RESEARCH ARTICLE

An approach to prepare uniform graphene oxide/aluminum composite powders by simple electrostatic interaction in water/alcohol solution

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ABSTRACT: The homogenous dispersion of graphene in Al powders is a key challenge that limits the development of graphene-reinforced metal matrix composites with high performance. Here, uniform distribution of graphene oxide (GO) coated on flake Al powders were obtained by a simply stirring and ultrasonic treatment in the water/alcohol solution. The effect of water volume content on the formation of GO/Al composite powders was investigated. The results showed that GO adsorbed with synchronous reduction on the surface of Al powders, but when the water content was higher than 80% in the solution, Al powders were totally changed into $Al(OH)_3$. With optimizing the water content of 60% in the solution, reduced GO was homogenously coated onto the surface of flake Al powders. The formation mechanism can be ascribed to the balance control between the liquid/solid interaction and the hydrolysis reaction.

KEYWORDS: graphene; Al powder; composite; morphology; electrostatic interaction

Contents

1 Introduction

During the fabrication of metal matrix composites by the powder metallurgy method, micro- or nano-scale compo-

site powders are generally used to prepare bulk composites. Over past decades, Al-based metal matrix composites have attracted great attention due to their high specific strength [1–3]. Compared with traditional ceramic particle, fiber and whisker reinforcements, graphene is considered as an ideal reinforcement for its two-dimensional (2D) structure, high Young's modulus (1 TPa), and high fracture strength (125 GPa) [4]. However, the homogenous dispersion of graphene in Al powders is a key problem which limits the development of graphene-reinforced Al matrix composites with high performance [5].

Co-milling of metal powders with graphene is regarded as an effective way to uniformly disperse graphene into the metal matrix [6]. However, the integrity of graphene would be seriously damaged, and it will promote the interfacial reaction [7–8]. Compared with graphene, graphene oxide (GO) sheets are typically functionalized with epoxide and

hydroxyl groups on their basal plane and carboxyl groups at edges. These functional groups make GO hydrophilic and it can be dispersed in the aqueous media easily. As a result, GO is often used as the original material negatively charged in the aqueous solution [9]. From previous report, the Al powder suspension with positive charge is firstly obtained by some cation surfactants such as polyvinyl alcohol [10] and hexadecyltrimethyl ammonium bromide [11]. Then the modified Al powder suspension is mixed with the GO aqueous solution. This method can improve the dispersibility of GO in Al powders, but it requires surfactant and the process is complex. Moreover, the residual surfactant cannot be easily disposed clearly. In the aqueous solution, the fresh surface of Al powders can become ionized (Al^{3+}) because of the negative standard reduction value of Al/Al^{3+} [12–13]. Meanwhile, micron Al powders could directly react with water and generate hydrogen at mild conditions (atmosphere pressure, temperature < 100 °C) [14]. The hydrolysis reaction can be accelerated due to the size of Al powders, and a large amount of the Al powder surface would be changed into bayerite $Al(OH)_3$. It is also found that graphite would promote the reaction of hydrogen generation too [15]. Therefore, for micro-sized Al powders mixing with GO in the aqueous solution, how to balance the GO/Al oxide electrostatic attraction and the hydrolysis reaction of Al powders is a challenge to prepare the uniform distribution of GO/Al composite powders in aqueous solution.

In this paper, GO/Al powders were prepared by stirring and ultrasonic treatment in different ratios of the water/alcohol solution. The influence of the water content of the water/ethyl alcohol solution on the formation of GO/Al composite powders was investigated. The microstructure and the formation mechanism of GO/Al composite powders were analyzed. It is expected that this research could offer useful information for preparing high-quality GO/Al composite materials.

2 Experimental

GO was prepared through a modified Hummers method [16]. In brief, graphite powders were first oxidized into graphite oxide using $KMnO_4/H_2SO_4$, and then the graphite oxide was exfoliated into GO sheets by ultra-sonication in water. Spherical Al powders with the particle size of 10 μm were used as the starting material. The morphology of Al powders was shown in Fig. 1(a). Only the Al phase was observed in the X-ray diffraction (XRD) pattern of Al powders, as shown in Fig. 1(d). Spherical Al powders were ball-milled in pure ethanol at a rotation speed of 380 r·min^{-1} for 4 h in a stainless steel mixing jar with the ball-to-powder mass ratio of 20:1. Then, the obtained Al flakes were filtered with ethanol for four times. The morphology of Al flakes was shown in Fig. 1(b), and energy dispersive X-ray spectroscopy (EDX) results were
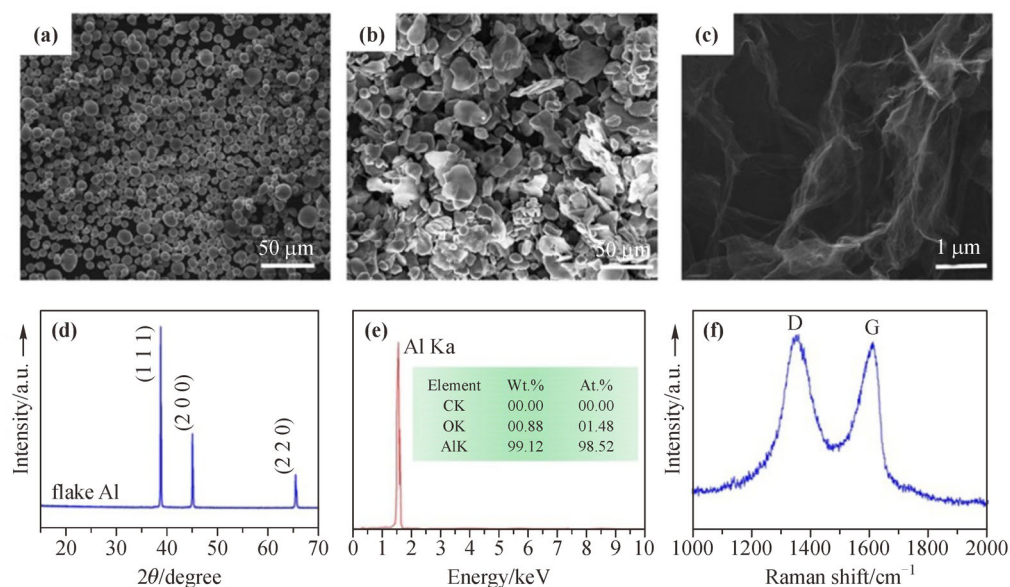

Fig. 1 Characterization of Al powders and GO: **(a)** morphology of spherical Al powders; **(b)** morphology of flake Al powders; **(c)** morphology of GO powders; **(d)** XRD pattern of flake Al powders; **(e)** EDX spectrum of flake Al powders; **(f)** Raman spectrum of GO powders.

shown in Fig. 1(e), in which 0.88 wt.% oxygen element was detected on the surface of Al flakes, indicating that the surface of flake Al powders was partly oxidized during the ball milling process. The typical morphology of GO after freeze-drying was shown in Fig. 1(c). The Raman spectrum of GO in Fig. 1(f) exhibited two intensive peaks at 1350 and 1600 cm^{-1}, corresponding to D and G bands, respectively, and the intensity ratio of I_D/I_G was 1.02.

To obtain uniform GO/Al composite powders, 0.3–1.0 wt.% of GO aqueous solution was poured into water/ethyl alcohol solutions with different water/ethyl alcohol ratio (0%, 20%, 40%, 60%, 80%, 100%). Then the slurry was stirred at 200 r·min^{-1} for a few minutes, following by ultrasonic treatment (300 W, 40 kHz) at ambient temperature, and then it was placed for deposition. After the completion of the adsorption process, all of the as-fabricated flake GO/Al composite powders were filtered with alcohol for several times, and then vacuum-dried at 50 °C for 3 h. The fabrication procedures for GO/Al composite powders were shown in Fig. 2.

Scanning electron microscopy (SEM) equipment with an energy dispersive spectrometer was used to characterize the morphology of Al and GO/Al composite powders. The phase of GO/Al powders was identified by Bruker D8 XRD. Raman spectroscopy (HORIBA HE) with an Ar$^+$ laser wavelength of 532 nm and X-ray photoelectron spectroscopy (XPS) were used to prove the adsorption mechanism of GO, as well as to characterize the reduction degree of the final GO/Al composite powders.
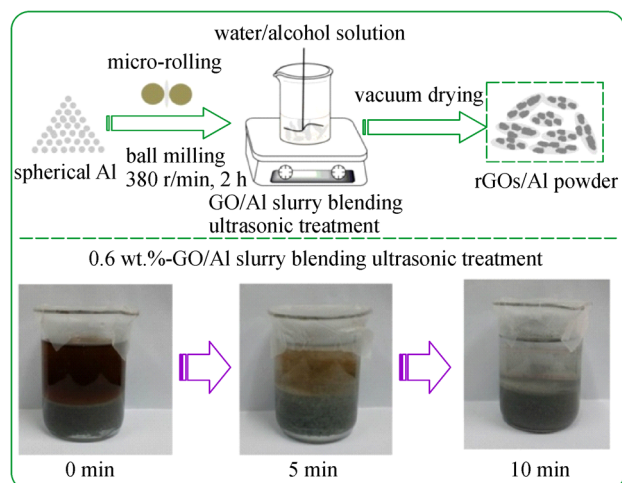

Fig. 2 Fabrication procedures for GO/Al composite powders.

3　Results and discussion

Figure 3 shows the morphology of GO/Al powders treated in different water/ethyl alcohol solutions. It can be seen from Fig. 3(a) that the surface of flake Al powders was very clear when the water content in the mix solution was 0%. This was because there was no hydrolysis reaction between ethanol and Al powders. When the water content in the mix solution was less than 40%, which was shown in Figs. 3(b) and 3(c), Al powders only partially hydrolyzed to form a small amount of positive Al^{3+} ions, and the resulting positive Al^{3+} ions were insufficient to absorb excess
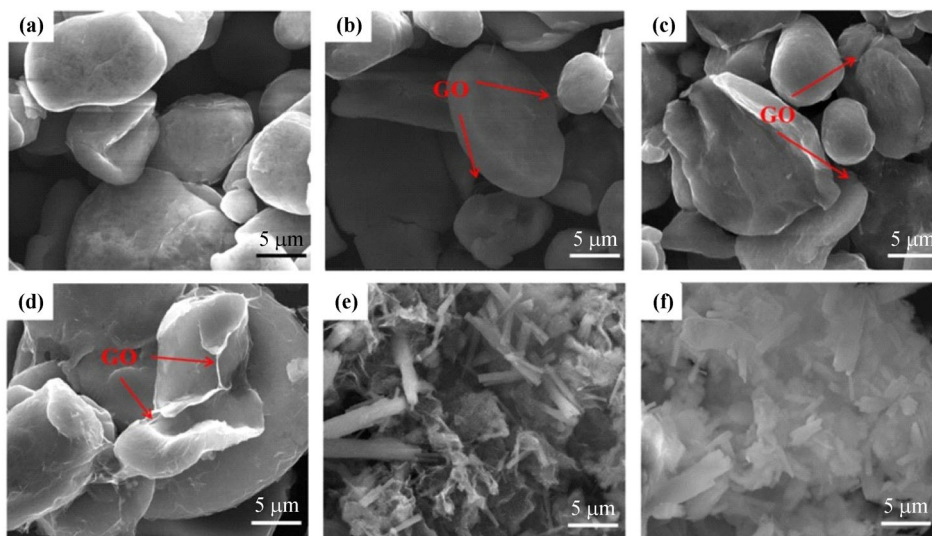

Fig. 3 Morphologies of GO/Al powders treated in different water/ethyl alcohol ratio solutions: **(a)** 0%; **(b)** 20%; **(c)** 40%; **(d)** 60%; **(e)** 80%; **(f)** 100%.

negative GO, so the surface of Al powders was relatively clear. But when the water content was 60%, the surface of flake Al was obviously coated by GO, which was shown in Fig. 3(d). The absorption of GO onto the surface of flake Al powders was greatly related to the degree of Al powders' hydrolysis reaction, since positive Al^{3+} ions can be formed on the Al particle surface and the electrostatic adherence between negative GO and Al^{3+} could promote the adsorption process. This result was conforming to previous research, which showed that GO could be adsorbed onto the surface of Al foils through the water/Al interface [17]. With the increase of the water content higher than 80%, flake Al powders seriously hydrolyzed, which was shown in Figs. 3(e) and 3(f). The shape of flake Al powders totally vanished, and compounds with the columnar shape were formed. The phase structure of all the samples was analyzed.

Figure 4(a) shows XRD patterns of GO/Al powders treated in different water/ethyl alcohol solutions. The standard Al phase was detected in GO/Al composite powders when the water content in the mixing solution was lower than 60%, and no new phase was found. Especially,
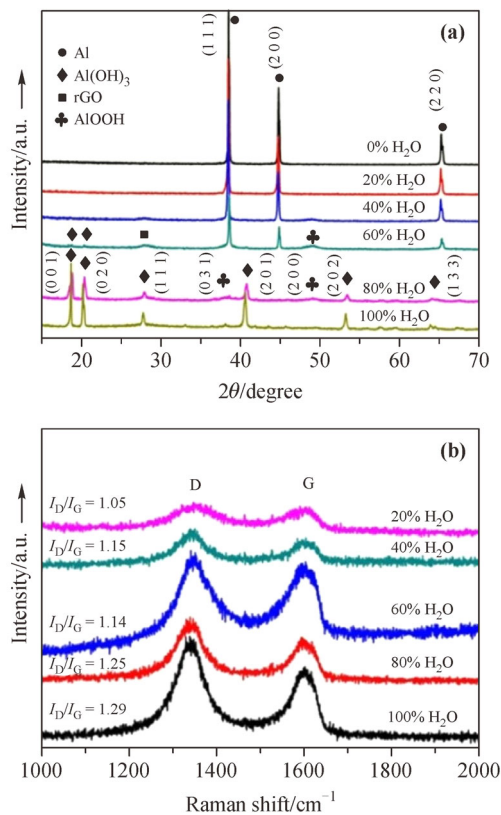

Fig. 4 **(a)** XRD patterns and **(b)** Raman spectra of GO/Al powders treated in different water/ethyl alcohol solutions.

the weak peak of the graphene phase was observed in GO/Al composite powders when the water content was 60%. But, when the water content in water/alcohol mix solutions was higher than 60%, Al powders were totally changed into bayerite $Al(OH)_3$ and little boehmite $AlOOH$. This meant that during the preparation of GO/Al composite powders by this method, the water content in the mixing solution was very important, and the appropriate water content of in the mixing solution was about 60%. This result was in accordance with the morphology of GO/Al composite powders as shown in Fig. 3. Raman spectra were also taken to measure GO in GO/Al powders, which was shown in Fig. 4(b). Two main peaks are around 1350 and 1600 cm^{-1}, which raised from the lattice disorder at edges of sp^2 clusters and in plane stretching of the graphene lattice. The intensity ratio of I_D/I_G was used to indicate the integrity of graphene. GO in GO/Al composite powders treated in water/alcohol mixing solutions with different water contents (20%–100%) exhibited two intensive peaks. No peak was detected on the surface of flake Al powders when the solution was total alcohol.

The intensity ratio of I_D/I_G was gradually increased (from 1.05 to 1.29) when the water content was from 20% to 100%. The increased intensity ratio of I_D/I_G meant a reduction of GO surface functional groups, indicating a partial reduction of GO during the adsorption. The fraction of reduced graphene oxide (rGO) was directly correlated with the amount of transferred electrons, in which GO can be adsorbed and reduced to form rGO. With the increase of the water content in the mixing solution, the possibility of the hydrolysis reaction between Al powders and water was increased. Therefore, more amounts of Al powders were changed into $Al(OH)_3$, which is beneficial for the adsorption and reduction process of GO, resulting in an increase of the intensity ratio I_D/I_G.

The partial reduction of GO by flake Al powders was further confirmed by XPS. Figure 5 shows the XPS spectrum of GO/Al composite powders treated in the water/alcohol solution with the water content of 60%. The degree of GO reduction can be described by the analysis of C 1s spectrum as well. The peaks of O 1s, C 1s and Al 2p were detected in XPS general spectra in Fig. 5(a) to prove that GO was successfully coated onto flake Al powders. The C 1s peak appearing in Fig. 5(b) consisted of various components, which were assigned to C = C/C − C, C − O, C − O − C, C = O and − COOH, close to previous report [13]. As shown in Fig. 5(c), four different peaks of GO are centered at 284.7, 286.2, 287.8 and 289.1 eV,

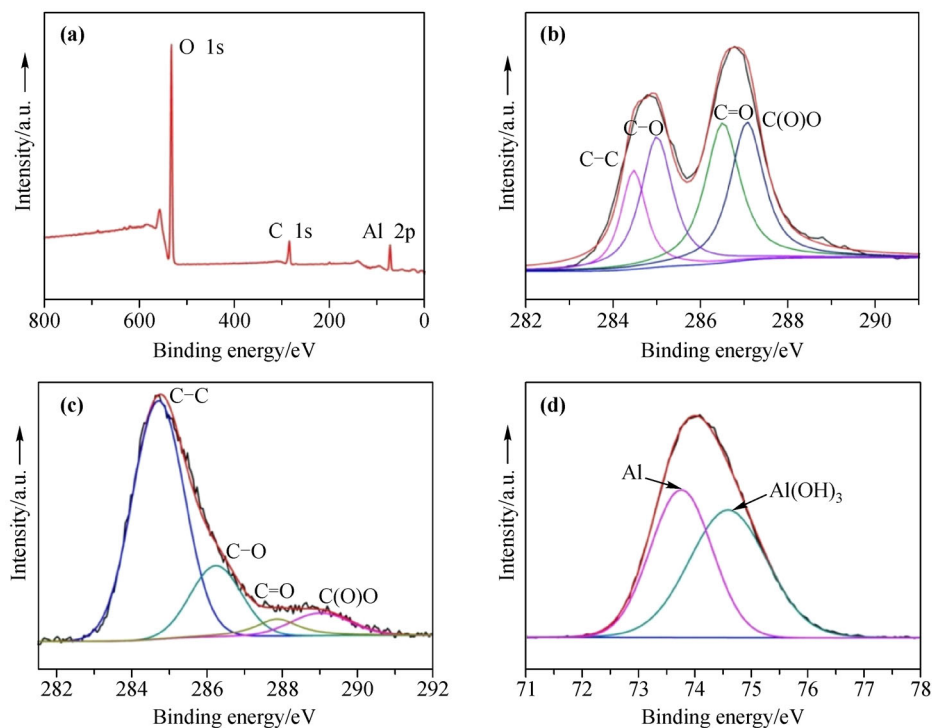**Fig. 5** XPS spectra of GO/Al composite powders treated in the water/alcohol solution with the water content of 60%: **(a)** general survey; **(b)** curve fits of original GO; **(c)** curve fits of C 1s of GO on the surface of Al powders; **(d)** curve fit of Al 2p.

corresponding to $C=C/C-C$ in aromatic rings, $C-O$ (epoxy and alkoxy), $C=O$ and COOH groups, respectively. The intensities of peaks, assigned to oxygen functional groups, were much lower than those in Fig. 5 (b), indicating that most of the oxygen functional groups were removed. Two peaks in the XPS spectrum of Al 2p shown in Fig. 5(d) are centered at 73.5 and 74.6 eV, corresponding to Al 2p and $Al(OH)_3$, respectively, indicating that $Al(OH)_3$ was formed at the surface of flake Al powders.

It was found that there was strong liquid/solid interfacial interaction between fresh Al powders and the GO aqueous solution, which promoted a fast sedimentation GO on the surface of Al powders [13]. The fresh surface of flake Al powders was transferred into Al^{3+} through the hydrolysis reaction and GO was adsorbed on the surface. Additionally, GO could be partially reduced on the surface of flake Al powders. It has been supposed that Al^{3+} can act as a cross-linker due to the interaction between negative charges of GO and Al^{3+}. Meanwhile, GO sheets acted like a surfactant, which could be adsorbed on the interfaces and decreased the surface or interfacial tension, leading to its self-assembly on the Al surface [17]. Moreover, some hydroxyl groups always existed on the surface of flake Al powders because of the formation of $Al(OH)_3$, leading to the hydrogen-bonding interaction between hydroxyls on the Al surface and oxygen-containing groups of GO sheets [18].

It was well known that there was a dense passivation oxide film on the surface of Al powders, which lowers the surface activity of Al powders. Therefore, the passivation oxide film on the surface should be destroyed as much as possible before the hydrolysis reaction of Al occurs. The ball-milling process used can eliminate most of the oxide layer on the surface of Al powders to obtain a fresh surface of flake Al powders, which can be verified by a very low content of oxygen element in Fig. 1(e). The fresh, highly active aluminum surface will hydrolyze in water, helping GO to adsorb on the surface of flake Al powders. The specific adsorption mechanism was shown in Fig. 6. There were two processes during the adsorption: one was the Al powder hydrolysis reaction, and the other was the GO adsorption on the Al surface. As shown in Fig. 6(a), when Al particles were added into water, a hydration reaction would take place, even the oxide film remained on the Al surface. This process involved disrupting the $Al-O-Al$ bond by hydrolysis to form an $Al-OH$ species [19–20]. The reaction equation was as follow:
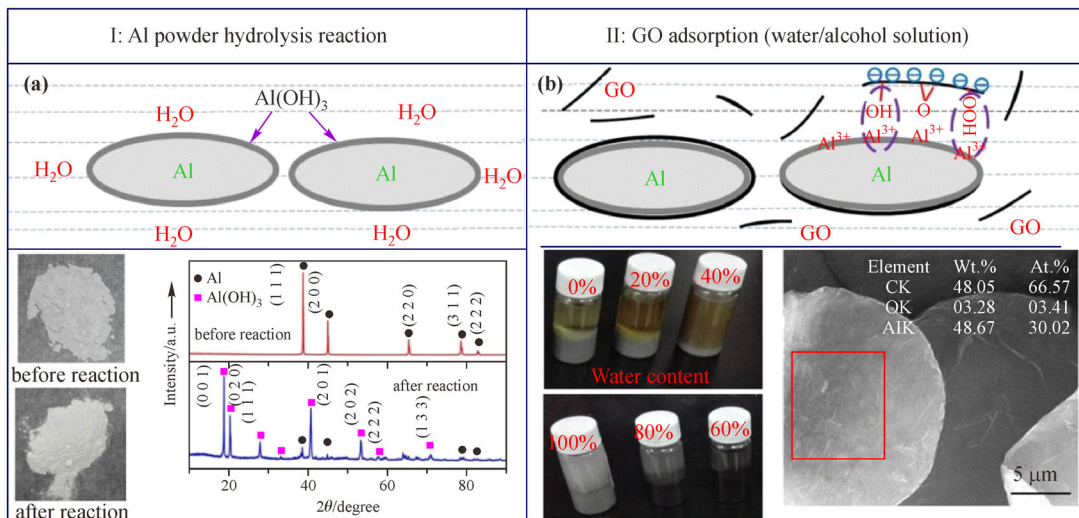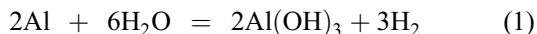
Fig. 6   The mechanism of GO adsorption on the flake Al surface: **(a)** Al powder hydrolysis reaction; **(b)** GO adsorption in the water/alcohol solution.

$$2Al \ + \ 6H_2O \ = \ 2Al(OH)_3 + 3H_2 \qquad (1)$$

The following XRD pattern showed the change of the substance before and after the total hydrolysis reaction in 100% water solution. Only the typical Al peak was detected before the reaction. Meanwhile, after the reaction the color of sample powders becomes whiter than that before the reaction, which proved the formation of a new substance, as shown in Fig. 6(a).

The adsorption process of GO was shown in Fig. 6(b). In aqueous solution, a negatively charged GO functional group ($-O$, $-OH$, $-COOH$, etc.) will be tight coupling by electrostatic interaction with positively charged Al^{3+}, which was ionized from $Al(OH)_3$, leading to self-assembly on the Al surface. In addition, some of hydroxyl groups ionized by $Al(OH)_3$ always existed on the surface of flake Al powders, resulting in a hydrogen-bonding interaction between hydroxyl groups on the Al surface and oxygen-containing groups of the GO sheet. This would further enhance the interfacial bonding strength of GO/Al.

The effect of the water content in the water/ethanol solution on the GO adsorption process was shown at the bottom of Fig. 6(b). When the water content was less than 60%, the amount of Al^{3+} produced by the hydrolysis reaction was not enough to completely absorb negatively charged GO. Using this method, when the water content reached 60%, it can be seen from the small vial experiment that 1.0 wt.% GO can be uniformly distributed on the surface of flake Al powders by this simple method. The SEM image of the adsorbed powder was shown in

Fig. 6(b). GO was uniformly adsorbed onto the surface of flake Al powders, and the carbon content could reach as high as 48.05 wt.%, suggesting that when preparing GO/Al composite powders in the aqueous medium, the balance between the electrostatic interaction and the hydrolysis reaction should be considered.

4   Conclusions

Uniform Al/GO composite powders were prepared in the water/alcohol mixing solution by the stirring and ultrasonic treatment method. The hydrolysis reaction of Al powders and the reduction of GO were detected during the treatment. When the water content was higher than 80%, Al powders were totally changed into bayerite $Al(OH)_3$. However, rGO was homogenously coated onto the surface of flake Al powders when the water content was 60%. Different contents of GO were dispersed into the water/alcohol mixing solution with the water content of 60%, and uniformly distributed GO/Al composite powders with 1.0 wt.% GO was obtained by this simple electrostatic interaction method. The mechanism was ascribed to multiple contributions including the liquid/solid interfacial interaction and the hydrophobicity reaction.

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