instrument) at a heating rate of 10 °C/min under air or nitrogen. The surface area was measured by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method on Micromeritics ASAP 2504 N. X-ray photoelectron spectra (XPS) were recorded on a Thermo Fisher K-alpha XPS spectrometer. Elemental analysis (EA) was conducted with Thermo Scientific Flash 2000. X-Ray diffraction (XRD) patterns were recorded with a Rigaku D/MAZX 2500V/PC with Cu-Kα radiation (35 kV, 20 mA, λ = 1.5418 Å).

3. Results and discussion

As schematically represented in Fig. 1a, aluminated graphene nanoplatelets (AlGnPs) were prepared by a mechanochemical reaction between graphite (5.0 g) and Al beads (5.0 g) in a planetary ball-milling machine (Fritsch) in the presence of stainless steel balls (500 g). High-speed metal balls in a ball-mill container generate enough kinetic energy to dissociate graphitic C—C bonds of graphitic frameworks and Al—Al bonds of solid Al beads. When such bonds are broken, active carbon and Al species lead to the formation of covalent C—Al bonds along the broken edges of graphene nanoplatelets (GnPs).

Before and after ball-milling, the visual appearances of the components were significantly different. Shiny graphite powder (Fig. S1a) and Al beads (Fig. S1b) turned to a fine black powder (Fig. S1c). Scanning electron microscopy (SEM) images further indicate the morphology change. The grain size of the graphite (<150 μm, Fig. 1b) was dramatically reduced after ball-milling (<1 μm, Figs. 1c and S2) and the work-up procedures to completely etch off unreacted Al and other metallic residues (See details in the Experimental section). The presence of Al in the AlGnPs was observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS, Fig. 1d) with element mapping (Fig. S3). The content of Al was approximately 35.11 wt% (19.65 at%, Table S1), suggesting that significant amounts of Al were incorporated into the AlGnPs.

High-resolution transmission electron microscopy (HR-TEM) (Fig. S4a) and atomic-resolution TEM (AR-TEM) images (arrows, Fig. S4b) further indicate that AlGnPs have significant amounts of