The Reaction Thermodynamics during Plating Al on Graphene Process

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Abstract: This research explored a novel chemical reduction of organic aluminum for plating Al on a graphene surface. The thermodynamics of the Al plating reaction process were studied. The Al plating process consisted of two stages: the first was to prepare (C\(_2\)H\(_5\))\(_3\)Al. In this reaction, the \(\Delta H\) (enthalpy) was 10.64 kcal/mol, the \(\Delta G\) (Gibbs free energy) was 19.87 kcal/mol and the \(\Delta S\) (entropy) was 30.9 cal/(mol·K); this was an endothermic reaction. In the second stage, the (C\(_2\)H\(_5\))\(_3\)Al decomposed into Al atoms, which were gradually deposited on the surface of the graphene and the Al plating formed. At 298.15 K, the \(\Delta H\) was \(-20.21\) kcal/mol, the \(\Delta G\) was \(-54.822\) kcal/mol, the \(\Delta S\) was \(116.08\) cal/(mol·K) and the enthalpy change was negative, thus indicating an endothermic reaction.

Keywords: density functional theory (DFT); thermodynamics; graphene/aluminum composites

1. Introduction

Graphene/aluminum composites have high strength, high conductivity and high toughness. Thus, graphene/aluminum composites have wide application potentiality in the electronics, automotive and aerospace industry [1–8]. However, graphene/aluminum composites are difficult to prepare; because of the poor wettability between Al and graphene, the graphene aggregates easily in the Al matrix, which can decrease the mechanical properties of the composites [9,10]. In order to improve the wettability between graphene and Al, the ideal method is to coating melt on the surface of the graphene, by methods including self-assembly, chemical reduction, electrochemical deposition, redox method and chemical vapor deposition. For instance, Bagheri et al. prepared graphene-gold nanocomposites by self-assembly [11]. Tsai et al. coated the Cu nanoparticles on the graphene surface through coalescence and epitaxial self-assembly and studied molecular dynamics during the process [12]. Muszynski et al. synthesized gold nanoparticles through the chemical reduction of AuCl\(_4^−\) (Aldrich) with NaBH\(_4\) and coated the gold nanoparticles on the surface of graphene [13]. Zhao et al. prepared graphene nanplatelets by reinforcing copper matrix composites with electrochemical deposition and the composites’ hardnes and conductivity reached 111.2 HV and 89.2% IACS [14]. Kim et al. prepared single-atomic-layer graphene film on the surface of Cu through chemical vapor deposition (CVD), then obtained multi-layer graphene/copper composites with the strength of 1.5 GPa [15]. According to previous investigations, gold, copper, or nickel nanoparticles were usually coated on the graphene. However, these metal nanoparticles may be viewed as impurities in Al alloys, which can affect their properties. Plating Al on graphene is an effective method to improve graphene’s wettability and reduce these impurities. Because the Al is active, it is difficult to displace Al atom from conventional Al salt solution [16].

Selective laser melting (SLM), through melting successive layers of metal powder, is a promising metal additive manufacturing method [17,18], it has huge advantages compared to traditional
processing methods [19–24] and therefore has been widely used in the fields of medical, military, aerospace and automobile manufacturing [25]. The purpose of this new method is to increase the weight of graphene by plating Al on its surface, which solves the problem of uneven dispersion of graphene in Al powder for SLM. Considering that plating Al on graphene is difficult, we explored a novel chemical reduction of organic aluminum for plating Al on the graphene surface [19]. The Al plating process consisted of two stages. In the first stage, the Al powders were added to the C\textsubscript{2}H\textsubscript{5}Br solution, to produce (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Al. In the second stage, the (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Al decomposed into Al atoms, which were gradually deposited on the surface of the graphene and the Al plating formed [26]. The microstructure evolution was reported [26].

However, the reaction mechanism was unclear, especially the thermodynamics of the reaction process. Density functional theory (DFT) is a quantum mechanical method for studying the electronic structure of multi-electron systems [27–29]. DFT has a wide range of applications in physics and chemistry, especially for studying the properties of molecules and condensed states [30–32]. It is one of the most commonly used methods in computational materials and computational chemistry [30]. The objective of the study described here is to elucidate the thermodynamics of the Al plating reaction process and it provides guidance for process optimization.

2. Experiment and Simulation

2.1. Experiment

The Al powders and the graphene were employed as raw materials, as shown in Figure 1. During the Al plating reaction process, H\textsubscript{2} gas was pumped into the reaction vessel and the Al powder (1.5 g), aluminum chloride (0.1 g) and iodine (0.1 g) were dried and added into the C\textsubscript{2}H\textsubscript{5}Br (29 mL) at 39 °C. Al reacted with C\textsubscript{2}H\textsubscript{5}Br and the (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr and C\textsubscript{2}H\textsubscript{5}AlBr\textsubscript{2} were obtained as follows [26]:

\begin{equation}
3\text{C}_2\text{H}_5\text{Br} + 2\text{Al} \rightarrow (\text{C}_2\text{H}_5)_2\text{AlBr} + \text{C}_2\text{H}_5\text{AlBr}
\end{equation}

The Al reacted with C\textsubscript{2}H\textsubscript{5}AlBr\textsubscript{2} to produce (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr, Al and AlBr\textsubscript{3} [26]:

\begin{equation}
2\text{C}_2\text{H}_5\text{AlBr} + \text{Al} \rightarrow (\text{C}_2\text{H}_5)_2\text{AlBr} + \text{Al} + \text{AlBr}_3
\end{equation}

The (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr and Al further reacted to produce Al, (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Al and AlBr\textsubscript{3} via Equation [26]:

\begin{equation}
3(\text{C}_2\text{H}_5)_2\text{AlBr} + \text{Al} \rightarrow 2(\text{C}_2\text{H}_5)_3\text{Al} + \text{Al} + \text{AlBr}_3
\end{equation}

After reaction, the solution temperature was kept at 0 °C for 1 h. The tetrahydrofuran was added to the solution. The solution was filtered after the reaction and the alkyl aluminum solution was obtained. Then, the graphene (0.05 g) was added to the alkyl aluminum solution. The temperature was kept at 70–100 °C for 1–1.5 h and the (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Al was decomposed into Al, H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} [26]:

\begin{equation}
2(\text{C}_2\text{H}_5)_3\text{Al} \rightarrow 6\text{C}_2\text{H}_4 + 3\text{H}_2 + 2\text{Al}
\end{equation}

The Al atoms were gradually deposited on the surface of the graphene and the Al plating formed. Al atoms absorbed on graphene may form upon (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Al/graphene collisions. This reaction is initiated by ethane elimination from the (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Al molecule, similar to the observations reported for (CH\textsubscript{3})\textsubscript{3}Al/graphene [33]. Microstructure observation was carried out using a scanning electron microscope (SEM) (Zeiss Ultra 55, Carl Zeiss Microscopy, Jena, Germany) equipped with energy dispersive spectroscopy (EDS).
H1C1C2 increased from 109.471° to 111.590°, ∠C1C2Br increased from 109.469 ° to 111.496°  and ∠BrC2H5 decreased from 109.472° to 103.736°. The bond length of H 1–C1 decreased from 1.14 Å to 1.1 Å, the C1–C2 bond was reduced from 1.54 Å to 1.517 Å, the C 2–Br bond as increased from 1.91 Å to 2.025 Å and the C2–H5 bond was reduced from 1.14 Å to 1.095 Å. During the structure optimization process, the bond angle and bond length of atom s tended to be stable through the vibration displacement and the total energy was gradually minimized.

Figure 1. Scanning electron microscopy (SEM) image and energy dispersive spectrometer (EDS) analysis of Graphene/aluminum composites with different reaction times: (a) Graphene/aluminum composites prepared with reaction time of 1 h; (b) Graphene/aluminum composites prepared with reaction time of 1.5 h; (c) Low-magnification SEM image of composite prepared with reaction time of 1.5 h; (d) map analysis of (c).

2.2. Computation Details

During the process of plating Al on the graphene, the thermodynamics of the chemical reduction of organic aluminum were simulated by density functional theory (DFT) methods implemented in the Dmol3 package of Materials Studio. The structure of the reaction products was analyzed through the DFT, revealing the thermodynamic properties and reaction types of the chemical reactions. Spin-unrestricted DFT in the generalized gradient approximation (GGA) with the Revised Perdew-Burke-Eruzerhof (RPBE) exchange-correlation functional approach and double numerical plus polarization atomic orbitals was employed as the basis set. The Brillouin zone was sampled using the 4 × 4 × 1 k-point grid thickness, which presented a good approximation of the model below the article. In addition, the energy tolerance accuracy, maximum force and displacement were set as 1 × 10^{-5} Ha, 2 × 10^{-3} Ha/Å and 5 × 10^{-3} Å, respectively, to ensure high accuracy in all calculations.

During the Dmol3 simulation process, the relationship between thermodynamic properties (entropy S, enthalpy H, heat capacity Cp, Gibbs free energy G) and temperature can be calculated from the vibration frequency. The total energy at 0 K was obtained during the simulation. The translational energy, rotational energy and vibration energy were used to calculate the thermodynamic properties at an instantaneous temperature. The instantaneous enthalpy H is:

\[
H(T) = E_{vib}(T) + E_{rot}(T) + E_{trans}(T) + RT
\]

where \(E_{vib}(T)\), \(E_{rot}(T)\) and \(E_{trans}(T)\) are vibration energy, rotational energy and translational energy respectively at temperature \(T\) and \(R\) is an ideal gas constant.
The contribution of vibration to enthalpy is:

\[ E_{\text{vib}}(T) = \frac{R}{2} \sum_i h\nu_i + \frac{R}{K} \sum_i \frac{h\nu_i \exp(-h\nu_i / kT)}{1 - \exp(-h\nu_i / kT)} \]  

(6)

The contribution of vibration to entropy is:

\[ S_{\text{vib}} = R \sum_i \frac{(h\nu_i / kT) \exp(-h\nu_i / kT)}{1 - \exp(-h\nu_i / kT)} - R \sum_i \ln[1 - \exp(-h\nu_i / kT)] \]  

(7)

The contribution of vibration to heat capacity at normal pressure is:

\[ C_{\text{vib}} = R \sum_i \frac{(h\nu_i / kT)^2 \exp(-h\nu_i / kT)}{[1 - \exp(-h\nu_i / kT)]^2} \]  

(8)

where \( k \) is the Boltzmann constant, \( h \) is the Planck constant and \( \nu_i \) is the vibration frequency of the \( i \)th atom. Each of the chemical bond vibrational frequencies was calculated by DFT at 298.15 K and then assumed to remain constant with Temperature.

3. Results and Discussions

3.1. Preparation and Reaction Mechanism of Al-Coated Graphene

During the Al plating process, with the increase of reaction time, more Al was deposited on the graphene, as shown in Figure 1a,b. When the chemical reduction reaction was at 1.5 h, abundant Al atoms were deposited on the graphene uniformly, the Al plating was formed and the content of the Al element was 71%, as shown in Figure 1c,d.

3.2. Reaction Thermodynamics during Plating Al on Graphene Process

The molecular model of each substance was established and its structure optimized during the chemical reduction reaction process. The vibration frequency was calculated and the thermodynamic properties of each substance were analyzed. The thermodynamics of the formation and decomposition of (C\( _2 \)H\( _5 \))\( _3 \)Al were calculated according to the laws of thermodynamics.

During the process of plating Al on grapheme, based on the reaction Equations (1) and (3), the structural optimization and thermodynamic calculation of C\( _2 \)H\( _5 \)Br, (C\( _2 \)H\( _5 \))\( _2 \)AlBr, C\( _2 \)H\( _5 \)AlBr\( _2 \), (C\( _2 \)H\( _5 \))\( _3 \)Al and AlBr\( _3 \) were carried out through the Al cluster (Al\( _3 \)) molecular model [34].

3.2.1. Structure Optimization and Thermodynamic Properties of C\( _2 \)H\( _5 \)Br

Figure 2 shows the structure of the C\( _2 \)H\( _5 \)Br molecule. The initial structure of the C\( _2 \)H\( _5 \)Br molecule built in MS is shown in Figure 2a; the stable molecular structure after structure optimization is shown in Figure 2b. After structure optimization, \( \angle H_1 C_1 C_2 \) was reduced from 109.471° to 108.747°, \( \angle H_1 C_1 C_2 \) increased from 109.471° to 111.590°, \( \angle C_1 C_2 Br \) increased from 109.469° to 111.496° and \( \angle BrC_2 H_5 \) decreased from 109.472° to 103.736°. The bond length of H\( _3 \)–C\( _1 \) decreased from 1.14 Å to 1.1 Å, the C\( _1 \)–C\( _2 \) bond was reduced from 1.54 Å to 1.517 Å, the C\( _2 \)–Br bond as increased from 1.91 Å to 2.025 Å and the C\( _2 \)–H\( _5 \) bond was reduced from 1.14 Å to 1.095 Å. During the structure optimization process, the bond angle and bond length of atoms tended to be stable through the vibration displacement and the total energy was gradually minimized.

Figure 3 shows the relationship between the thermodynamic properties (entropy \( S \), enthalpy \( H \), heat capacity \( C_p \), Gibbs free energy \( G \)) of the C\( _2 \)H\( _5 \)Br and temperature was obtained through Equations (5)–(8). In the range of 25–1000 K, the enthalpy of the C\( _2 \)H\( _5 \)Br molecule had a linear relationship with the temperature and the enthalpy value increased with the increase of temperature. The heat capacity of C\( _2 \)H\( _5 \)Br gradually increased with the increase of temperature, although the free
energy decreased. At 298.15 K, the enthalpy, entropy, free energy and heat capacity of C\textsubscript{2}H\textsubscript{5}Br molecules were 43.533 kcal/mol, 68.433 cal/(mol·K), 15.174 cal/(mol·K) and 23.127 kcal/mol respectively, as shown in Table 1.

![Molecular model of C\textsubscript{2}H\textsubscript{5}Br molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).](image)

**Figure 2.** Molecular model of C\textsubscript{2}H\textsubscript{5}Br molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).

![Graph showing the relationship between the thermodynamic properties of C\textsubscript{2}H\textsubscript{5}Br and temperature.](image)

**Figure 3.** The relationship between the thermodynamic properties of C\textsubscript{2}H\textsubscript{5}Br and temperature.

| Property Value | Temperature/°C |
|----------------|----------------|
| 100            |                |
| 90             |                |
| 80             |                |
| 70             |                |
| 60             |                |
| 50             |                |
| 40             |                |
| 30             |                |
| 20             |                |
| 10             |                |
| 0              |                |
| -10            |                |
| -20            |                |
| -30            |                |
| -40            |                |
| -50            |                |
| -60            |                |
| -70            |                |
| -80            |                |
| -90            |                |
| 100            |                |

**Table 1.** The total energy and the thermodynamic properties at 298.15 K of each component.

| Substance     | E (\textsuperscript{1}Har/at) | H (kcal/mol) | G (kcal/mol) |
|---------------|--------------------------------|--------------|--------------|
| C\textsubscript{2}H\textsubscript{5}Br | -423.7794203                  | 43.533       | 23.127       |
| Al            | -727.1831592                  | 4.348        | -16.613      |
| (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr | -745.5311183                  | 85.548       | 56.435       |
| C\textsubscript{2}H\textsubscript{5}AlBr\textsubscript{2} | -1010.8496025                 | 46.425       | 18.226       |

\textsuperscript{1}1 Har/at = 627.5 kcal/mol.

### 3.2.2. Structure Optimization and Thermodynamic Properties of (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr

Figure 4 shows the structure of (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr. After structure optimization, ∠H\textsubscript{1}C\textsubscript{1}H\textsubscript{2} decreased from 109.415° to 107.039°, ∠C\textsubscript{1}C\textsubscript{2}Al increased by 9.965°, ∠H\textsubscript{4}C\textsubscript{2}H\textsubscript{5} decreased by 5.254° and ∠C\textsubscript{2}AlC\textsubscript{3} decreased by 5.254°. The length of the Al–C\textsubscript{3} bond increased from 1.88 Å to 1.98 Å, the length of the C\textsubscript{3}–H\textsubscript{7} bond decreased by 0.03 Å, the length of the C\textsubscript{3}–C\textsubscript{4} bond increased by 0.009 Å and the length of the C\textsubscript{4}–H\textsubscript{9} bond decreased by 0.026 Å.

![Molecular model of (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr molecule.](image)

**Figure 4.** Molecular model of (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlBr molecule.
increased by 2.571°. The length of the Br–Al bond increased from 2.250 Å to 2.331 Å, the length of the Al–C₃ bond increased from 1.88 Å to 1.98 Å, the length of the C₃–H₂ bond decreased by 0.03 Å, the length of the C₃–C₄ bond increased by 0.009 Å and the length of the C₄–H₉ bond decreased from 1.140 Å to 1.102 Å. Figure 5 shows the relationship between the thermodynamic properties of (C₂H₅)₂AlBr and temperature. It can be seen that the enthalpy, entropy and heat capacity of (C₂H₅)₂AlBr increased with the increase of temperature in the range of 25–1000 K and the free energy decreased with the increase of temperature. At 298.15 K, the enthalpy, entropy, heat capacity and free energy were 85.548 kcal/mol, 97.648 cal/(mol·K), 33.078 cal/(mol·K) and 56.435 kcal/mol, respectively, as shown in Table 1.

![Molecular model of (C₂H₅)₂AlBr molecule. (a) Initial model; (b) Optimized model.](image)

**Figure 4.** Molecular model of (C₂H₅)₂AlBr molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).

**Figure 5.** The relationship between the thermodynamic properties of (C₂H₅)₂AlBr and temperature.

### 3.2.3. Structure Optimization and Thermodynamic Properties of C₂H₅AlBr₂

Figure 6 shows the original and the optimal structure of C₂H₅AlBr₂. After structure optimization, the angle of H₁–C₂–H₂ decreased from 109.511° to 104.953°, the angle of H₃–H₀–H₄ decreased from 109.52° to 107.514°, the angle of C₁–Al increased from 109.239° to 117.439°, the angle of C₁–AlBr₁ increased by 0.3° and the angle of Br₁AlBr₁ decreased by 3.685°. The bond length of H₂–C₁ decreased from 1.14 Å to 1.102 Å and the bond length of C₁–C₂ increased by 0.007 Å, indicating that the C–C bond was relatively stable. The bond length of C₁–Al was increased by 0.085 Å and the bond length of Al–Br₁ was increased by 0.45 Å. Figure 7 shows the relationship
between the thermodynamic properties of C₂H₅AlBr₂ and temperature. It can be seen that the enthalpy, entropy and heat capacity of C₂H₅AlBr₂ increased with the increase of temperature in the range of 25–1000 K. The free energy decreased with the increase of temperature. At 298.15 K, the enthalpy, entropy, heat capacity and free energy were 46.425 kcal/mol, 94.579 cal/(mol·K), 26.606 cal/(mol·K) and 18.226 kcal/mol respectively (Table 1).

![Figure 6. Molecular model of C₂H₅AlBr₂ molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).](image)

Figure 6. Molecular model of C₂H₅AlBr₂ molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).

![Figure 7. The relationship between the thermodynamic properties of C₂H₅AlBr₂ and temperature.](image)

Figure 7. The relationship between the thermodynamic properties of C₂H₅AlBr₂ and temperature.

3.2.4. Structure Optimization and Thermodynamic Properties of (C₂H₅)₃Al

Figure 8 shows the structure of (C₂H₅)₃Al. After structure optimization, ∠C₂AlC₃ was reduced from 119.992° to 118.949°, ∠C₂AlC₅ decreased from 119.805° to 119.593°, ∠C₃AlC₅ increased from 119.891° to 121.407°, ∠AlC₅C₆ increased from 108.858° to 117.775°, ∠H₁₁C₅H₁₂ decreased from 109.536° to 103.956° and ∠H₁₃C₆H₁₄ decreased from 109.447° to 107.13°. The H₁–C₁ bond length was reduced from 1.14 Å to 1.105 Å, the C₁–C₂ bond length increased from 1.54 Å to 1.551 Å, the C₆–Al bond length increased from 1.879 Å to 1.997 Å and the C₂–H₄ bond length was reduced from 1.14 Å to 1.112 Å. During the optimization process, the C–Al bond rotated, the bond angle had large variation, the bond length changed little and the initial structure was significantly different from the optimized structure. Figure 9 shows the thermodynamic properties of (C₂H₅)₃Al. In the range of 25–1000 K, the enthalpy, entropy and heat capacity of (C₂H₅)₃Al increased with the increase of temperature. The free energy
decreased with the increase of temperature. At 298.15 K, the enthalpy, entropy and heat capacity were 125.294 kcal/mol, 102.836 cal/(mol·K), 41.264 cal/(mol·K) and 94.634 kcal/mol, respectively.

![Molecular model of (C2H5)3Al molecule.](image)

Figure 8. Molecular model of (C2H5)3Al molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).

![Thermodynamic properties of AlBr3](image)

Figure 8. Molecular model of (C2H5)3Al molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).

![Thermodynamic properties of AlBr3](image)

Figure 9. The relationship between the thermodynamic properties of (C2H5)3Al and temperature.

3.2.5. Structure Optimization and Thermodynamic Properties of AlBr3

Figure 10 shows the structure of AlBr3. It can be seen that after optimization of the AlBr3 structure, the bond angle of AlBr3 increased from equal 120° to 120.687°, 120.173° and 119.14°. The Br1–Al bond length increased from 2.25 Å to 2.267 Å, the Br2–Al bond length increased from 2.254 Å to 2.264 Å and the Br3–Al bond length increased from 2.25 Å to 2.267 Å. Figure 11 shows the thermodynamic properties of AlBr3. It can be seen that in the range of 25–1000 K, the enthalpy and entropy of the AlBr3 molecule increased with the increase of temperature, the heat capacity tended to be stable with the increase of temperature and the free energy decreased with the increase of temperature. The free energy was 0 kcal/mol at 25 K, which gradually decreased to a negative value with the increase of temperature. At 298.15 K, the enthalpy, entropy, heat capacity and free energy were 6.478 kcal/mol, 88.04 cal/(mol·K), 18.250 cal/(mol·K) and −19.771 kcal/mol, respectively.
Br

was

preparation process (reaction Equation (3)). At 298.15 K, the

∆H was 30.9 cal/(mol K) and the enthalpy change was greater than 0; indicating

this was an exothermic reaction.

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Table 2 shows the thermodynamic properties during Al reacting with C2H5Br to produce

(C2H5)2AlBr and C2H5AlBr2. It can be seen that when the reaction temperature was 298.15

K, the ΔH was −160.77 kcal/mol, ΔG was −139.83 kcal/mol and ΔS was −70.2 cal/(mol K); it was thus an

exothermic reaction.

Table 2. The thermodynamic properties during Al reacting with C2H5Br to produce (C2H5)2AlBr and

C2H5AlBr2.

| 1ΔH (kcal/mol) | 2ΔG (kcal/mol) | 3ΔS (cal/mol·K) |
|---------------|---------------|---------------|
| −160.77       | −139.83       | −70.2         |

1ΔH = ∑(E + H)_{product} − ∑(E + H)_{reactant};
2ΔG = ∑(E + H)_{product} − ∑(E + H)_{reactant};
3ΔS = (ΔH − ΔG) / T.

Table 3 shows the total energy and thermodynamic properties of each component during

(C2H5)3Al preparation at 298.15 K. Table 4 shows the thermodynamic properties during the (C2H5)3Al

preparation process (reaction Equation (3)). At 298.15 K, the ΔH was 10.64 kcal/mol, the ΔG was

19.87 kcal/mol, the ΔS was 30.9 cal/(mol·K) and the enthalpy change was greater than 0; indicating

this was an endothermic reaction.
Table 3. Total energy and thermodynamic properties of each component during (C₂H₅)₃Al preparation at 298.15 K.

| Substance       | E (Har/at)       | H (kcal/mol) | G (kcal/mol) |
|-----------------|------------------|--------------|--------------|
| (C₂H₅)₃Al       | −480.2022142     | 125.294      | 94.634       |
| AlBr₃           | −1276.1579299    | 6.478        | −19.771      |

Table 4. The thermodynamic properties during preparing (C₂H₅)₃Al process.

| Property       | Value |
|----------------|-------|
| ∆H (kcal/mol)  | 10.64 |
| ∆G (kcal/mol)  | 19.87 |
| ∆S (cal/mol·K) | 30.9  |

3.2.6. Structure Optimization and Thermodynamic Properties of C₂H₄

Figure 12 shows the structure of C₂H₄. After structural optimization, ∠H₂C₂H₄ was reduced from 120.001° to 116.504°. The bond length of C–H decreased from 1.14 Å to 1.094 Å and the bond length of C=C was reduced from 1.54 Å to 1.342 Å. Figure 13 shows the thermodynamic properties of C₂H₄. It can be seen that the enthalpy, entropy and heat capacity of C₂H₄ increased with the increase of temperature in the range of 25–1000 K. The free energy decreased with the increase of temperature. At 298.15 K, the enthalpy, entropy, heat capacity and free energy were 33.759 kcal/mol, 55.228 cal/(mol·K), 10.372 cal/(mol·K) and 17.293 kcal/mol respectively (Table 5).

Figure 12. Molecular model of C₂H₄ molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).

Figure 13. The relationship between the thermodynamic properties of C₂H₄ and temperature.
3.2.7. Structure Optimization and Thermodynamic Properties of H\(_2\)

Figure 14 shows the structure of H\(_2\). It can be seen that after structural optimization, the bond length of H–H increased from 0.74 Å to 0.747 Å. Figure 15 shows the relationship between the thermodynamic properties of H\(_2\) and temperature. The enthalpy, entropy and heat capacity of H\(_2\) increased with the increase of temperature and the free energy decreased with the increase of temperature. At 298.15 k, the enthalpy, entropy, heat capacity and free energy were respectively 8.367 cal/mol, 32.531 cal/(mol·K), 6.955 cal/(mol·K) and −1.332 kcal/mol (Table 5).

![Molecular model of H\(_2\) molecule. (a) Initial model; (b) Optimized model. The unit of the angle in the image is (°), and the unit of the bond length is angstrom (Å).](image)

![The relationship between the thermodynamic properties of H\(_2\) and temperature.](image)

Table 5. The total energy and thermodynamic properties of each component during (C\(_2\)H\(_5\))\(_3\)Al decomposition at 298.15 K.

| Substance | E (Har/at) | H (kcal/mol) | G (kcal/mol) |
|-----------|------------|--------------|--------------|
| C\(_2\)H\(_4\) | −78.6243401 | 33.759 | 17.293 |
| H\(_2\) | −1.2899789 | 8.367 | −1.332 |

Table 5 shows the thermodynamic properties during the (C\(_2\)H\(_5\))\(_3\)Al decomposition process (reaction Equation (4)). At 298.15 K, the \(\Delta H\) was −20.21 kcal/mol, the \(\Delta G\) was −54.822 kcal/mol, the \(\Delta S\) was 116.08 cal/(mol·K) (Table 6) and the enthalpy change was less than 0, this was an endothermic reaction.

Table 6. The thermodynamic properties during preparing (C\(_2\)H\(_5\))\(_3\)Al process.

| \(\Delta H\) (kcal/mol) | \(\Delta G\) (kcal/mol) | \(\Delta S\) (cal/mol·K) |
|------------------------|------------------------|------------------------|
| −20.21                 | −54.822                | 116.08                 |
4. Conclusions

We explored a novel chemical reduction of organic aluminum for plating Al on a graphene surface. The thermodynamics of the Al plating reaction process were studied. The Al plating process consisted of two stages: the first was to prepare \((\text{C}_2\text{H}_5)_3\text{Al}\); the \(\Delta H\) was 10.64 kcal/mol, the \(\Delta G\) was 19.87 kcal/mol, the \(\Delta S\) was 30.9 cal/(mol·K); this was an endothermic reaction. In the second stage, the \((\text{C}_2\text{H}_5)_3\text{Al}\) decomposed into Al atoms, which were gradually deposited on the surface of the graphene and the Al plating formed. At 298.15 K, the \(\Delta H\) was \(-20.21\) kcal/mol, the \(\Delta G\) was \(-54.822\) kcal/mol, the \(\Delta S\) was 116.08 cal/(mol·K) and the enthalpy change was negative, thus indicating an endothermic reaction. The results show that the reaction efficiency can be improved significantly by increasing the reaction temperature and reaction time appropriately.

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