

**Novel process of coating Al on graphene involving organic aluminum  
accompanying microstructure evolution**

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**Abstract:** A novel chemical reduction of organic aluminum for coating Al on the graphene surface is proposed. During the process, Al powder reacted with the  $(C_2H_5)_2Br$  solution to produce  $(C_2H_5)_3Al$  solution, followed by gradual decomposition of  $(C_2H_5)_3Al$  into Al atoms. Al atoms gradually deposited on the surface of graphene, nucleated, grew up, until Al coating was formed on the surface of graphene. With the increase of reaction temperature, the decomposition rate of  $(C_2H_5)_3Al$  increased, which was beneficial to the formation of Al atoms and Al coating. The reducing agent, NaH, promoted the reaction and formation of Al coating. When the reaction temperature was optimized to  $100^\circ C$ , and the reaction time was 1.5 h, with NaH added to the solution, high quality Al-coated graphene was obtained.

**Keyword:** Al, graphene, nanocomposites, microstructure, coating

## 1. Introduction

Graphene exhibits excellent mechanical properties and high conductivity. These superior properties render graphene as ideal reinforcement for Al matrix composites for use in automotive, aerospace, and packaging applications. Previous research has shown that the addition of few-layer graphene [1], graphene oxide [2, 3], or graphene nanoplatelets improved the mechanical properties of Al alloys [4, 5]. However, due to the density difference and poor wettability between graphene and Al, graphene is difficult to disperse in Al matrix, and the homogeneous distribution of graphene in metals continues to be challenging [6-8]. Activation of graphene has been proposed to improve wettability between graphene and Al. Coating metal on graphene surface is an important activating treatment [9, 10]. Currently various activating treatment methods have been developed, including chemical reduction, self-assembly, electrochemical deposition, vapor deposition and redox method. Muszynski et al. decorated graphene sheets with gold nanoparticles [11]. Hong et al. prepared gold-coated graphene by

self-assembly [12]. Luo et al. potentiostatically electrodeposited metallic Cu nanoparticles on graphene sheets [13]. These methods are mainly used to coat precious metals, copper or nickel on the surface of graphene [14, 15]. After these activating treatments, precious metals, copper or nickel were coated on the graphene surface. If the graphene was added in Al alloy, these precious metals, copper or nickel may be viewed as impurities, which can affect properties of Al alloys. The effective method to reduce these impurities and improve wettability of graphene, is to coat Al on the surface of the graphene. This is difficult via conventional liquid chemical reduction reaction because Al is active and Al atom is difficult to displace from the Al salt solution [16, 17]. A novel chemical reduction of organic aluminum for coating Al on the graphene surface is proposed. The objective of the study described here is to elucidate the microstructure evolution during coating Al on the graphene that has not been previously explored.

## **2. Experimental procedure**

Al powder with an average size of 15-50  $\mu\text{m}$  (1.5g), bromoethane (29 mL), iodine (0.1 g) and aluminum chloride (0.1 g) was added to a reaction vessel under a  $\text{H}_2$ -shielded atmosphere. The reaction solution was heated to 39  $^\circ\text{C}$ , and uniformly stirred. After the reaction was completed, the reaction solution temperature was reduced to 0  $^\circ\text{C}$  and held for 1 h, and tetrahydrofuran was added to the reaction solution. After the solution reacted completely, it was filtered, and alkyl aluminum solution was prepared. Subsequently, graphene (0.05 g) was added to the alkyl aluminum solution while stirring, and the solution was heated at 70-100  $^\circ\text{C}$ . After reaction time of 1-1.5 h, Al-coated graphene was prepared after cleaning and drying.

The microstructure of Al-coated graphene were observed by scanning electron microscope

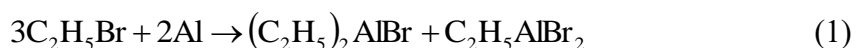
(SEM) equipped with energy dispersive spectroscopy (EDS). X-ray diffraction was used to analyze precipitates in Al-coated graphene. The Al-coated graphene was placed on a high resolution transmission electron microscopy (HRTEM) grid holder for HRTEM observations.

### 3. Results and discussion

Fig. 1 shows the SEM images and EDS analysis of Al-coated graphene after different reaction time. During coating of Al on graphene, mechanical stirring had little effect on the structure of graphene. The graphene maintained irregular curls and folds (Fig. 1). At the beginning of the reaction process (0.5 h), a few heterogeneous particles deposited on the surface of graphene (Fig. 1b), EDS (Fig. 1d) and XRD (Fig.2) confirmed that these heterogeneous particles were composed of Al particles, but the Al particles distributed inhomogeneously. As the reaction progressed, more Al particles deposited on the surface of the graphene, and the distribution gradually became homogeneous (Figs. 1c and e). When the reaction time was increased to 1.5 h, a number of Al particles were homogeneously distributed on the surface of graphene. The Al coating formed, had area coverage 61%, as shown in Figs. 3a and b.

The reaction process of coating Al on the surface of graphene consisted of two stages: The first stage was to prepare the  $(C_2H_5)_3Al$  solution. The second stage was gradually decomposition of  $(C_2H_5)_3Al$  into Al atoms. The Al atoms gradually deposited on the surface of graphene, nucleated, grew up, and coated evenly on the surface of graphene.

The Al powder was added to the  $C_2H_5Br$  solution. Al reacted with  $C_2H_5Br$  to produce  $(C_2H_5)_2AlBr$  and  $C_2H_5AlBr_2$ , according to the reaction:

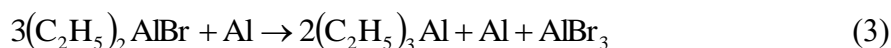


The  $C_2H_5AlBr_2$  further reacted with Al to produce  $(C_2H_5)_2AlBr$ , Al and  $AlBr_3$ . The reaction

equation may be written as follows:



The reaction product  $(\text{C}_2\text{H}_5)_2\text{AlBr}$  and  $\text{Al}$  further reacted, and  $(\text{C}_2\text{H}_5)_3\text{Al}$ ,  $\text{Al}$  and  $\text{AlBr}_3$  were obtained via equation:



The  $(\text{C}_2\text{H}_5)_3\text{Al}$  easily decomposed into  $\text{Al}$ ,  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  at high temperatures, according to the reaction:

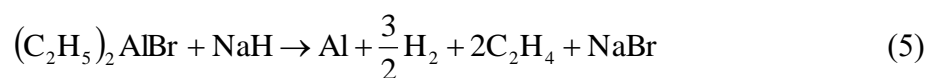


During coating  $\text{Al}$  on graphene,  $(\text{C}_2\text{H}_5)_3\text{Al}$  decomposed, and  $\text{Al}$  atoms gradually deposited on the surface of graphene. In the beginning of reaction (0.1 h), a small content of  $\text{Al}$  formed and distributed discontinuously on the surface of graphene (Fig. 4a). With progress in reaction, more  $\text{Al}$  particles nucleated and grew up, and  $\text{Al}$  particles (Fig. 4b), coated evenly on the surface of graphene (Fig. 3).

The content of  $\text{Al}$  coating on the surface of graphene increased with the increase of reaction temperature. When the reaction temperature was increased to  $100\text{ }^\circ\text{C}$ , the area coverage of  $\text{Al}$  coating was increased to 77%, as shown in Figs. 3c and d. This was because the reaction temperature had significant effect on the decomposition rate of  $(\text{C}_2\text{H}_5)_3\text{Al}$ . Higher reaction temperature led to faster decomposition rate of  $(\text{C}_2\text{H}_5)_3\text{Al}$ , and more  $\text{Al}$  atoms deposited on the surface of graphene, with increased nucleation and growth rate. When the reaction was higher than  $100\text{ }^\circ\text{C}$ , the reaction process was unstable. An optimum reaction temperature of  $100\text{ }^\circ\text{C}$  was considered appropriate.

When the reaction time was 1.5 h, the reaction temperature was  $100\text{ }^\circ\text{C}$ ,  $\text{NaH}$  was added

as a reducing agent into the solution. The Al coating was uniformly distributed, and the area coverage of Al was increased to 84% (Figs. 3e and f). Graphene/Al interface was relatively stable, and high quality Al-coated graphene was obtained. The chemical reduction of organic aluminum for coating Al on graphene surface was promoted effectively by addition of NaH. During the reaction process, the reaction product  $(C_2H_5)_2AlBr$  of chemical equation (1) and (2) reacted with NaH to produce Al,  $H_2$ ,  $C_2H_4$  and NaBr, according to the equation:



Therefore, the precipitation rate of Al atom increased with the addition of NaH, which was beneficial for coating Al on the graphene.

#### 4. Conclusions

A novel chemical reduction of organic aluminum for coating Al on the graphene surface is proposed. During the process, the Al powders reacted with  $(C_2H_5)_2Br$  solution to produce  $(C_2H_5)_3Al$  solution, followed by gradual decomposition of  $(C_2H_5)_3Al$  into Al atoms. The Al atoms gradually deposited on the surface of graphene, nucleated, grew, until the Al coating was formed on the surface of graphene. With the increase of reaction temperature, the decomposition rate of  $(C_2H_5)_3Al$  was increased, which was beneficial to coat graphene with Al. The reducing agent NaH promoted the reaction and the formation of Al coating. When the reaction temperature was  $100^\circ C$ , the reaction time was 1.5 h, and NaH was added to the solution, and high quality Al-coated graphene was obtained.

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### **Figure Captions**



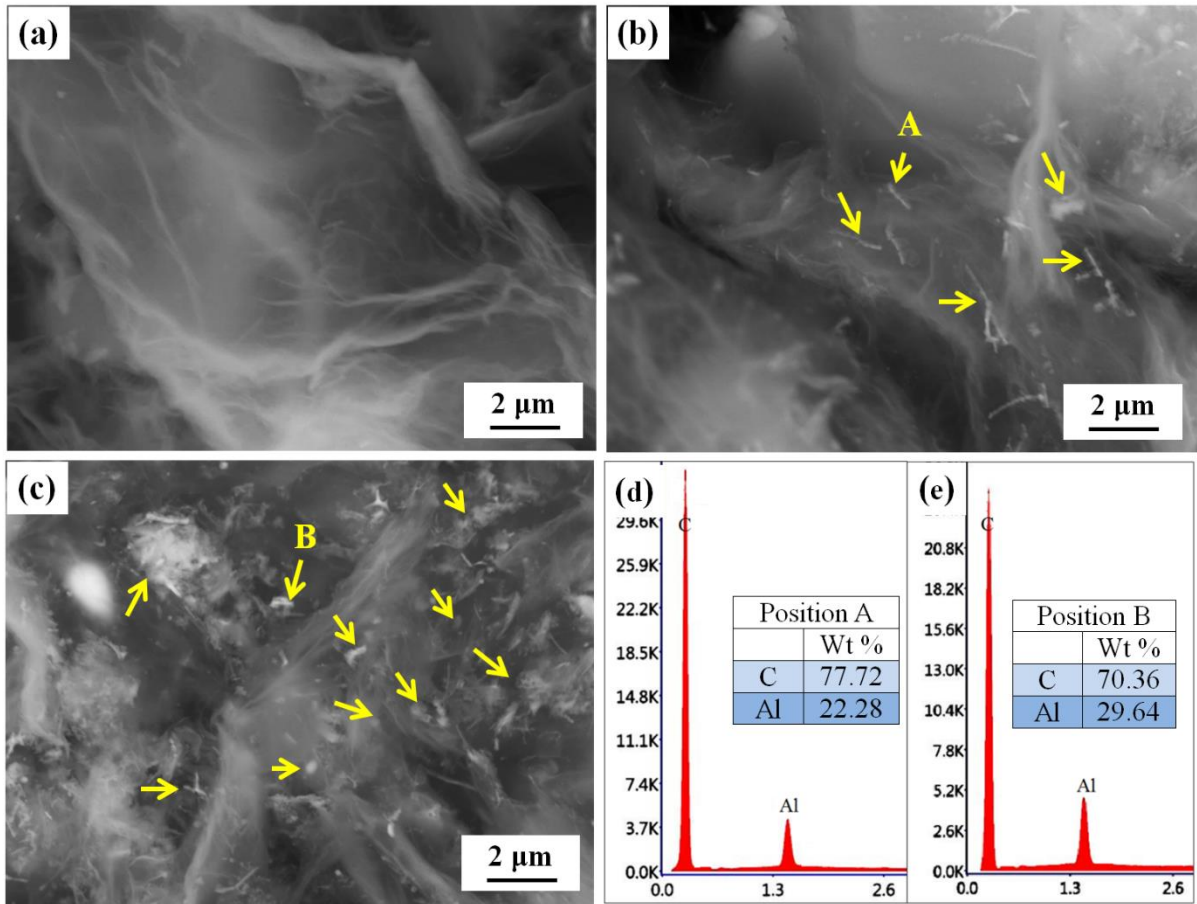


Fig. 1. SEM observations show the morphologies of (a) graphene, (b) Al-coated graphene after reaction for 0.5 h, (c) Al-coated graphene after reaction for 1 h, (d, e) composition analysis at point A and B.

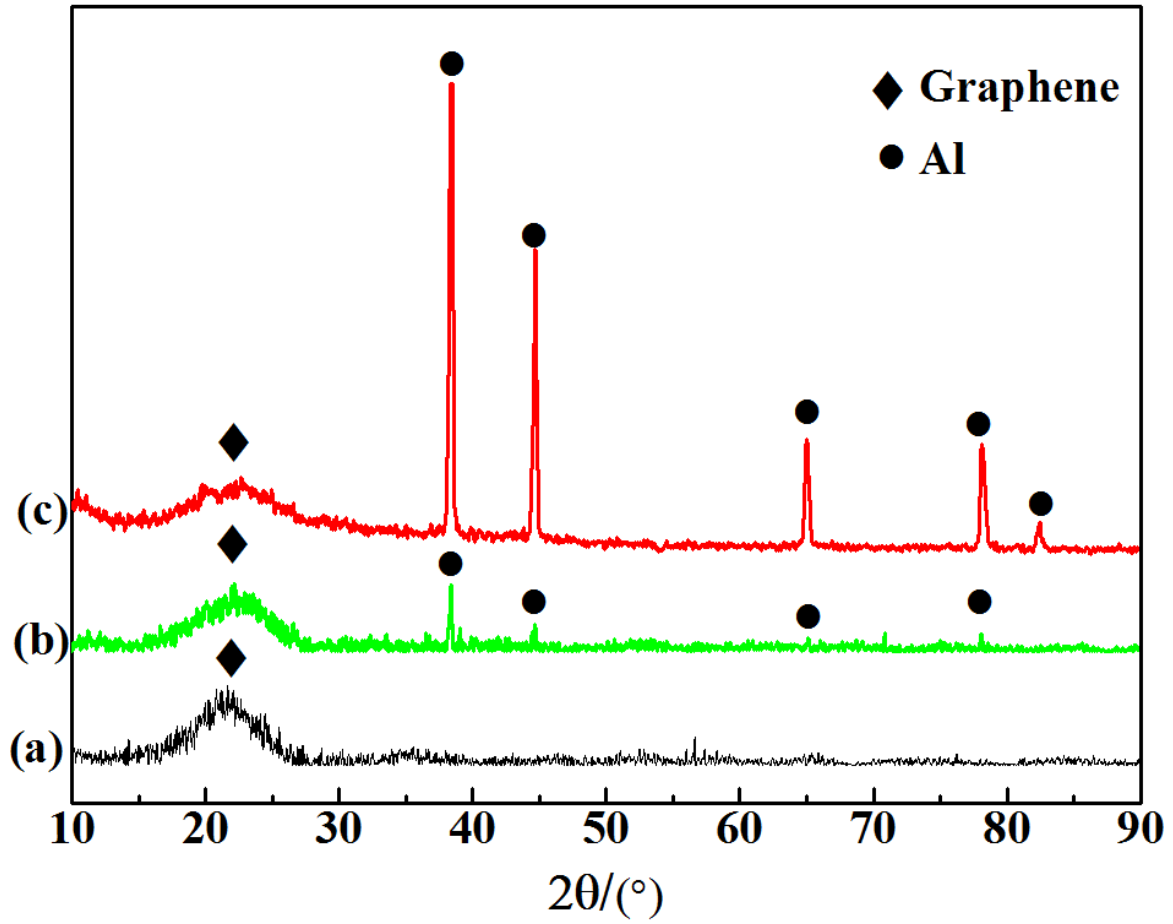


Fig. 2. XRD patterns for Al-coated graphene after different reaction time, (a) 0 h, (b) 0.5 h, (c) 1 h.

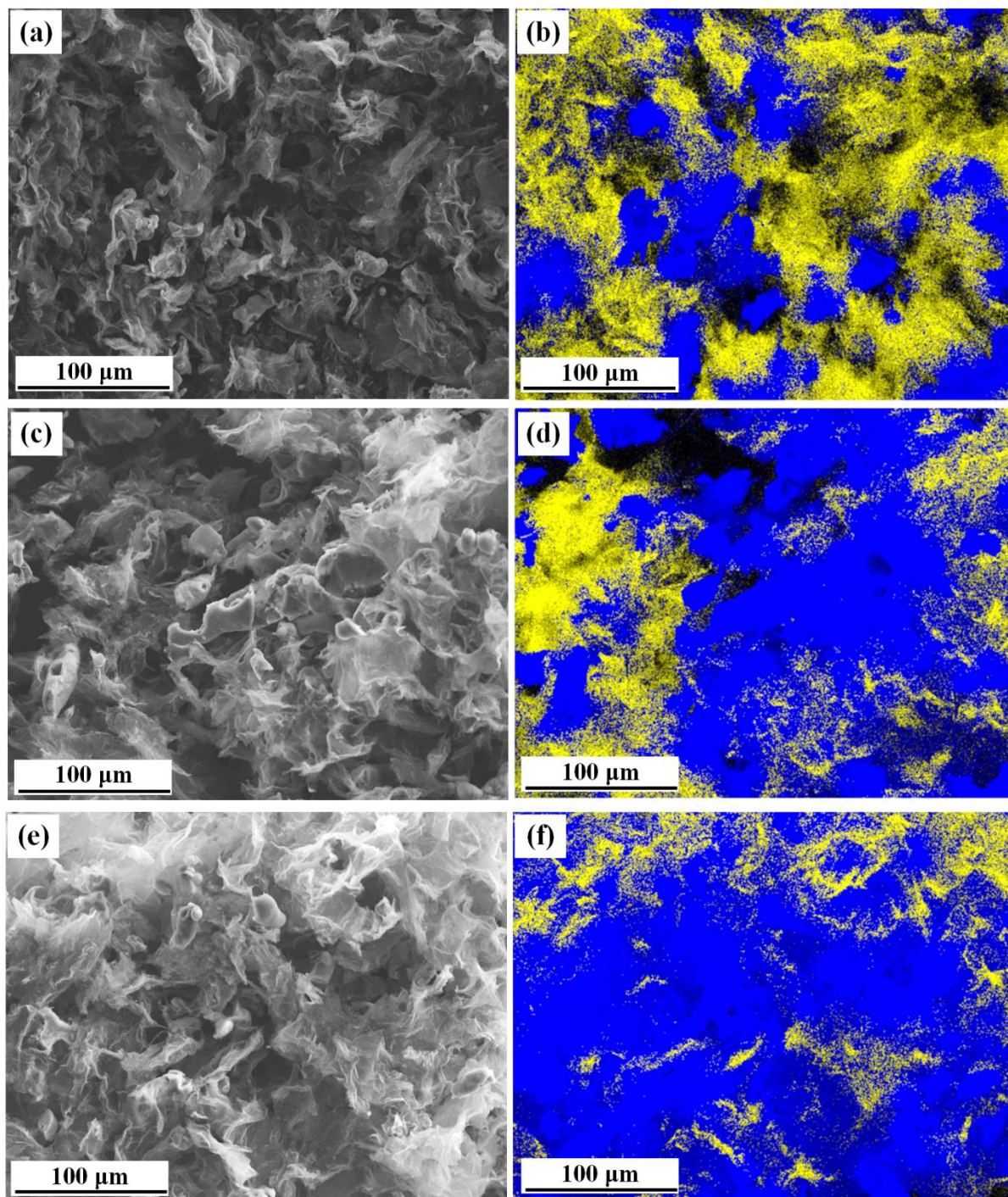


Fig. 3. The SEM images and the EDS analysis of Al-coated graphene during the different reaction process (■ Al element, ■ C element): (a) the reaction temperature 70 °C, without NaH, (b) the reaction temperature 100 °C, without NaH, (c) the reaction temperature 100 °C, with NaH.

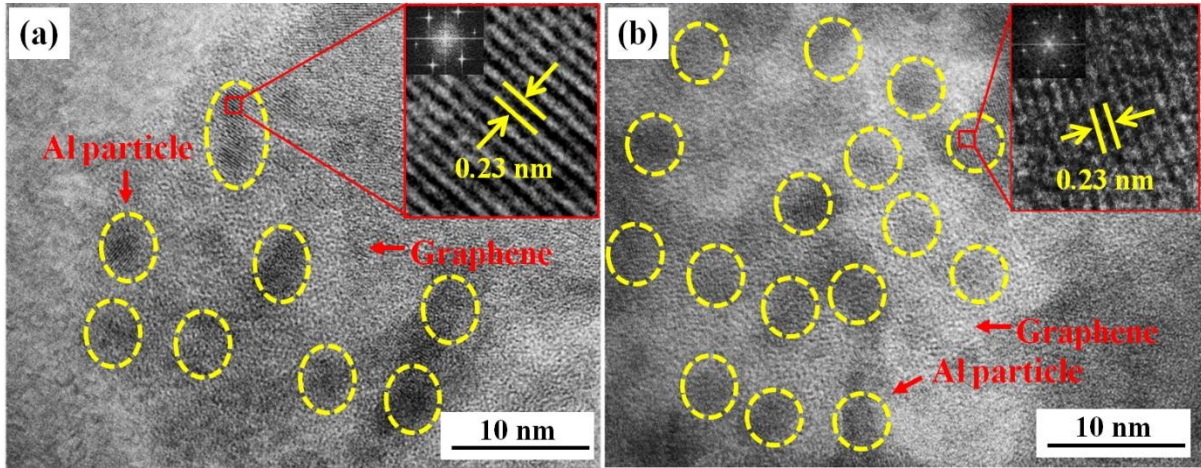


Fig. 4 High-resolution TEM images the morphologies of Al-coated graphene, (a) after reaction for 0.1 h, (b) after reaction for 0.3 h.