## **Dispersion of Chemically-Modified Graphene and its Applications**

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## ABSTRACT

The solution processability of chemically-modified graphene solution is most important for its application in electronics and conductive inks. Here, we decribe several method to fabricate the stable reduced graphene oxide solution by using metal cation- $\pi$  interactions and polymeric metal oxide sol.

*Keywords*: chemically-modified graphene, dispersion, metal ion, metal oxide sol

## **1 INTRODUCTION**

Chemically exfoliated graphene sheets show promise for use in high performance electronics and sensor applications because they are solution processable and display unique electrical properties.[1-8] The solution processability of graphene oxide (GO) permits application of GO to substrates via spin-coating, spray-casting, dropcasting, or inkjet printing for the large-scale production of graphene electronic circuits. Subsequent reduction of GO sheets can proceed through deoxygenation by thermal or by chemical reduction. The direct fabrication of uniform reduced GO (rGO) films is difficult because rGO sheets are not easily dispersed in solvents, and they form wrinkled structures during spin-coating, spraving, or printing. Thus, the solution processability of rGO solution is most important for its application in printed electronics because we can exclude the post reduction process considering the cost.

In this work, we present a straightforward method for addressing the problems associated with dispersing rGO nanosheets in organic solvents by introducing stabilizing metal ions and hydrophobic interfacial interactions between the rGO surfaces and an acetylacetone (acac) stabilizer in a  $TiO_2$  precursor solution. Metal ion-modified graphene sheets promise the mass production of easy-dispersible graphene powder. Moreover,  $TiO_2$ -modified rGO solutioin produces wrinkle-free rGO/TiO<sub>2</sub> hybrid multilayer films by air spraying onto large substrates with enhanced electrical properties.

## **2 EXPERIMENTAL**

Graphene oxide was prepared from natural graphite (Alfa Aesar, 99.999% purity, -200 mesh) by a modified

Hummers method. Briefly, 20 g graphite and 460 mL  $H_2SO_4$  were mixed in a flask. Then, 60 g KMnO<sub>4</sub> were slowly added over 1 h. Stirring was continued for 2 h in an ice-water bath. After the mixture was stirred vigorously for 18 h at room temperature, 920 mL deionized water was added, and the solution was stirred for 10 min in an ice-water bath. Fifty milliliters of  $H_2O_2$  (30 wt% aqueous solution) was then added, and the mixture was stirred for 2 h at room temperature. The resulting mixture was precipitated and filtered to obtain the graphite oxide powder.

# **2.1** Dispersion by monovalent cation-π interaction

The synthesized graphite oxide was immersed in aqueous NaOH or KOH at pH 10 to a concentration of 300 mg/L, and exfoliation and dispersion were carried out by sonicating for 1 h. Aqueous hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>, 4 mM) was added dropwise to the GO solutions, followed by heating at 100°C for 16 h. To confirm the dispersion stability of RGO in various solvents with respect to cation- $\pi$  interacting and non-interacting GO, the GO solution were diluted in dimethylsulfoxide (DMSO), dimethylformamide (DMF), and DI water to a concentration of 90 wt%, followed by hydrazine reduction.

#### 2.2 Dispersion by titania precursor

The TiO<sub>2</sub> precursor sol was prepared using TIP/ acac (in a 1:5 molar ratio), ethanol, HCl, and water by stirring at 60°C for 10 h, followed by solvent exchange with DMF. Next, the GO solution was mixed with various amounts of the TiO<sub>2</sub> precursor sol, and hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>) was added dropwise to the GO/TiO<sub>2</sub> precursor sol solutions to a final concentration of 4 mM, followed by heating at 100°C for 24 h. GO and rGO/TiO<sub>2</sub> hybrid films were fabricated at room temperature using an automatic spray coater (NCS Co., NCS400) with a nozzle 1.2 mm in diameter. The GO films were then reduced by heating under hydrazine fumes at 100°C for 2 h to fabricate rGO films. The prepared rGO/TiO<sub>2</sub> hybrid films were heated at 200°C to cure the TiO<sub>2</sub> sol and remove any remaining chemicals, such as solvents or TiO<sub>2</sub> sol stabilizers.

## 2.3 Characterization

Source and drain electrodes were deposited by evaporating Au through a shadow mask. The channel length

and width of a typical device were 1 m. respectively. The transistor current-voltage characteristics were measured using Keithley 2400and 236 source/measure units under vacuum ( $10^{-5}$  Torr). The temperature-dependent transport measurements were conducted in a cryostat (ST-500, Janis) with a base pressure of  $10^{-5}$  Torr over the range 80–290 K. The morphologies of the rGO and rGO/TiO<sub>2</sub> hybrid films were imaged by AFM (Park Systems XE-100 Multi-modes), and field emission scanning electron microscopy (FE-SEM, HITACHI S4800). The absorbance of the prepared films and the GO solution during reduction were measured by UV-vis spectroscopy (Varian, Cary 5000). The structural characteristics of the RGO sheets were investigated by by confocal Raman spectrometer (NTEGRA SPECTRA, NT-MDT) with an excitation wavelength of 532 nm. To confirm the change in the carbon to oxygen atomic ratio in the functional groups of the films after reduction, XPS analysis was conducted using a Multilab2000 (Thermo VG Scientific Inc.) spectrometer with monochromatized Al XK -rav radiation as the X-Ray excitation source.

### **3 RESULTS AND DISCUSSION**

First, a schematic diagram in Figure 1 shows our strategy to stabilize the RGO dispersion by monovalent cation– $\pi$  interactions. The interactions between alkali metal ions and sp<sup>2</sup> carbons on the GO sheets do not form immediately after sonication since the cations preferably interact with carboxylic acid and hydroxyl groups on highly oxidized GO (as described in Figure 1a, b, and c). Therefore, mild reduction process of GO sheets and an aging process without mechanical perturbation are necessary to permit the monovalent cation- $\pi$  interactions (Figure 1a, b, d, and e route). Longer aging times vielded the CIGO, as shown in Figure 1e. The dispersibilities of the non-interacting GO and cation- $\pi$  interacting GO (CIGO) were similar in aqueous solutions due to the presence of oxygen functional groups in each sample. However, the significant differences between the GO and CIGO were revealed after hydrazine reduction, which desorbed the oxygen functional groups from graphene, as illustrated in Figure 2. Hydrazine reduction of CIGO over 16 h at 100°C rendered a homogeneous CIRGO dispersion in solution after an aging time of 2 h for (3), whereas the RGO aggregated and precipitated in solution due to hydrophobic interactions for the samples not permitted to age, as in (1). The monovalent cation– $\pi$  interactions induced a change in the chemical shifts of the graphitic carbon atoms  $(sp^2)$  due to electrostatic interactions with sodium ions. Highresolution <sup>13</sup>C SSNMR using magic angle spinning (MAS) provided signal assignments and specific structural information for the non-interacting GO and the CIGO (Figure 3). Unlike previous reports of GO, the main  $sp^2$ peak was split to give signals at 132.7 and 129.1 ppm, as shown in the inset of Figure 3a. The existence of an upfield chemical shift peak (132.7 ppm) for the  $sp^2$  carbons reveals the presence of interactions with Na<sup>+</sup> ions.



Figure 1: (a)Schematic diagram of fabrication of metal cation interacted graphene oxide nanosheets. (b) FE-SEM image of CIGO on a silicon wafer (inset: AFM images of CIGO sheets). The scale bars in (b) indicate 2 µm.



Figure 2:UV absorbance spectra as a function of aging time for a GO solution in DI water, DMSO, or DMF.



Figure 3: <sup>13</sup>C NMR analysis of the non-interacting GO and CIGO, (inset: the split sp<sup>2</sup> peaks at 132.7 and 129.1 ppm).

Raman spectra for RGO and CIRGO. Second-order zone boundary phonon (2D) peaks were observed at 2658 and 2662 cm<sup>-1</sup> with a symmetric line shape, confirming the presence of single-layered graphene. The intensity ratios of the 2D and G ( $I_{2D}/I_G$ ) bands were 0.51 and 0.37, respectively. The charge transfer from the sodium ions to graphene significantly downshifted the 2D peak from RGO to CIRGO. Moreover, in the CIRGO, the  $I_{2D}/I_G$  ratio was reduced by cation adsorption due to the introduction of ionic scattering. These results demonstrated the presence of *n*-type doping effect and phonon scattering due to charge transfer and ionic adsorption, which introduced electrostatic interactions between cations and the aromatic  $\pi$  system. The doping effect was characterized by fabricating an RGOfield effect transistor (FET).

The electrical properties of the single layered RGO were measured for deposited Au source and drain electrode widths of 2  $\mu$ m. The I<sub>ds</sub>-V<sub>gs</sub> curves were observed over a gate voltage range of -100 to 100 V with a constant V<sub>ds</sub> of 0.2 V. Despite the similar atomic percentage of oxygen functional groups with RGO, the Dirac point of CIRGO was shifted to the negative gate bias region indicating the *n*-type doping effect in terms of cation adsorption on the  $\pi$  system as shown in Figure 4d.

Second, we introduced titania precursor sol prepared with titanium isopropoxide (TIP) and acetyl acetone (acac) via hydrophobic interaction as shown in Figure 5a.



Figure 4: . a) Raman spectra with respect to the noninteracting RGO and CIRGO (inset: the gray arrow reveals the down-shift of the G band). The down-shift and decreased intensity of the 2D band confirmed the presence of n-type doping effects. b) The 2D and G peak positions revealed a down-shift compared to the RGO and CIRGO. (d), (e)  $I_{ds}$ - $V_{gs}$  characteristics of the non-interacting RGO and CIRGO in the gate bias range from -100~100 V at a constant  $V_{ds}$  (0.2 V).

Figure 5b shows that the UV absorbance of the GO/TiO<sub>2</sub> precursor sol solution increased during hydrazine reduction in the presence of the TiO<sub>2</sub> precursor sol, and precipitation was not observed. This strategy enabled us to directly deposit rGO/TiO<sub>2</sub> multilayer films by air spraying over a large area onto a desired substrate without the need for additional reduction procedures. The straightforward buildup of rGO/TiO<sub>2</sub> hybrid multilayer films by air spraying was monitored by UV-vis absorption spectroscopy. A higher absorption cross-section was assigned to the cumulative layering of rGO and TiO<sub>2</sub> layers, as shown in Figure 5c. The linear increase in the peak absorbance at 241 nm with the number of rGO/TiO<sub>2</sub> solution spray applications, as shown in the inset of Figure 1c, indicates that the deposition was uniform. Figure 5d shows an X-ray photoelectron spectroscopy (XPS) analysis of GO, rGO, rGO/TiO<sub>2</sub> precursor sol, and rGO/TiO<sub>2</sub> multilayer films, which indicates that the oxidative groups were reduced by hydrazine reduction and the acac molecules stabilized the TiO<sub>2</sub> sol in films prior to thermal treatment at 200°C. Importantly, reduction of the GO sheets by hydrazine in solution was not influenced by the presence of the TiO<sub>2</sub> precursor sol.



Figure 5: (a) Proposed mechanism by which the rGO sheets are dispersed in the presence of the  $TiO_2$  precursor sol. (b) Absorbance of the GO solution at 550 nm during reduction with hydrazine monohydrate. The inset images in (b) show vials containing the GO solution as a function of the reduction time. (c) UV-vis absorption spectra of the rGO/TiO<sub>2</sub> hybrid multilayer films, and plot showing the linear relationship between the absorbance at 241 nm and the number of spraying applications. (d) XPS C1s spectra of GO, rGO reduced by hydrazine vapor (H-rGO), rGO/TIP:acac (before thermal treatment ), and rGO/TiO<sub>2</sub> (after thermal treatment at 200°C) films.

Figure 3a presents the transfer characteristics ( $I_D vs. V_G$ ) of the graphene FETs based on the rGO and rGO/TiO<sub>2</sub> hybrid films. As the TiO<sub>2</sub> content was increased, the hole mobility of the rGO FETs increased dramatically by as much as a factor of 9, whereas the electron mobility increased only slightly (Figure 3b).

Importantly, the threshold voltages of these devices shifted by +16 V from 12 to 28 V (Figure 3d), and the asymmetry between the hole and electron mobilities increased dramatically upon addition of the TiO<sub>2</sub> sol. Both rGO/TIP0.5 and rGO/TIP0.7 FETs exhibited unipolar-like transport characteristics.



Figure 6: (a) Transfer characteristics and (b) mobility of rGO and rGO/TiO<sub>2</sub> hybrid multilayer films as a function of the GO/TIP ratio. (c) Raman spectra of rGO and rGO/TiO<sub>2</sub> hybrid multilayer films for varying amounts of TiO<sub>2</sub>. 2D Raman spectra were magnified for easy visualization. 2D/G intensity ratios of rGO and rGO/TiO<sub>2</sub> hybrid films are 0.074 and 0.0598, respectively. (d) The threshold voltage of the films from the transfer curves and Raman G-bands as a function of the GO/TIP ratio.

## 4 CONCLUSIONS

We demonstrated that the stable dispersion of RGO nanosheets in orgaic solvents can be achieved by introducing metal cation- $\pi$  interactions and titania precursor sol. First, noncovalent binding interactions between monovalent cations (monopole) such as Na<sup>+</sup> or K<sup>+</sup>, and sp<sup>2</sup> carbons (quadrupole) on graphene were obtained by simple aging process with adding an alkaline solution to the aqueous GO solution. The RGO dispersion stability was sensitive to the GO solution aging time after the exfoliation

process, regardless of the solvent. Second, a stable dispersion of rGO sheets in an organic solvent was achieved as a result of hydrophobic interactions between  $sp^2$  carbons in rGO surfaces and acac stabilizer ligands in the TiO<sub>2</sub> precursor sol. Addition of TiO<sub>2</sub> resulted in hole doping of the rGO.

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