Materials Research Bulletin 50 (2014) 73–78

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Nitrated graphene oxide and its catalytic activity in thermal decomposition of ammonium perchlorate

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ARTICLE INFO

Article history:
Received 24 July 2013
Received in revised form 1 October 2013
Accepted 13 October 2013
Available online 21 October 2013

Keywords:
Nanostructures
Infrared spectroscopy
Nuclear magnetic resonance
Catalytic properties

ABSTRACT

Nitrated graphene oxide (NGO) was synthesized by nitrifying homemade GO with nitro-sulfuric acid. Fourier transform infrared spectroscopy (FTIR), laser Raman spectroscopy, CP/MAS ^{13}C NMR spectra and X-ray photoelectron spectroscopy (XPS) were used to characterize the structure of NGO. The thickness and the compositions of GO and NGO were analyzed by atomic force microscopy (AFM) and elemental analysis (EA), respectively. The catalytic effect of the NGO for the thermal decomposition of ammonium perchlorate (AP) was investigated by differential scanning calorimetry (DSC). Adding 10% of NGO to AP decreases the decomposition temperature by 106 °C and increases the apparent decomposition heat from 875 to 3236 J/g.

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1. Introduction

Graphene has been found to be an extremely promising material in various fields, such as nanoelectronics, sensor for biomolecules, transistors, solar cells, and catalysts, due to its unique electronic, chemical and mechanical properties [1–4]. However, the strong Van der Waals interaction and chemical inertness fade it in various applications [5]. Graphene oxide (GO), an oxidized form of graphene, has plenty of oxygen atoms on the basal plane and the edge of the sheets in the form of epoxy, hydroxyl, and carboxyl groups, which offer tremendous opportunities for access to derived graphene-based materials [6,7]. Besides, GO has been successfully utilized as support to prepare hybrids with Fe_3O_4, ZnO, and Mn_3O_4, etc., which display high activity as catalysts, mainly involving chemical, photocatalytic, and electrocatalytic applications [8–10]. Furthermore, the presence of nucleophilic oxygen-containing functionalities impart multifunctionality to the use of GO in fuels as chemically active sites and may provide catalytic behavior during combustion [11,12]. It has been proved that the GO can be an excellent substitution for a majority of nanocatalytic fuel additives involving some metals and/or metal oxides such as aluminum, for which the GO does not have nonenergetic oxide passivation layers on the surface, and produce solid oxide reaction products in combustion process [13,14]. However, Justin et al. have found that the additives have a negligible or negative effect on the total heat release by diluting the mixture [14]. Therefore, the development of a novel energetic burning rate catalyst and the improvement of the catalysis efficiency are still demanded. To the best of our knowledge, covalent functionalization of carbon-containing species with nitro groups could provide materials with enhanced energetic performance. Carbon nanotubes, with nano-sized diameter and tubular microstructure, have been used to obtain nitro-functionalized carbon materials [15,16]. Unfortunately, the research is always being confined by the presence of metal contamination in the CNTs [17–19]. Also, the CNTs do not disperse well in fuels and the active surface is constrained to only the outer regions of the nanotubes. In contrast, GO is highly dispersible in fuels and its catalytic activity occurs on both sides of the sheet [20–22]. Therefore, all aforementioned advantages suggest that nitro-functionalized GO could be an energetic burn rate modifier replacement for nitro-functionalized CNTs.

With this in mind, we expect that the NGO may exhibit excellent catalytic activity upon AP decomposition. This is because AP is one of the main oxidizing agents that have been used in solid propellant and the burning behaviors of propellants are highly relevant to the thermal decomposition of AP [23].

At present, the catalytic behaviour of nitro-functionalized carbon-containing species in the thermal decomposition of AP has rarely been reported and to the best of our knowledge there have not been any nitro-functionalized GO reported till now. In this work, we first report the synthesis of NGO by the nitration of GO in

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0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.10.023

nitro-sulfuric acid. The preparation of NGO is based on the electrophilic substitution reaction of benzene ring hydrogen and hydroxy hydrogen and also cycloaddition of epoxy group. We also demonstrate that the NGO can facilitate the decomposition of AP and release much heat. This study may provide a novel and energetic burning rate catalyst for composite solid propellant.

2. Experimental

2.1. Reagents

Raw materials used in the experiment as following: Graphite powder ($\geq$99.85%, ~30 μm particle size, Shanghai Huayuan China), $KMnO_4$ ($\geq$99.5%), $NaNO_3$ ($\geq$99.0%), 30% H_2O_2, H_2SO_4 (95–98%), HNO_3 (68–70%), HCl (36–38%), and absolute ethyl alcohol ($\geq$99.7%) were provided by Chengdu Kelong Chemical Reagent Company (Sichuan China). AP was received from Sinopharm. Aqueous solutions were prepared with deionized water (18.25 MΩ cm) from an ultrapure water purification system.

2.2. Synthesis of NGO

The pathway for the formation of NGO is depicted in Fig. 1. The process began with preparation of GO according to a modified Hummers method [24,25]. The obtained GO was grinded to use. Adding 50 ml concentrated sulfuric acid solution into 25 ml concentrated nitric acid solution slowly, the resulting mixed acid was cooled down to room temperature with cold water. In the moment, 100 mg GO and 25 ml concentrated H_2SO_4 solutions were added into a beaker and sonicated for 30 min. Thereafter, the mixed acid was slowly dropped into the beaker through a filling funnel, the obtained reaction system was stirred for 5 h at 45 °C, and then diluted and cooled with a certain amount of deionized water to terminate the reaction. Finally, the resulting lower sediment was centrifuged, washed with deionized water until pH of 7, and dried at 60 °C overnight under vacuum.

2.3. Characterization

Fourier transform infrared (FTIR) spectrometer (Spectrum One, Perkin Elmer Crop, U.K.) was used to study the structures of the GO and NGO using KBr pallets at room temperature. Compositions were analyzed with an element analyzer (Vario EL CUBE, Elementar). Raman spectra were measured with a inVia spectrometer using a Ar laser (λ = 514.5 nm) and CP/MAS ^{13}C NMR experiments were performed on a Bruker AVANCE III spectrometer (working frequency: 400 MHz). The X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250 (Thermo Scientific) spectrometer operated at 15 kV and 10 mA at a pressure of about 2×10^{-9} mbar using Al Kα as the exciting source. Atomic force microscopy (AFM) images were recorded on a SPI 3800N system (SEIKO) with a silicon cantilever by using the tapping mode. Before AFM measurement, the diluted colloidal suspension (0.01 mg/ml) was sprayed onto a freshly cleaved mica surface and then dried in air for 1 h. DSC curves were conducted with United States SDT Q600 synchronous thermal analyzers at a heating rate of 20 °C/min in Ar atmosphere over the range 20–500 °C with Al_2O_3 as reference.

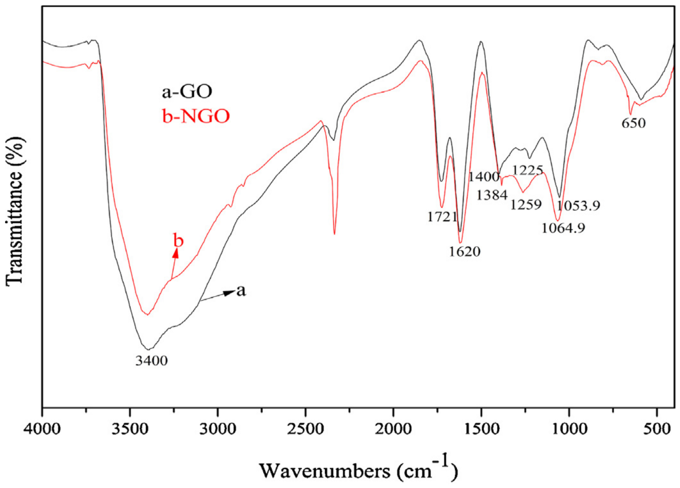

Fig. 2. IR spectra of GO and NGO, (a) GO, (b) NGO.

3. Results and discussion

The FTIR spectra were obtained from GO and NGO (Fig. 2). In the spectrum of GO (Fig. 2a), the peaks at 3400 cm^{-1}, 1620 cm^{-1} and 2925/2855 cm^{-1} are separately ascribed to the –OH, aromatic C=C bond and CH/CH_2 groups. Besides, it also shows that the bands attributed to carboxyl C=O and C–O (1721 and 1400 cm^{-1}), epoxy C–O (1225 cm^{-1}) and alkoxy C–O (1053 cm^{-1}) groups locate at the edges of the GO sheets [26]. In contrast to the GO, C–O stretching at 1225 cm^{-1} and O–H bending vibration at 1400 cm^{-1} are greatly reduced for NGO, which signifies that the hydroxyl and epoxy groups are partly reacted with the nitryl groups. Additionally, there are two new peaks at 1384 cm^{-1} ($C{-}NO_2$ stretching vibrations) and 1259 cm^{-1} ($O{-}NO_2$ stretching vibrations) in the NGO sample, which testifies to the presence of nitryl groups [27,28]. While the characteristic asymmetric stretching mode of $-NO_2$ in the 1600–1650 cm^{-1} [29] region is not observable in the spectrum of NGO which is likely due to the overlapping bands from aromatic C=C bond. In the meanwhile, the shift of the peak for alkoxy C–O from 1053 cm^{-1} in GO to 1064 cm^{-1} in NGO indicates the strong electron-withdrawing performance of $-NO_2$ groups. Furthermore,

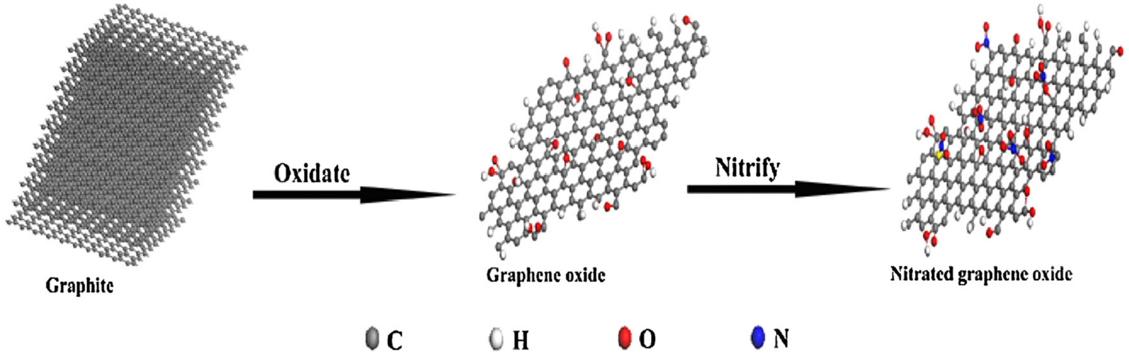

Fig. 1. The scheme of the preparation of NGO.

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