Enhanced Mechanical Properties of Graphene/Copper Nanocomposites Using a Molecular-Level Mixing Process

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Graphene, which has a 2D layered structure of carbon atoms, is of great interest because of its excellent mechanical[1,2] and electrical properties.[3,4] Monolayer graphene has a Young’s modulus of 1 TPa and a tensile strength of 130 GPa. The electron mobility of suspended graphene is 200 000 cm² V⁻¹ s⁻¹.[4] Graphene also has a large surface area (~2600 m² g⁻¹) and a low density (2.2 g cm⁻³), which makes it suitable as a reinforcement for nanocomposites. Numerous graphene/polymer composites have been studied for that reason. Stankovich et. al. first reported possibilities of graphene-based polymer composites with homogeneous dispersion of graphene at relatively low percolation threshold of ~0.1 vol% in polystyrene matrix. Since then, graphene/polymer nanocomposites have been reported based on epoxy,[5,6] poly(methyl methacrylate) (PMMA),[7] poly styrene (PS),[8] polyurethane (PU),[9] and polypropylene (PP)[10] polymers. Recently, our research group also introduced non-covalent,[11–13] PBA functionalization to graphene flakes and synthesized graphene/epoxy composite resulting in enhanced thermal conductivities and mechanical properties.[12]

Graphene could be an ideal 2D reinforcement nanomaterial not only for polymer matrix but also to metal matrix. However, only few work on graphene/metal nanocomposites have been reported[14–17] and, sometimes, exhibited even lower mechanical properties with the addition of graphene flakes.[14] Two major reasons for this behavior are: i) poor bondings between graphene flakes and metals and ii) relatively high processing temperature (over 1000 °C in case of copper) at which the graphene is easily decomposed or damaged. Previous work of graphene/metal composites was mostly based on the traditional process of powder metallurgy, which cannot effectively prevent agglomeration of the graphene in the metal matrix because graphene is prone to segregate from the metal particles due to its poor affinity to metal in the absence of any binding sites and the formation of agglomerates of graphene by van der Waals forces. Furthermore, general sintering and melting process are not easily applicable to graphene/metal nanocomposites because the process temperatures of most metals are beyond the decomposition temperature of reduced graphene oxide (RGO) (~600 °C) found from TGA (Figure S1, Supporting Information). Also, the large density difference between the metal and graphene causes the graphene to float on top of the melt. To achieve the best mechanical properties, graphene flakes must be homogeneously dispersed in metal matrix without significant thermal damage or conversion into metal carbides during densification and sintering.

We propose here a molecular-level mixing process and spark plasma sintering (SPS) process to investigate the strengthening effects of graphene in a metal matrix. The suggested method avoids the issues of dispersion and thermal damage of graphene flakes during the synthesis of graphene/metal nanocomposite. The first key process is a molecular-level mixing process that consists of attaching functional groups onto graphene flakes and making chemical bondings between graphene and composite matrix. The second key process is SPS that consolidate metal powders through local joule heating and spark plasma generated between individual powders. Fast heating and cooling rate of SPS process not only limits grain growth and diffusion but also lowers average sintering temperature due to localized heating at the contact point of the powders. The strategies was proven successfully for carbon nanotube (CNT)/metal nanocomposites by our previous work[18] and for graphene/ceramic nanocomposites.[19] Because graphene has the same surface characteristics with CNTs except curvature, the application of molecular-level mixing process to graphene/metal nanocomposites is very promising.

To the best of our knowledge, our result is the first report proving that graphene flakes can be effective nanofillers to significantly enhance mechanical properties of metal composites. Graphene/copper (Cu) nanocomposites containing 2.5 vol% RGO had an elastic modulus of 131 GPa and a yield strength of 284 MPa, which are 1.3 and 1.8 times higher, respectively, than those of pure Cu. The strengthening mechanism was studied by measuring the adhesion energy between graphene and Cu using a double cantilever beam (DCB) test.[20] The adhesion energy between sintered graphene and Cu was 164 J m⁻², which is much stronger than the adhesion energy of 0.72 J m⁻² for as-grown graphene on a Cu substrate. We believe the successful application of molecular level mixing process...
results in the strong adhesion energy between graphene and Cu. Even though the adhesion energy is not greater than Cu/Cu adhesion energy, combined effects of dislocation blocking and pinning even by single layer of graphene\cite{21} and more than 200 times enhancement of adhesion energy from the molecular level mixing can explain the strengthening effects of graphene in Cu matrix.

RGO used here was produced by oxidation and reduction processes. Graphene oxide (GO), which is oxidized from graphite through modified Hummers method, has functional groups such as hydroxyl, epoxide, carbonyl, and carboxyl groups.\cite{5} These functional groups render GO hydrophilic, which reduces agglomeration and improves dispersion in solvents such as deionized water. Also, these functional groups can enhance the bonding between graphene and a polymer matrix by additional hydrogen bonds\cite{7} or the bonding between CNTs and metals by covalent oxygen bonds bridging metal and carbon atoms.\cite{22,23}

However, the tendency of agglomeration between GO (or RGO) powders during mixing with metal powders need better dispersion methods. We produced RGO/Cu nanocomposite powders by molecular-level mixing technique to enhance dispersion of RGO in Cu matrix and bonding strength between RGO and metal matrix. A schematic diagram of the fabrication process is given in Figure 1. First, GOs and metal ions were homogeneously mixed in deionized water (Figure 1c); chemical bonds formed between the functional groups of the GOs and the Cu ions. Before producing RGO/Cu nanocomposite powders, mixtures of GOs and Cu ions were oxidized to GO/CuO nanocomposite powders by NaOH solution to prevent reducing functional groups of the GOs before forming the chemical bonds to Cu ions (Figure 1d). RGOs decorated with Metal particles were produced after thermal reduction with H$_2$ (Figure 1e). Once metal particles are attached on the RGO, no further agglomeration of individual RGOs are possible. Finally, the powders are sintered and densified by spark plasma sintering (Figure 1f).

Figure 2a shows an atomic force microscopy (AFM) image of GOs that were fabricated using Hummers method. They were not agglomerated and had thickness of $\approx 1$ nm, which is the typical monolayer thickness of GO.\cite{5} The mixture of GO and Cu(II) acetate powders obtained by solution mixing is shown in Figure 2b: the GO layer was not agglomerated and was homogeneously mixed with the Cu(II) acetate salts. The GO/Cu oxide (CuO) nanocomposite powders were produced after oxidation (Figure 2c). The CuO particles were ellipsoidal and about 500 nm in size. Note that distinguishing the GO from the 1 vol% GO/CuO particles in SEM images was difficult because the GO particles were fully covered by CuO particles. Only above 80 vol% of the GO/CuO composition one could find GO in the matrix. This proves that no decomposition or damage of GO were made during the oxidation process and the CuO conformally wetted the surface of GO. Furthermore, high-resolution scanning electron microscopy (HR-SEM) revealed that the smooth surfaces of the GO flakes were covered with small CuO particles (Figures S2a,b). RGO/Cu nanocomposite powders were obtained by thermal treatment of the GO/CuO powders at 450 °C in H$_2$ (Figure 2d). CuO particles which were formed on GO were reduced to form Cu islands with average size of 30 nm, while CuO particles which were formed without GO were reduced to form large Cu particles and connect each other during the thermal treatment. The fine size of Cu particles on RGOs originated from the difficulty of Cu diffusion on the surface of RGOs.\cite{24}

Raman spectroscopy of the nanocomposite powders indicates changes of oxidation status in the RGO during processing (Figure 2e). The ratio of the D band (1355 cm$^{-1}$) to the G band (1603 cm$^{-1}$; $I_D/I_G$) is a measure of defects present in the GO and RGO; a higher value may indicate higher defect density. The $I_D/I_G$ ratio increased from 0.78 for GO to 0.81 for GO/Cu ions. The GO with Cu ions could be more defective because the interaction of Cu ions to GO surface could damage sp$^2$ bonding network of graphene further. A continuous, conformal coating of CuO on the GO flakes right after oxidation process, as
shown in Figure 2c, blocked the characteristic Raman signals of GO (i.e. D, G bands) from the GO/CuO samples. However, Raman bands at 289, 623, and 1119 cm\(^{-1}\) from crystalline CuO (Figure S3, Supporting Information) proves the stable formation of continuous CuO films on GO.[23] The \(I_D/I_G\) ratios of the RGO/Cu nanocomposite powders were markedly lower (i.e., 0.40) because the reduction process removed functional groups and partially recovered the graphene structure. Remaining defects in the RGO even after reduction serve as chemical bonding sites between the RGO and Cu. Figure 2f shows the Fourier transform infrared (FTIR) spectrum of the nanocomposite powders in each processing step. Characteristic peaks of GO and RGO were observed for the O–H stretching vibration at \(\approx 3350\), C=O (carboxyl/carbonyl) stretching at \(\approx 1740\), C=C (aromatic ring) stretching at \(\approx 1640\), C–O (carboxyl) stretching at \(\approx 1410\), C–O (epoxide/ether) stretching at \(\approx 1230\), and C–O (alkoxy) stretching at \(\approx 1060\) cm\(^{-1}\). The carboxyl (C=O) and epoxide peaks of GO disappeared after mixing with the Cu salts while alkoxy bands appeared. Decreasing C–O stretch intensities is an evidence for carboxylic acid coordinates to a Cu\(^{2+}\) ion. Also, ring-opening of the epoxide by Cu\(^{2+}\) reduces the relative intensity of the epoxy stretch and increases the intensity of alkoxy stretch.[26,27] These phenomena support that chemical interactions between RGO and Cu occur during molecular-level mixing process and Cu nanoparticles are nucleated both at basal plane and edges of RGO due to each epoxide group and carboxyl groups are generally attached on basal plane and edges of RGO.[28]

Sintering and densification of solid RGO/Cu nanocomposites by SPS is shown in Figure 3a. SPS process provides low sintering temperature and fast sintering time, so thermal decomposition of graphene can be minimized during consolidation. Thin RGO layers were dispersed in the Cu matrix without further agglomeration because the RGOs were bonded to the Cu particles before sintering and the consolidation time was too short for carbon diffusion to the matrix. The SEM images showing the surfaces of etched RGO/Cu nanocomposites proves that the RGOs were homogeneously dispersed in the Cu matrix (Figure 3b). RGOs were also observed at the fracture surface of the RGO/Cu nanocomposites (Figure 3c). Raman spectroscopy of the RGO/Cu nanocomposites confirmed that graphenes were existed in Cu matrix after SPS (Figure S4, Supporting Information). The tensile properties of the RGO/Cu nanocomposites are shown in Figure 3d. The tensile strength of the 2.5 vol% RGO/Cu nanocomposite (\(\approx\)335 MPa) was about 30% greater than that of pure Cu (\(\approx\)255 MPa). Elastic modulus and yield strength of the sample increased by \(\approx\)30% (from 102 to 131 GPa) and by \(\approx\)80% (from 160 to 284 MPa), respectively. Enhanced mechanical properties of the nanocomposite can be explained by the high load-transfer efficiency of RGO in the Cu matrix. The high load-transfer is possible with strong bonding between Cu and graphene mediated by oxygen.[22] The remaining oxygen of RGO in our nanocomposites can supply the strong bonding sites between RGO and Cu. Figure 3e shows strengthening effect as a function of reinforcement amounts in the Cu matrix. The strengthening efficiency of a reinforcement can be expressed as:

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R = \frac{(\sigma_t - \sigma_m)}{V_r \sigma_m}
\]

where \(\sigma_t\) is the yield strength of the composite, \(\sigma_m\) is the yield strength of the matrix, and \(V_r\) is the volume fraction of the
reinforcement. The mechanical properties and strengthening efficiencies of several reinforcing materials in a Cu matrix are summarized in Table S1 in the Supporting Information. The strengthening efficiency of RGO is about 45, which is four times higher than that of TiB₂ because RGOs have outstanding mechanical properties, large surface areas, and strong RGO–Cu interfacial strengths. Compared to RGO, the strengthening effect of CNT, processed by molecular-level mixing with metal, is similar and this could be easily expected considering that RGO and functionalized CNT have similar surface chemical structures. However, if RGO and CNT show similar strengthening effects, RGO is more desirable for practical applications because RGOs are more cost-effective. Furthermore, the electrical and thermal conductivity of RGO/Cu nanocomposite were measured. (Figure S5,S6, Supporting Information) The RGO/Cu nanocomposites have similar electrical resistivity and thermal properties compared with pure Cu.

Adhesion between reinforcement materials and matrix is very important for the mechanical strength of composites. Because interfacial bond strength affects the load-transfer efficiency of composites, precise value of adhesion energy between graphene and Cu could explain whether graphene acts as reinforcements or defects in Cu matrix. Recently, we reported the measurement of adhesion energy between graphene and Cu as grown from CVD by DCB Test. The adhesion energy between graphene and Cu substrate, as expected, was low without any chemical bonding. Graphene, simply in areal contact with Cu foil, cannot enhance mechanical properties in composite. However, the RGO/graphene composite presented here underwent through spark plasma sintering to consolidate the Cu and graphene with heating and plasma at the interface. To prove the effect of spark plasma sintering to adhesion energy between graphene and Cu, a model composite was prepared and studied because precise and direct measurement of the adhesion energy from the RGO/Cu composite is impossible. Figure 4a shows the fabrication process for the model sample composed of Cu/graphene/Cu. The use of CVD-graphene enables to control the thickness of graphene layer in large area which is not achievable from RGO samples. The use of monolayer is also important to measure the interfacial bond strength between the graphene and Cu, not between graphene layers. Figures 4b,c show exposed graphene after partial etching in FeCl₃ solution from the sidewall of SPS processed graphene/Cu sandwich sample. The existence of continuous graphene sheet proves that graphene can remain without severe tearing or fragmentation. The adhesion energy between graphene and Cu substrate, as expected, was low without any chemical bonding. Graphene, simply in areal contact with Cu foil, cannot enhance mechanical properties in composite. However, the RGO/graphene composite presented here underwent through spark plasma sintering to consolidate the Cu and graphene with heating and plasma at the interface. To prove the effect of spark plasma sintering to adhesion energy between graphene and Cu, a model composite was prepared and studied because precise and direct measurement of the adhesion energy from the RGO/Cu composite is impossible. Figure 4a shows the fabrication process for the model sample composed of Cu/graphene/Cu. The use of CVD-graphene enables to control the thickness of graphene layer in large area which is not achievable from RGO samples. The use of monolayer is also important to measure the interfacial bond strength between the graphene and Cu, not between graphene layers. Figures 4b,c show exposed graphene after partial etching in FeCl₃ solution from the sidewall of SPS processed graphene/Cu sandwich sample. The existence of continuous graphene sheet proves that graphene can remain without severe tearing or fragmentation. The adhesion energy between graphene and Cu could not be easily etched because graphene has a strong chemical resistance and blocks the flow of the etching solution.

The adhesion energy between the Cu and graphene was measured using DCB fracture test. Each side of the model sample was loaded and unloaded by micromechanical tester and the applied load was measured with the applied displacement. A graph of the displacement and applied load is shown in Figure 4d. The crack length and adhesion energy were calculated using a compliance-based model. The calculated adhesion energy value for graphene and Cu was 164.47 ± 28.47 J m⁻², which is much greater than the adhesion...
results that RGOs enhance the mechanical properties of the Cu matrix. In conclusion, we successfully demonstrated RGO as a reinforcement for a metal matrix nanocomposite to improve the mechanical properties by the molecular-level mixing process. Functional groups of GO helped to disperse the GO flakes and form chemical bonds with metal ions, which lead to fabrication of homogeneously dispersed RGO/Cu nanocomposite powders. The mechanical properties of the RGO/Cu nanocomposite were enhanced due to uniform dispersion of RGOs in the Cu matrix and the high adhesion energy between RGO and Cu, which was induced by intermediate oxygen and the SPS process. The elastic modulus and the yield strength of the 2.5 vol% RGO/Cu nanocomposite were 131 GPa and 284 MPa, respectively, which were \( \approx 30\% \) and \( \approx 80\% \) higher than the values for pure Cu. Furthermore, the obtained adhesion energy between the graphene and Cu was 164 J m\(^{-2}\), which could be the evidence of strong interfacial bonding of graphene and Cu. By these results, graphene can be an excellent candidate for the reinforcement of metal matrix nanocomposites.

Experimental Section

Fabrication of GO: GO was made by the Hummers method. Graphite (1 g) and \( \text{H}_2\text{SO}_4 \) (40 mL) were mixed in an ice bath. \( \text{KMnO}_4 \) (3.5 g) was slowly added as an oxidizing agent to the graphite solution. Once the solution was homogenous, deionized water was added as the oxygen source. \( \text{H}_2\text{O}_2 \) (10 mL) was added to remove Mn ions, and the solution was vacuum-filtered. Finally, to remove the remaining residual, it was rinsed with a HCl solution (100 mL) and dried in a vacuum oven without heating.

Fabrication of the RGO/Cu Nanocomposite Powders: The GOs (75 mg) were dispersed in deionized water (500 mL) by sonicing for 2 h. An aqueous solution (2000 mL) of \( \text{Cu(CH}_3\text{COO)}_2 \cdot \text{H}_2\text{O} \) (96.24 g) was added with mixing to the GO suspension. The mixed solution was
heated to 80 °C and then aqueous 2 M NaOH (500 mL) was added. The chemical reaction reduced the Cu ions to CuO and formed the GO/Cu nanocomposite powders. The powders were isolated by centrifugation, rinsed with deionized water, and dried at 80 °C under vacuum. The powders were then reduced at 400 °C for 3 h under a hydrogen atmosphere to form the graphene/Cu nanocomposite powders.

Consolidation of the RGO/Cu Nanocomposite Powders: The RGO/Cu nanocomposite powders were compacted in a graphite mold. The powders were consolidated at an applied pressure of 50 MPa and spark plasma sintered at 600 °C for 3 min under vacuum. The consolidated RGO/Cu nanocomposite was 20 mm in diameter and 1 mm thick.

Characterization of the RGO/Cu Nanocomposite: The microstructures of the RGO/Cu nanocomposite powders and consolidated nanocomposite were observed by AFM (Seiko) and SEM (Hitachi S-4800). Tensile tests were performed using a microforce testing system (Instron Model 8848). The tensile dogbone specimens had a 7 mm gauge length, 1.5 mm width, and 0.3 mm thickness.

Synthesis of Cu/Graphene/Cu Model Material: CVD-graphene was grown on a Cu-block substrate. The width, thickness, and length of the Cu beam were 5 mm, 3 mm, and 30 mm, respectively. The Cu block was reduced with H2 gas to remove residual oxygen and increase the grain size of the Cu. The graphene was grown at 1000 °C using CH4 as the carbon source gas. Once the reaction was complete, rapid cooling was needed to obtain the graphene. A graphene/Cu block was stacked on a heat-treated Cu block and the assembly was placed in a graphite mold. The stacked blocks were consolidated by spark plasma sintering at 500 °C for 5 min in vacuum at an applied pressure of 5 MPa.

DCB Test of Cu/Graphene/Cu Model Material: The DCB test comprised three steps. Firstly, the tensile motion was applied to the specimen, and the load increased linearly. Secondly, the crack propagation occurs when the load starts to decrease. The critical load is defined at this point when the crack growth starts. Finally, the compressive motion is applied to seize the crack and corresponding crack length can be calculated by the slope of the load-displacement curve. The adhesion energy was also calculated by combining the crack length with the critical load. These steps were conducted multiple times during the crack propagation, therefore, multiple values of adhesion energy could be obtained in a specimen.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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