



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

Z.Y. Zhao^a, R.D.K. Misra^{b,*}, P.K. Bai^{a,*}, J.F. Gao^a, Y.J. Li^c, R.G. Guan^d, Z.H. Guo^e, H. Liu^{e,f}

^a School of Materials Science and Engineering, North University of China, Taiyuan 030051, China

^b Department of Metallurgical and Materials Engineering, 500 W. University Avenue, University of Texas at El Paso, TX 79968, USA

^c Department of Materials Science and Engineering, Norwegian University of Science and Technology, Alfred Getz vei 2 B, N-7491 Trondheim, Norway

^d School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

^e Integrated Composites Laboratory, Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

^f National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou 450002, China

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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 °C, and the reaction time was 1.5 h, with NaH added to the solution, high quality Al-coated graphene was obtained.

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1. Introduction

Graphene exhibits excellent mechanical properties and high conductivity. These superior properties render graphene as ideal reinforcement for Al matrix composites. 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 poor wettability between graphene and Al, graphene is difficult to disperse in Al matrix [6–8]. Coating metal on graphene surface has been proposed to improve wettability between graphene and Al [9,10], including chemical reduction, self-assembly, electrochemical deposition, vapor deposition and redox method [11–13]. These methods are mainly used to coat precious metals, copper or nickel on the surface of graphene [14,15]. 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

The graphene nanoplates was synthesized by the modified Hummers methods [18], in which the graphite particles (99.2%, <12 μm) were employed as raw material. Al powders (99.9%, 15–50 μm) were taken as matrix material. Al powder (1.5 g), bromoethane (29 mL), iodine (0.1 g) and aluminum chloride (0.1 g) was added to a reaction vessel under a H_2 -shielded atmosphere. The reaction solution was heated to 39 °C, and uniformly stirred. After the reaction was completed, the reaction solution temperature was reduced to 0 °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 °C. After reaction time of 1–1.5 h, Al-coated graphene was prepared after cleaning and drying.

* Corresponding authors.

E-mail addresses: dmsira2@utep.edu (R.D.K. Misra), baipeikang@nuc.edu.cn (P.K. Bai).

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. 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 (Fig. 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 Fig. 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:

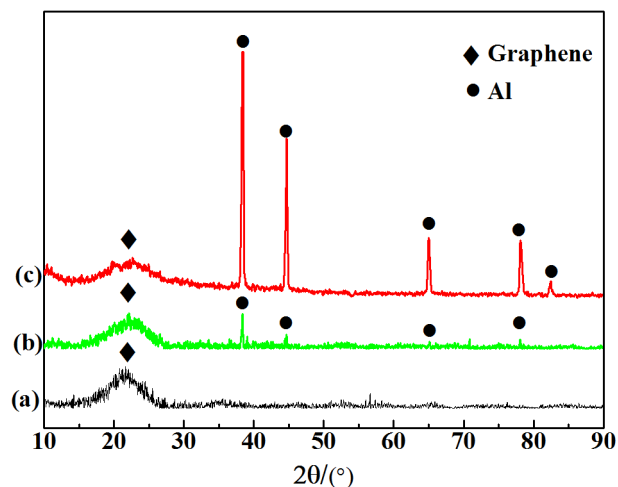
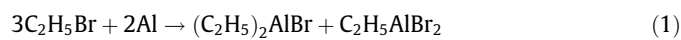
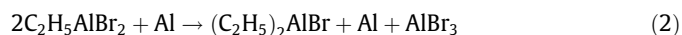
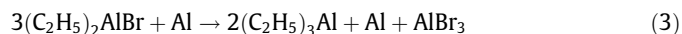


Fig. 2. XRD patterns for Al-coated graphene after different reaction time, (a) 0 h, (b) 0.5 h, (c) 1 h.

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 $(C_2H_5)_2AlBr$ and Al further reacted, and $(C_2H_5)_3Al$, Al and $AlBr_3$ were obtained via equation:



The $(C_2H_5)_3Al$ easily decomposed into Al, H_2 and C_2H_4 at high temperatures, according to the reaction:

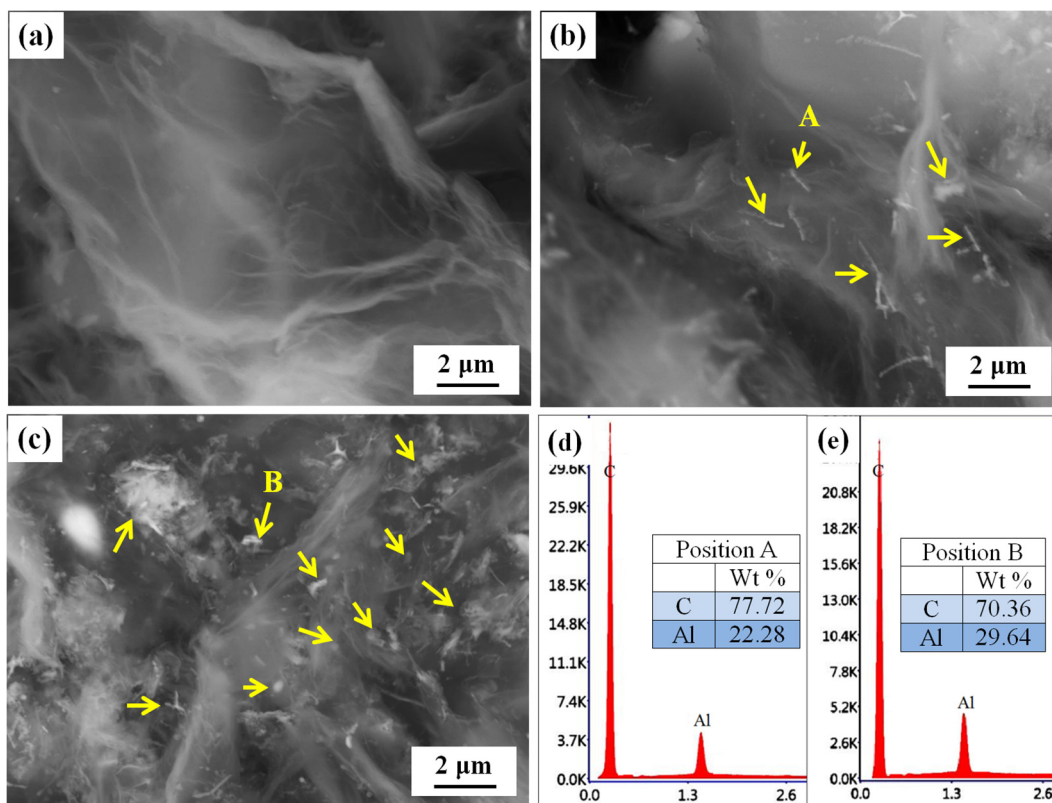


Fig. 1. SEM observations show the morphologies of (a) graphene, (b) Al-coated graphene after reaction for 0.5 h, (c) Al-coated graphene after reaction for 1 h, (d, e) composition analysis at point A and B.

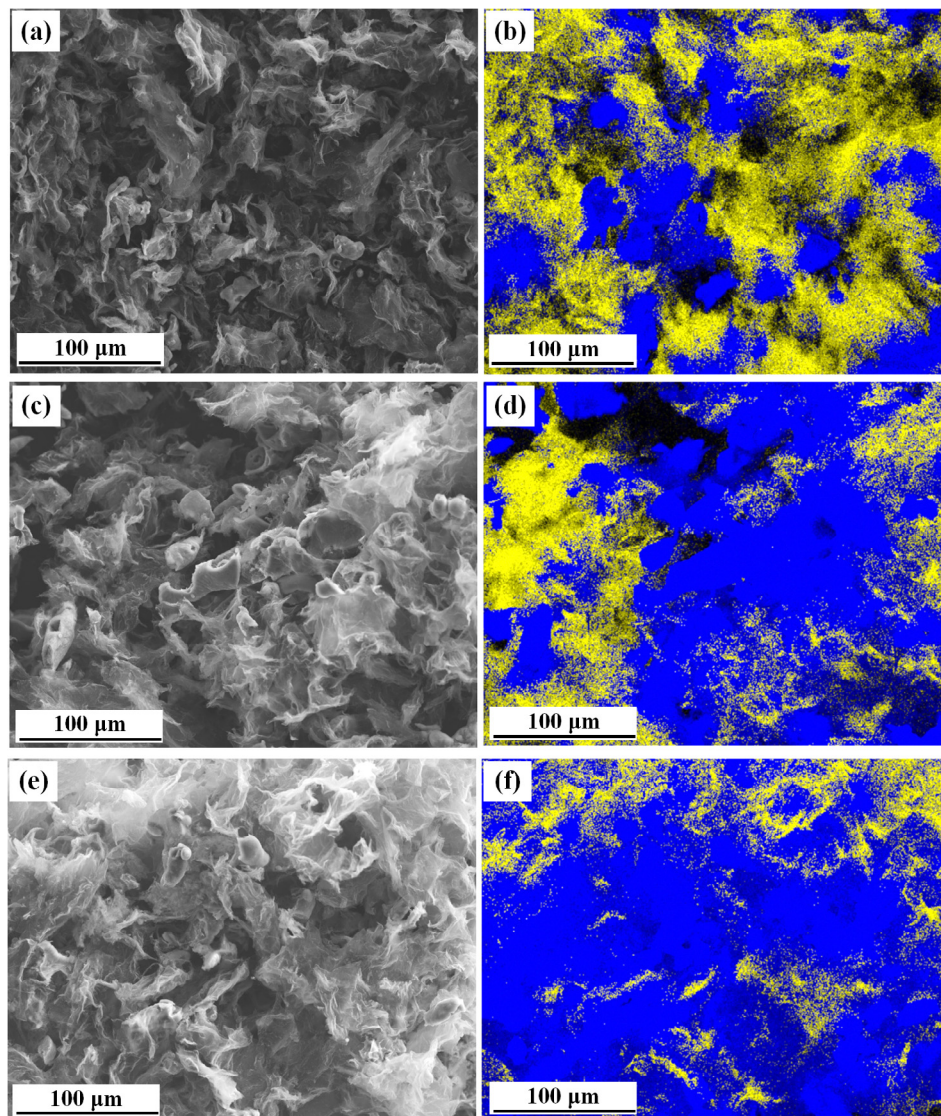


Fig. 3. The SEM images and the EDS analysis of Al-coated graphene during the different reaction process (■ Al element, ■ C element): (a) the reaction temperature 70 °C, without NaH, (b) EDS mapping of Fig. 3a, (c) the reaction temperature 100 °C, without NaH, (d) EDS mapping of Fig. 3c, (e) the reaction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

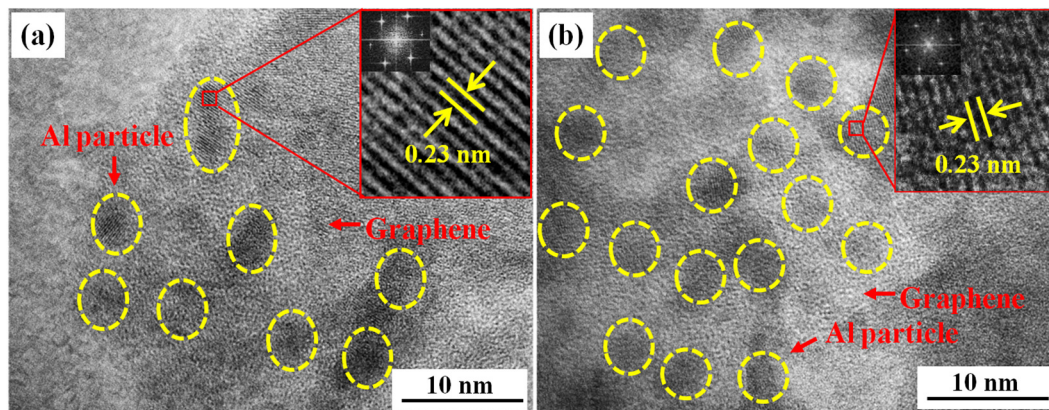


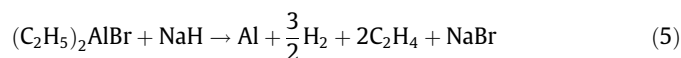
Fig. 4. High-resolution TEM images the morphologies of Al-coated graphene, (a) after reaction for 0.1 h, (b) after reaction for 0.3 h.



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

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

When the reaction time was 1.5 h, the reaction temperature was 100 °C, 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% (Fig. 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 $(\text{C}_2\text{H}_5)_2\text{AlBr}$ of chemical Eqs. (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 $(\text{C}_2\text{H}_5)_2\text{Br}$ solution to produce $(\text{C}_2\text{H}_5)_3\text{Al}$ solution, followed by gradual decomposition of $(\text{C}_2\text{H}_5)_3\text{Al}$ 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 $(\text{C}_2\text{H}_5)_3\text{Al}$ 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 °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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