Two-steps synthesis of sandwich-like graphene oxide/LLM-105 nanoenergetic composites using functionalized graphene

Peng Deng a,b,c, Yi Liu a,c, Ping Luo b, Junxia Wang b, Yu Liu c, Dunju Wang a,⇑, Yi He a,⇑

⇑Corresponding author.
E-mail addresses: wangdunju@swust.edu.cn (D. Wang), yhe2014@126.com (Y. He).

A R T I C L E   I N F O

Article history:
Received 29 October 2016
Received in revised form 10 February 2017
Accepted 12 February 2017
Available online 16 February 2017

Keywords:
Structural Nanocomposites
Graphene oxide
LLM-105
Thermal analysis

A B S T R A C T

The sandwich-like graphene oxide/LLM-105 nanoenergetic composites were successfully prepared via a facile two-steps method, including building functionalized graphene nanosheets with surface modification and cooling deposition of LLM-105 microparticles. Characterization results indicated the composites possess sandwich-like sheets-particles-sheets stacking structures. Furthermore, a tentative formation mechanism of sandwich-like graphene oxide/LLM-105 composites was proposed. More interestingly, thermal analysis demonstrated these novel structured nanoenergetic composites are much easier to be activated and have a higher reacting rate than the raw LLM-105.

1. Introduction

As a hot research topic, the 2D graphene-based functional nanomaterials have recently attracted considerable attention in many fields [1–4], due to the unique electrical, physical, mechanical, thermal properties and so on.

In energetic materials, nanoenergetic composites with fantastic performances based on functionalized graphene become a new field of research [5] and it reveals the applicable potential towards improved stability and/or enhanced performance [6–8]. For instance, Zhang [9] demonstrated the primary explosive Lead azide coated with graphene nanosheets exhibited excellent anti-electrostatic performance under electrostatic discharge; Thiruvengadathan [10] had reported functionalized graphene nanosheets could be used to prepare self-assembly nanoenergetic thermite with excellent combustion properties; More interestingly, Cohen [11] recently designed novel structured layer-by-layer energetic coordination polymers using functionalized graphene nanosheets with Cu²⁺ modified as substrates, which possess favorable stability as well as superior detonation performances. These indicated that the development of novel nanoenergetic composites using functionalized graphene is of great significance.

Although there still exist some challenges for practical applications at present, positive attempts are necessary to be made towards exploring and extending novel graphene-based nanoenergetic composites [5,8]. Herein, we report a facile two-steps synthesis method to prepare sandwich-like graphene oxide/LLM-105 nanoenergetic composites (SGLC) through using functionalized graphene nanosheets. Based on the experimental process and results, the possible formation mechanism of sandwich-like sheets-particles-sheets nanomaterials was discussed. Thermal analysis exhibited attractive decomposition properties of nanoenergetic composites. In addition, this simple method towards preparing unique nanostructured energetic composites may offer a new idea to design and fabricate new structured nanomaterials in other fields.

2. Experimental section

In a typical experimental, graphene oxide (GO) were obtained by the modified hummers method [10]. 10 mg GO and 0.12 ml 0.1 mol/l FeSO₄ solution were added into 50 ml deionized water with moderate stirring overnight. After centrifugation, functionalized graphene nanosheets with Fe²⁺ modified were obtained and dispersed in 25 ml deionized water. 50 mg LLM-105 were dissolved into 25 ml DMSO. Heat to 60 °C respectively and mix together for 1 h with energetic stirring. Then, cool spontaneously to the room temperature and remove precipitations. SGLC samples

http://dx.doi.org/10.1016/j.matlet.2017.02.038
0167-577X/© 2017 Elsevier B.V. All rights reserved.
were obtained by centrifuging and rinsing repeatedly, drying by freezer dryer at –65 °C.

Field-Emission Scanning Electron Microscopy (FE-SEM) images were obtained by an Ultra 55 microscope (ZEISS Company, The Germany). Powder X-ray diffraction (XRD) patterns were collected on a Philips X’Pert Pro X-ray diffractometer (PAAnalytical, Holland). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-5700 FT-IR spectrometer (Bruker, The Germany). The thermal decomposition process was further detected by thermo-gravi
metric/differential scanning calorimetry (TG-DSC) using Mettler Toledo TGA-DSC1-1100LF (heating rate: 10 °C/min).

3. Results and discussions

The morphology of as-prepared samples was showed in Fig. 1. Pure and modified GO nanosheets exhibited two-dimensional planar structures in Fig. 1a and b, respectively. Compared with smooth surfaces of the former, the latter modified by Fe²⁺ possessed the coarse stratiform wrinkles, which indicated functionalized graphene nanosheets were prepared successfully [12]. And raw LLM-105 twin crystals with uneven size distributions were seen in Fig. 1c. Multi-lamellae, mono-lamellar and surface images of SGLC were obtained in Fig. 1d–f. Multi-lamellae nanoenergetic composites combined functionalized graphene and LLM-105 were displayed in Fig. 1d. LLM-105 microparticles were encapsulated by functionalized graphene nanosheets that still kept two-dimensional structures. Local strains around the microparticles appeared, which can be observed more distinctly in Fig. 1f. And Fig. 1e demonstrates giant mono-lamellar nanoenergetic composites. Only rare particles without functionalized graphene coated, as red arrow noticed, were exposed on the surface. Obviously, almost all the microparticles were encapsulated into the interfaces of two or more stacking nanosheets, which indicated that energetic composites possessed sandwich-like sheets-particles-sheets stacking structures.

Fig. 2a shows the XRD patterns of as-prepared samples. Pure GO exhibited only one strong diffraction peak at 8.8°. As the surficial wrinkles showed in Fig. 1b, the decreased d-spacing in local wrinkled areas would lead to shift of the characteristic peak at 9.5°. Raw LLM-105 had many diffraction peaks, implying different growth surfaces. The XRD pattern of SGLC suggested that the energetic composites consisted of LLM-105 and functionalized graphene. The only one peak at 28.3° in this pattern revealed preferred orientation (100) of LLM-105, agreed with the literature [13]. Interestingly, the graphene peak at 9.5° shifts to 8.4°. This is because most LLM-105 nanoparticles deposited and embedded on the interfaces of two or more functionalized graphene nanosheets, which may influence and extend the d-spacing of functionalized graphene.

FT-IR analyses were further investigated in the Fig. 2b. After Fe²⁺ modified, the positions of main containing oxygen functional groups of functionalized graphene shifted. Several types of functional groups in SGLC are in agreement with modified GO and raw LLM-105 by peak assignments discussed. Meanwhile, there are obvious peak shifts, which indicated the presence of chemical bonds at the surfaces and interfaces, such as hydrogen bonds and coordination bonds, due to functional groups and cations.

To gain insight into the formation mechanism of the SGLC, the compared experimental was designed. Pure GO without surface modification of Fe²⁺ was added directly into the typical experiment. The result in Fig. 3a showed dispersed GO nanosheets with smooth surfaces. But there didn’t exist LLM-105 nanoparticles, not to mention sheets-particles-sheets stacking structures. The SGLC was collected in Fig. 3b. As depicted in Fig. 3b, LLM-105 particles deposited randomly were found, and they were all encapsulated tightly by functionalized graphene.

Based on the above results and experimental progress, the formation mechanism of SGLC can be proposed as follows: as described in the schematic diagram in Fig. 3c, modified GO with coarse wrinkles were obtained through the surface modification. Subsequently, the method of mixed solvents heating-cooling was used. The higher concentration was caused in the local areas isolated by surrounding modified GO nanosheets. With solvents cooling, seed crystals precipitated, deposited randomly into the interfacial wrinkles of functionalized graphene nanosheets and then grew into microparticles (largest lateral size ~ 5 μm). In this
process, chemical bonding from the surface and interface between LLM-105 and functionalized graphene induced the formation of like-vacuum packaging structures, namely encapsulated sheets-particles-sheets stacking structures.

The thermal properties of the samples were further investigated by TG-DSC in Fig. 4. For raw LLM-105, the thermal decomposition process contained two weight loss stages and two relative exothermic peaks appeared at 286.7 °C and 358.7 °C in the TG-DSC curves. Subsequently, thermal analysis of SGLC was discussed. The relatively moderate weight loss before 218.4 °C was observed, which is mainly consistent with TG-DSC curves of pure and modified GO (Supplementary material Fig. S1). A quick thermal loss followed immediately, where the major reacting components are LLM-105 microparticles. It demonstrated novel energetic composites showed the lower decomposition activation temperature, because the presence of the functionalized graphene can decrease the reaction activation energy. Meanwhile, the violent behavior happened in a short range from 218.4 °C to 220.5 °C, implying that SGLC possessed enhanced thermal decomposition rate. Significantly, such interesting thermal properties suggested the special structured nanoenergetic composites may have potential applications in energetic materials.

![Fig. 2. (a) The XRD and (b) FT-IR patterns of as-prepared samples.](image1)

![Fig. 3. SEM images of (a) compared experimental and (b) SGLC; and (c) formation schematic of SGLC materials.](image2)
4. Conclusion

In summary, sandwich-like GO/LLM-105 nanoenergetic composites were prepared by a simple two-steps method, combined functionalized graphene sheets with surface modification and cooling deposition of LLM-105 microparticles. The tentative formation mechanism of sandwich-like sheets-particles-sheets stacking structures of SGLC was discussed by the experiment and results. And nanoenergetic composites showed attractive properties, which had potential applications. What’s more, this synthesis method may offer a new idea for designing and fabricating the novel structured nanomaterials.

Acknowledgments

This work was supported by Postgraduate Innovation Fund Project by Southwest University of Science and Technology (No. 16ycx003) and Scientific Research Fund of Sichuan Provincial Education Department (project: 13zd1114).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.matlet.2017.02.038.

References


