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Full Length Article

Atomic layer deposition of iron oxide on reduced graphene oxide and its catalytic activity in the thermal decomposition of ammonium perchlorate

Ning Yan [a,*], Lijun Qin [a,b], Jianguo Li [b], Fengqi Zhao [b], Hao Feng [a,c,*]

[a] Laboratory of Material Surface Engineering and Nanofabrication, Xi'an Modern Chemistry Research Institute, Shaanxi, China
[b] Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Shaanxi, China
[c] State Key Laboratory of Fluorine and Nitrogen Chemicals, Xi'an Modern Chemistry Research Institute, Shaanxi, China

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ABSTRACT

Reduced graphene oxide (rGO) decorated with finely dispersed Fe_2O_3 nanoparticles (rGO@Fe_2O_3) was prepared through a facile atomic layer deposition (ALD) route. Compositional and morphological characterizations were conducted using various techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). A uniform dispersion of densely packed Fe_2O_3 nanoparticles has been successfully achieved on the graphene nanosheets, leading to improved spatial distribution as well as increased number of active sites compared to unsupported Fe_2O_3 nanoparticles. Differential scanning calorimetry (DSC) results show that rGO@Fe_2O_3 composites exhibit excellent catalytic activities in the thermal decomposition of ammonium perchlorate (AP), which are probably due to the synergistic effect of the rGO nanosheets and the supported Fe_2O_3 nanoparticles. ALD has been proved to be an effective approach to design and develop new classes of materials as efficient combustion catalysts.

1. Introduction

As one of the most commonly used oxidizers in solid propellants, ammonium perchlorate (AP) has been extensively studied because its thermal decomposition characteristics, such as the decomposition temperature, activation energy, and reaction rate, remarkably affect the combustion and/or energy properties of AP-based propellants [1]. It is generally accepted that the burning efficiency of a propellant is dependent on the decomposition temperature of AP [2–4]. Therefore, tuning the thermal decomposition behavior of AP provides a pathway to modify the combustion properties of AP containing propellants. It is well known that the addition of transition metal oxides promotes the thermal decomposition of AP. In particular, metal oxides with dimensions in nanometer scale demonstrate superior catalytic activities in the thermal decomposition of AP [5–8], as smaller particles possess larger surface areas, which suggest more catalytically active sites for the thermal decomposition of AP. Nevertheless, freestanding nanoparticles are prone to aggregate into larger particles due to their high surface energy, which will result in decreased accessible surface areas and compromised catalytic activities.

Universal strategies to prevent nanoparticles from aggregating are mainly based on capping routes, wherein the nanoparticles are encapsulated by chemicals such as surfactants, polymers or ligands [9–11]. Although these methods are effective for the stabilization of nanoparticles, the capping agents usually impose spatial confinements to the nanoparticles, which may significantly affect chemical activities of the nanoparticles and substantially limit their applications. An alternative method of stabilizing nanoparticles is to anchor the nanoparticles onto a high surface area support. In the area of heterogeneous catalysis this has been proved to be a viable approach to preserve the chemical activities of nanoparticles [12].

Among numerous high surface area support materials, graphene, a single-atom-thick, two-dimensional carbon material, demonstrates many advantages including extraordinarily high specific surface area [13], exceptional electrical and thermal conductivity [14–16], and robust mechanical properties [17]. These unique advantages make graphene an ideal substrate for immobilization of metal oxide nanoparticles. In this context, considerable

* Corresponding authors at: Laboratory of Material Surface Engineering and Nanofabrication, Xi'an Modern Chemistry Research Institute, Shaanxi, China (H. Feng).
E-mail addresses: yanning_204@163.com (N. Yan), fenghao98@hotmail.com (H. Feng).

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interest has been focused on the growth of functional nanoparticles on graphene nanosheets. The obtained graphene-nanoparticle composites have been extensively used in a variety of fields including electrochemical catalysis, energy storage and electronic devices [18,19], wherein the nanoparticles were endowed with remarkable electrochemical or catalytic properties in combination with graphene nanosheets. Most recently, graphene and its derivatives have been proved to be effective for enhancing the burning rate of nitromethane, a monopropellant [20]. Besides, graphene nanoplatelets decorated with transition metal oxide, such as iron oxide (Fe_2O_3), cupric oxide (CuO), and manganese oxide (Mn_3O_4) nanoparticles, have been prepared by means of several conventional approaches including microwave irradiation, self-assembly, hydrothermal method, and so on [21–23]. Even though effective stabilization of nanoparticles on the graphene nanosheets has been achieved, the aforementioned methods usually suffer from non-uniform particle size as well as irregular spatial distribution of nanoparticles, due to the lack of precise control in the particle growth process.

To overcome these shortcomings, considerable attention have been paid to the controlled synthesis of metal oxides on graphene. Atomic layer deposition (ALD) is a thin film coating technology capable of producing nano films or nano particles in a highly controlled manner. ALD consists of two consecutive steps of self-limiting surface reactions. In a typical ALD cycle for the growth of a metal oxide, two precursors, including a reactive metal-containing compound and an oxidant, are alternatively dosed and chemically adsorbed onto the substrate. Each precursor dosing step is followed by a nitrogen purge for the removal of the excessive precursor. The thickness of the deposited oxide layer or the size of the nanoparticles can be precisely adjusted by varying the number of ALD cycle. To date, ALD has been applied to the synthesis of a variety of metal oxides which have demonstrated excellent performances in various fields including semiconductor, photovoltaics, energy storage [24], gas sensors [25], catalysis, and so on. As a naturally abundant and nontoxic transition metal oxide, Fe_2O_3 has long been recognized as a promising catalyst for promoting the decomposition of AP-based propellants. It is evidenced that reducing the particle size of Fe_2O_3 to nanometer scale contributes to decreasing the decomposition temperature of AP and lowering the reaction activation energy [26,27].

Herein, we present a facile ALD approach to synthesize conformal Fe_2O_3 films composed of ultrafine nanoparticles on graphene sheets. The as-prepared nano composites may combine the unique advantages of Fe_2O_3 nanoparticles and graphene nanosheets, making promising combustion catalysts for AP-based energetic materials.

2. Experimental section

2.1. Materials

Thermally reduced graphene oxide (rGO) was purchased from TimesNano Co., Chengdu, China. Ferrocene (99%) used as the iron source for ALD of Fe_2O_3 was purchased from Alfa Aesar. High purity (99.999%) oxygen and nitrogen gases used respectively as the oxygen source and as the carrier gas, were obtained from Xi'an Weiguang Gas Co., Shaanxi, China. Ammonium perchlorate (AP) with a particle size distribution of 100–150 μm was obtained from Gaojia Chemical Co., Dalian, China.

2.2. Synthesis of rGO@Fe_2O_3 nanocomposites by ALD

ALD experiments were conducted in a homemade viscous flow reactor built based on the design of Elam et al. [28]. The experiments were carried out under 1.0 torr at 350 °C. Ferrocene ($Fe(Cp)_2$) and high purity oxygen were used as the iron and the oxygen source, respectively. High purity nitrogen was used as the carrier gas. A typical ALD cycle consists of four sequential steps: a 60 s dosing of $Fe(Cp)_2$, a 60 s purge with N_2, a 60 s dosing of oxygen, and another 60 s purge with N_2. This ALD pulse sequence ensures saturated adsorption of $Fe(Cp)_2$ and oxygen precursors on the rGO substrate. rGO@(x)Fe_2O_3 nanocomposites with varied weight percentage (x) of Fe_2O_3 (on the rGO basis) were prepared by performing different cycles of Fe_2O_3 ALD on rGO. For comparison, a mixture of rGO/Fe_2O_3 was also prepared by drying the uniform suspension of rGO and Fe_2O_3 nanoparticles (Sinopharm Chemical, 99%) in anhydrous N, N-dimethylformamide (DMF, 99.8%).

2.3. Characterization

After ALD experiments the sample mass gains were measured using a Mettler Toledo electronic balance. A Thermo Scientific K-Alfa X-ray photoelectron spectrometer (XPS) with monochromatized Al Kα radiation (1486.6 eV) was used to analyze the surface compositions of the nanocomposites. Raman measurements were performed with an invia/reflex laser micro-Raman spectroscope (Renishaw, England). The spectra were collected from 100 cm^{-1} to 3000 cm^{-1} using an excitation laser wavelength of 514 nm. Fourier transform infrared (FTIR) spectra were recorded using a VERTEX 70v FTIR spectrometer in the attenuated total reflectance (ATR) mode. The sizes, shapes and detailed structures of the rGO@Fe_2O_3 samples were investigated using a FEI Tecnai G^2 transmission electron microscope (TEM), and the chemical compositions of rGO@Fe_2O_3 composites were relatively quantified using a high angle annular dark field scanning transmission electron microscope (STEM). Differential scanning calorimetry (DSC) analysis was conducted to measure the heat flow characteristics as a function of temperature using a NETZSCH Instruments SDT Q600 thermal analyzer. Prior to performing thermal analysis, each additive was evenly mixed with AP by using pestle and mortar. The measurements were carried out with a heating rate of 10 °C min^{-1} in a 200 sccm argon flow.

3. Results and discussion

3.1. Structural and compositional characterization

To gain insights into the growth of Fe_2O_3 on the rGO sheets, FTIR measurements of rGO before and after ALD of Fe_2O_3 were carried out, and the corresponding spectra are shown in Fig. 1. The GO

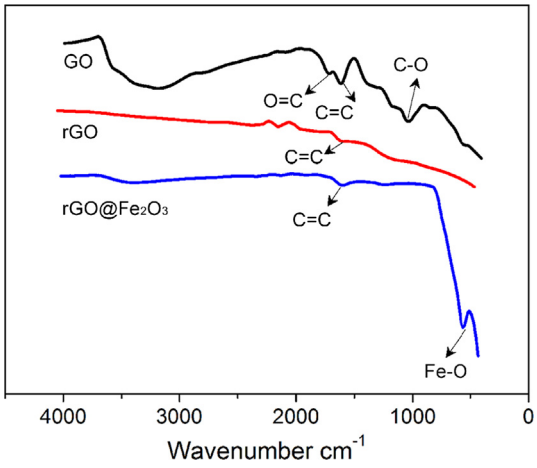

Fig. 1. FTIR spectra of GO, rGO and rGO@Fe_2O_3.