In-Situ Synthesis of Undulated Ni Anchored To Graphene/Al with One-Step Method

Xinghai Liu [a], Junwei Sha [a], Enzuo Liu [a, b], Qunying Li [a], Chunsheng Shi [a], Chunnian He [a, b], Jiajun Li [a], Naiqin Zhao [a, b]*

a School of Materials Science and Engineering and Tianjin Key Laboratory of Composites and Functional Materials, Tianjin University, Tianjin 300350, PR China

b Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, PR China

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ABSTRACT

Here we present a new approach for synthesizing the graphene nanosheets (GNS) on aluminum matrix by an in-situ chemical vapor deposition process assisted with the precursors of epoxy resin template and Ni catalysts as well as glucose carbon source. The results show that the GNS exhibits a vertical grid network structure with a high specific surface area of 703.38 m^2/g covered on aluminum powder since the epoxy resin enables forming three dimensional crosslinked network structures. In addition, a small amount of nano-sized Al_4C_3 intermediate phases was observed in the bulk materials that fabricated by powder metallurgy (PM) technology. Moreover, the effects of GNS and Al_4C_3 on the conductivity of the bulk materials show that the GNS/Al bulk composite with 2.5 vol % GNS exhibits the highest electrical conductivity of 38.0 MS/m compared to the pure aluminum of 34.4 MS/m. The mechanical properties test show that the GNS/Al composite with 2.5 vol % GNS exhibits the optimal comprehensive mechanical properties with a tensile strength of 307 MPa, more than 75% improvement compared to pure Al and favorable elongation of 13.7 %. The major enhancing mechanism of the composite was attributes to dislocation strengthening and load transfer. This new network-like structure of GNS herein presents promising application prospects in structural composites as the reinforcement and functional materials as the conductive substrate.

INTRODUCTION

The papers presented at the ICCM21 will be published Carbon nanomaterials, including carbon fiber (Cf), carbon nanotubes (CNTs), graphene (GN), and fullerene *et al*, which present excellent mechanical, electrical, and thermal properties including high specific surface area and low density, show good potential prospects in fields of energy storage device [1-6] and metal matrix structural composites. [7-9] Especially graphene, with a high theoretical Young's modulus (~ 1.1 TPa), tensile strength (> 130 GPa), low density (~ 2.2 g cm^{-3}), high specific surface area (~ 2630 m^2/g), and high electrical mobility (15000 cm/V·S), is considered as an ideal functional and reinforcing material, which has intercepted lots of attention in recent years.[10] As a result, more and more researchers have paid attention to the preparation of GN with various catalysts on different matrices ever since it appeared. [11-14] By using chemical vapor deposition (CVD) method, many researchers have synthesized thickness-controlled GN on Cu or Ni foil, Fe/MgO and SiO_2/Si matrices with excellent optical, electrical or thermal properties. [15-18] However, the typical synthesis temperature of GN *via* conventional CVD method is over 800 °C, which is higher than the melting points of Al, which would lead to the instability of the corresponding used devices and limit its application. [19] Therefore, Lee *et al.* have attempted the plasma-enhanced CVD (PECVD) method to prepare GN on SiO_2/Si bases at 600 °C and obtained notable conductivity of the composite. [20] To solve this problem, several efforts have been made by introducing reduced graphene oxide (rGO) into metal matrices to achieve enhanced mechanical and thermal performances in recent years. Li *et al.* reported the preparation of graphene/Al composites by direct electrostatic adsorption between graphene oxide and Al powder, which achieved relatively uniformly dispersion of rGO in Al matrix. [21] Jiang *et al.* have proposed the solvothermal-assisted method to encapsulate SiC nanoparticles with GN on Al matrix and acquired a high thermal conductivity of the composite. [22] However, the aggregation and structural integrity of graphene sheets, as well as weak interfacial bonding between graphene and metal matrices, still limit the thermal, electrical and other properties improvement of the composites. Thus, an easy and efficient strategy to achieve well dispersed and homogeneously distributed graphene on Al matrix with strong interfacial bonding was sought. Superior to the *ex-situ* regimes, He *et al*. developed an *in-situ* CVD process to prepare CNTs reinforced Al matrix composites, enabling the one-dimensional growth of CNTs on Al powders with a top growth model by activated Ni particles that anchored to aluminum surface, which acquire strong connection between CNTs and Al matrix. [23] By using the similar method, He *et al*., Li *et al* and Nasibulin et al. have successfully prepared CNTs and carbon nano-onion (CNOs) on Al and Cu matrices with the catalysis of Ni, Co or Cu. [24-26] Unlike the synthesis of CNTs, in the case of *in-situ* synthesizing two-dimensional graphene on Al, carbon source, catalyst and especially a planar template are of great importance. So far, it is still hard to *in-situ* prepare graphene on Al to fabricate the GN/Al composites, mainly ties in that the lack of an appropriate planar template on Al, non-catalytic instinct of Al and weak interfacial wettability between carbon and aluminum. [27] Furthermore, the interfacial reactive production Al_3C_4 between carbon and aluminum over 500 ºC [28, 29] would also restrict the development of graphene/Al composites. [30] Consequently, *in-situ* preparation of graphene on Al to avoid large amount of Al_4C_3 formation at a relatively low temperature remains a challenge.

Herein, a vertical grid like graphene nanosheet (GNS) was *in-situ* synthesized on Al matrix through a low temperature (~ 600 ºC) CVD approach, in which Ni nanoparticles were employed as catalyst, glucose as solid carbon source and especially the sticky epoxy resin as a network forming template. The synthesis mechanism of GNS on aluminum powders and interfacial bonding between GNS and Al matrix were investigated. The evolution law of electrical conductivity and mechanical properties of the composites with different fractions of GNS was studied to help understand the effect of the vertical grid like GNS and Al_4C_3 on the conductivity and mechanical strength.

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EXPERIMENTAL

Materials

Pure Al powder functionalized with nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) were used as the starting metal powder. The epoxy resin as the commercially available diglycidylether of bisphenol-A (DGEBA) supplied by Feichengdeyuan Chem. of China (E-51) and EDA were used as network forming template and curing agent. Glucose anhydrous and ethanol were used as solid carbon source and dispersant, respectively.

Fabrication of GNS/Al composite materials

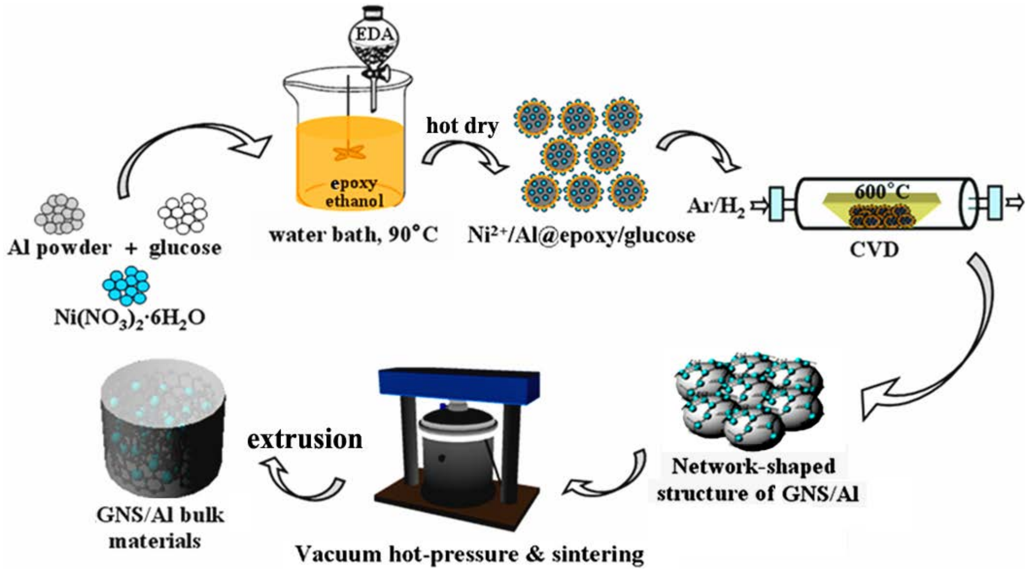

Fig. 1. Schematic of the preparation of GNS/Al composites.

FIGURES AND TABLES

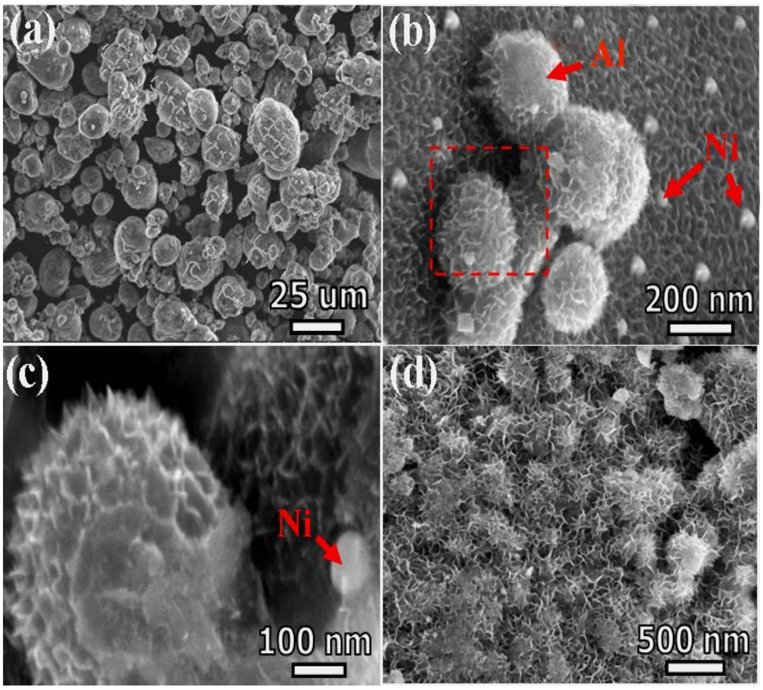

Figure 2: (a-c) SEM images of GNS/Al powders ((c) is the magnified image of the red dashed box in (b), Ni and Al are pointed by red arrows) and (d) epoxy/Al composite powders after CVD process at 400 °C.

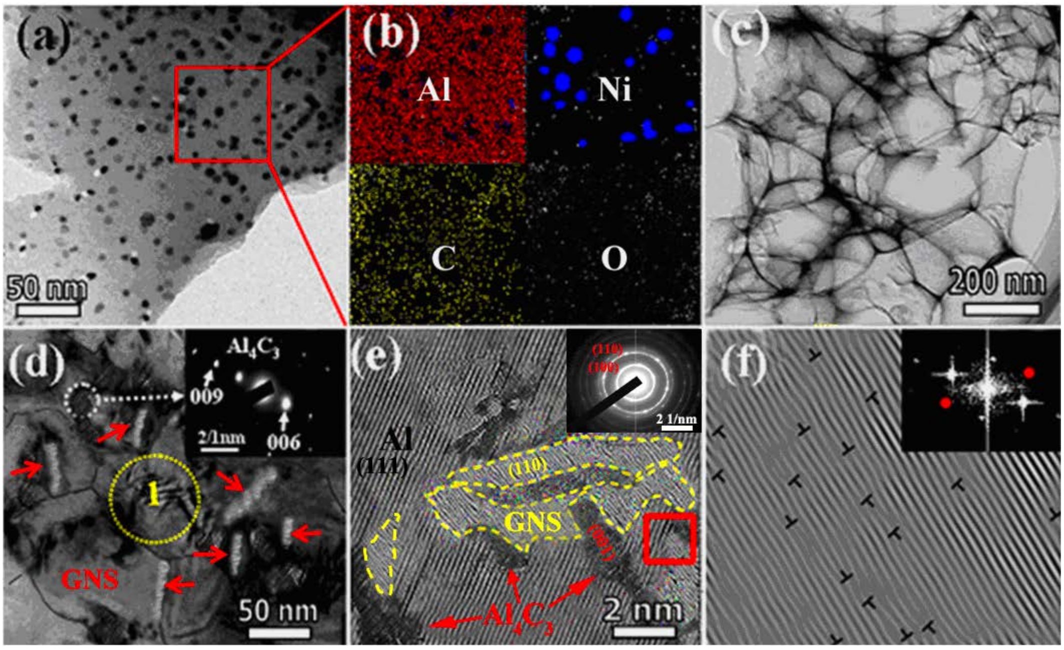

Fig. 3. TEM images of (a) Ni^{2+}@epoxy/Al composite powders before CVD process, (b) SEM-TEM element mapping image of the red solid box in (a), (c) the GNS/Al composite powders after erosion by hydrochloric acid (d) the GNS/Al bulk material (the inset is the SAED image of the white dash cycle, GNS are pointed by the red arrows), (e) the enlarged image of the yellow dash cycle in (d) (the inset is the SAED image of the yellow dash area, Al_4C_3 are pointed by the red arrows) and (f) IFFT image of the red solid box in (e) and the inset is the corresponding FFT image.

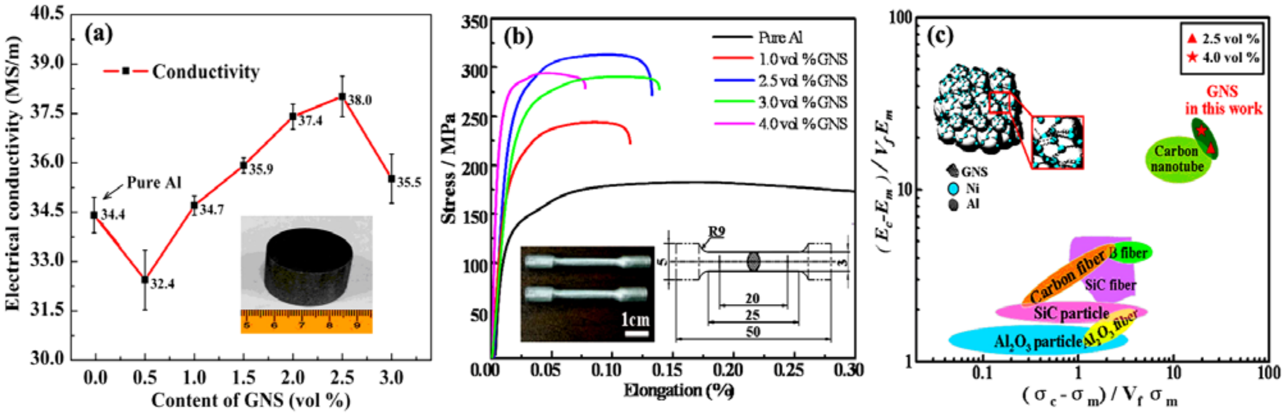

Fig. 3. (a) Electrical conductivity comparison of the GNS bulk composites with different content of GNS (insets are the test sample after hot pressure). (b) Engineering stress-strain curves for GNS/Al composites and the unreinforced Al matrix. The insets are the bulk sample and tensile test size after extrusion. (c) Comparison of the strengthening and stiffening efficiencies of GNS in GNS/Al composite with various reinforcements in Al matrix composites. Data was drawn based on the reviews articles.

EQUATIONS

$$\delta_m - \delta_0 = \Delta\,\delta = a\mu\, b\rho^{\,1/2} \tag{1}$$

$$\sigma_c = \left(\sigma_0 + a\mu b\rho^{1/2}\right)\left[\frac{V_f\left(S+4\right)}{4} + \left(1 - V_f\right)\right] \tag{2}$$

$$\sigma_c = \sigma_m\left[\frac{V_f\left(S+4\right)}{4} + \left(1 - V_f\right)\right] \tag{3}$$

CONCLUSIONS

A vertical grid like GNS with large specific surface was successfully *in-situ* synthesized on aluminum powders *via* a CVD method at relatively low temperature with the synergistic attributions mechanism of epoxy template, glucose carbon source and Ni catalyst. A small amount of nano-sized Al_4C_3 was formed in the bulk material between Al and GNS and was helpful to promote the Al/C interfacial bonding. The electrical conductivity of the composite was affected by the competitive effect of GNS and Al_4C_3, that is the conductivity increases with the increased content of conductive GNS while degrades with the increasing amounts of the nonconducting Al_4C_3 at room temperature. The mechanical properties tests indicate that GNS is an ideal reinforcement in structural composites. The main strengthening mechanism of the composite is ascribed to load transfer and dislocation strengthening. The vertical grid liked GNS on Al with more contacted sites and well connected interface would benefit to further applications such as energy storage materials and powder metallurgy molding of GNS reinforced Al matrix composites in the near future.

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