



## Preparation of Graphene Nanosheet/Alumina Composites†

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The introduction of graphene nanosheet into ceramic composites can be forseen the tantalizing foreground. Graphene nanosheet/alumina composite has been prepared by mixing solid powders process and *in situ* coating process. From the experimental results, it is suggested that *in situ* coating process overtakes mixing solid powders process at grains size and package density of graphene nanosheets.

**Key Words:** Graphene sheets, Alumina, Graphene/ceramic composites, Mixing solid powders process, *In situ* coating process.

### INTRODUCTION

Two-dimensional graphene nanosheets (GNS) have received significant attention in recent years due to their unique electronic, mechanical and thermal properties. One approach to harness these excellent properties for applications is to incorporate the material in composite materials. Incorporation of graphene into a ceramic to improve its performance would have great potential<sup>1</sup>.

It is well known that the graphene offers new opportunities with unusual electrical and mechanical properties. However, the big challenge of developing the composites is how to uniformly disperse graphene filler in the matrix. The exfoliated graphene often comes from the combination of graphite oxidation and sonication, followed by reduction through chemical methods<sup>2-4</sup>. The strong van der Waals interactions among these reduced graphene have an innate tendency toward aggregation in solutions<sup>5</sup>. In this paper the graphene/ceramic composites were synthesized by two different processes of mixing solid powders and *in situ* coating to reach the homo-dispersed graphene and alumina ceramics composites with crystalline grains refined.

### EXPERIMENTAL

**Preparation of graphene:** Graphite oxidation form was prepared from purified natural graphite (SP-1, 30- $\mu$ m nominal particle size) by the Hummers method<sup>6</sup>. GO (100 mg) was loaded in 100 mL water, sonicated. Hydrazine hydrate (85 %) was then added and the solution heated at 100 °C by constant stirring under a water-cooled condenser for 24 h. The reaction

product was washed copiously with water and methanol and dried.

**Preparation of 10 % graphene nanosheets/alumina composite powder:** 50 mg graphene nanosheets and 0.5 g alumina were dispersed in 50 mL absolute ethyl alcohol, respectively. Two dispersions were both sonicated for 0.5 h. The Al<sub>2</sub>O<sub>3</sub> suspension was heated in an oil bath at 100 °C, adding the graphene nanosheets suspension at a laggardly titration rate with constant stirring under a distillation device. Until the reaction for 6 h, an cooling for 12 h at room temperature. The reaction product was washed copiously with water and methanol and dried as sample 1.

The raw materials are analytically pure grade NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and NH<sub>4</sub>HCO<sub>3</sub>. The starting solution was obtained by dissolving 0.01 mol NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and 0.04 mol NH<sub>4</sub>HCO<sub>3</sub> into deionized water to concentrations of 0.2 and 2 mol/L, respectively. Graphene nanosheets (50 mg) were dispersed in aqueous solution of NH<sub>4</sub>HCO<sub>3</sub> *via* ultrasonication for 0.5 h, then adding hydrazine hydrate into aqueous solution of NH<sub>4</sub>HCO<sub>3</sub> until pH is 10. The NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub> solution was added into the NH<sub>4</sub>HCO<sub>3</sub> solution at a laggardly titration rate by incessantly stirring. The pH value was kept between 9 and 10 by adding ammonia, followed by an aging for 24 h at room temperature. When the precipitate was filtered and dried, the 10 % graphene nanosheets/alumina precursor power was obtained as sample 2.

### RESULTS AND DISCUSSION

**Graphite oxidation form and graphene nanosheets:** The crystal structure of graphite oxidation form and was

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characterized by XRD (Nikon E400), shown in Fig. 1. Compared graphite oxidation form with graphene nanosheets, the feature diffraction peak of exfoliated graphite oxidation form appears at  $11.8^\circ$  (002) is observed with interlayer space (d-spacing) of 0.75 nm. This value is larger than the d-spacing (0.34 nm) of the feature diffraction peak of graphite itself ( $2\theta = 26.5^\circ$ ), as a result of the introduction of oxygenated functional groups on carbon sheets. For the resulting graphene nanosheets the peak located at  $11.8^\circ$  disappeared, confirming the great reduction of graphite oxidation form and the exfoliation of the layered graphene nanosheets. Fig. 2 shows the TEM (JEM-2010) images of the large graphene nanosheets obtained by glucose reduction at different magnifications. There are some corrugations and scrollings on the edge of the graphene, which is consistent with previous works.

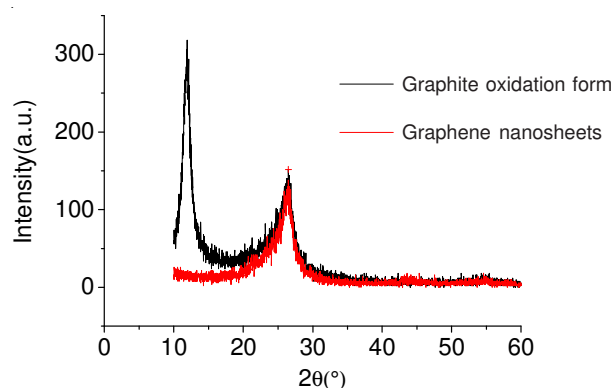


Fig. 1. XRD patterns of graphite oxidation form and graphene nanosheets

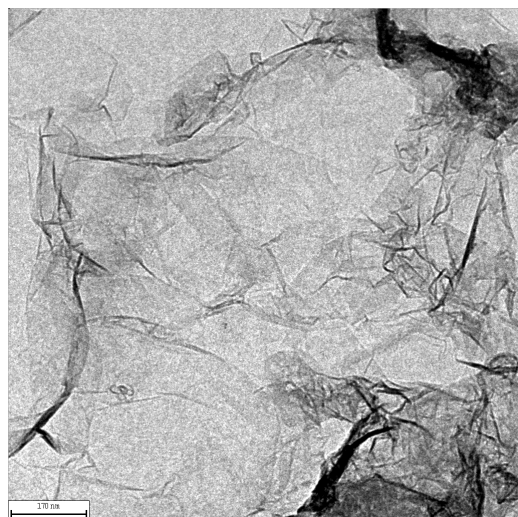


Fig. 2. TEM images of graphene nanosheets

**Graphene nanosheets/alumina composite powder:** Fig. 3 shows that the XRD patterns of sample 1(a) sample 2 (b). It is clear that the components of the sample 1 by mixing solid powders from Fig. 3(a). The XRD pattern of sample 2 is shown in Fig. 3(b). All the diffraction peaks can be ascribed to ammonium aluminum carbonate hydroxide (AACH) and no other phases except for graphene can be detected, indicating that the ammonium aluminum carbonate hydroxide obtained has a relatively high purity. The reaction involved can be expressed as follows:

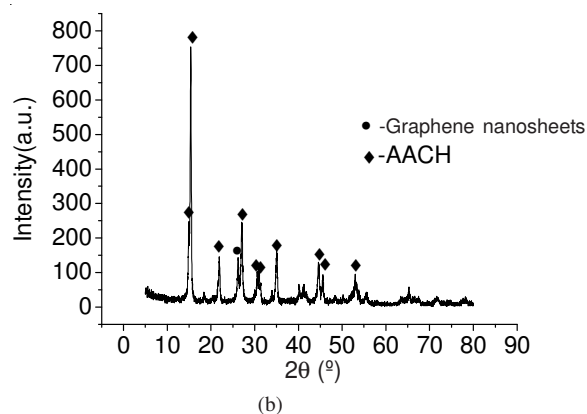
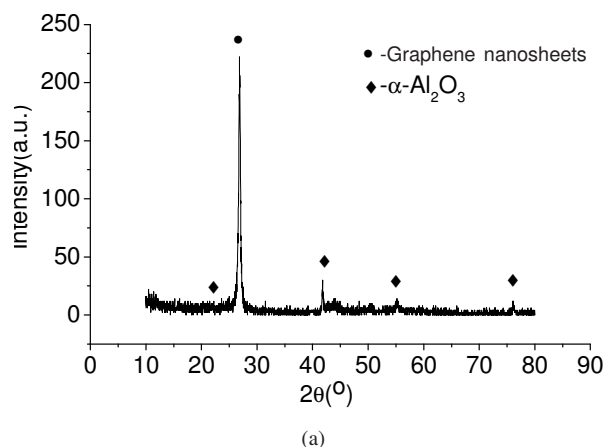
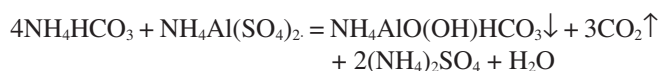


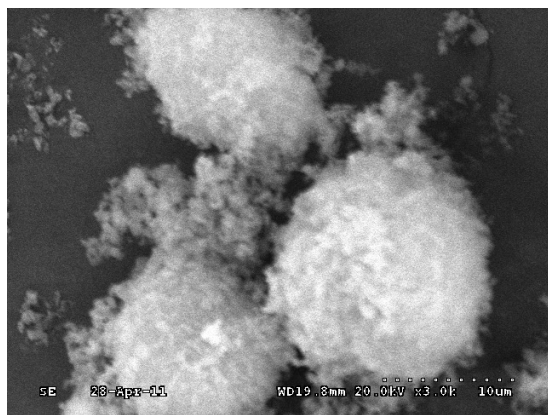
Fig.3 XRD patterns of sample 1(a) sample 2 (b)



Scanning electron microscopy images (S-3000N, Fig. 4a) of the powders by mixing solid powders processes shows that the agglomerate consists of hybrid multilayers with graphene nanosheets and alumina particles. The particles are of coarse size and reunite each other and the coagulation is evident. Fig. 4(b) shows the SEM images of the precursor prepared by *in situ* coating. The precursor is of uniform particle size distribution, regular morphology and good dispersion. It is obvious that particle size of alumina powder by mixing solid powders on graphene nanosheets multilayers much larger than the precursor by *in situ* coating.



(a)



(b)

Fig. 4. SEM images of sample 1(a), sample 2(b)

The TG-DSC curves of the precursor, as shown in Fig. 5, indicates that the sample 2 has two major weight loss events. The first weight loss below 150 °C is due to the desorption of physically adsorbed water. The second weight loss event in the temperature range of 150-260 °C, which also can be seen from the aculeated exothermic peak at 207 °C of the DSC curve, is associated with the decomposition of ammonium aluminium carbonate hydroxide, releasing CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O and forming AOOH particles. With the increase of the temperature in the thermal process, the TGA curve keep also on slightly decreasing, indicating the decomposition of AOOH and forming the alumina particles. It is worth mentioning that the DSC plot present the endothermic peaks at 882 °C. It may be associated with the phase transition process of the alumina.

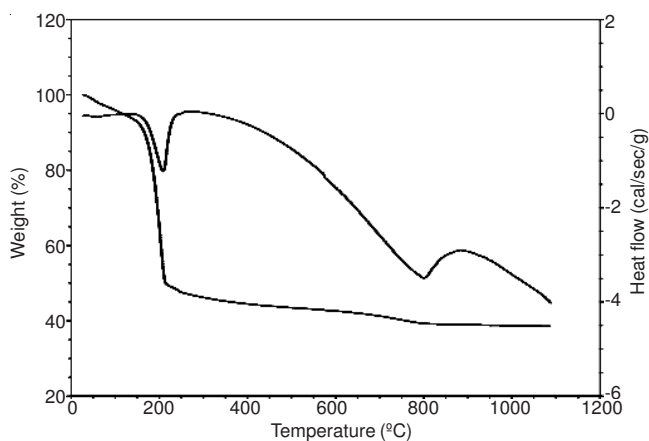


Fig. 5. TG-DSC curves of sample 2

## Conclusion

In summary, graphene nanosheets-reinforced alumina composite can be synthesized by mixing solid powders and *in situ* coating. The *in situ* coating process superior to the mixing solid powders process has been testified by experiment.

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