FABRICATION OF HYBRID FILM GRAPHENE/SINGLE-WALL CARBON NANOTUBE BY THERMAL TREATMENT

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1 Introduction
The market for display is expected to extremely expand various in coming years. Recently, it was published that single-walled carbon nanotube (SWCNTs)/graphene oxide hybrid films show reduced sheet resistance and improved transmittance relative to graphene only films. However many of these method include oxide process induce much defect of aromatic formation during exfoliate with nitric acid, sulfuric acid and potassium permanganate. And method to produce hybrid films comes from solution process, because it allows the formation of graphene/SWCNTs hybrid composite film through various processing methods, including filtration, spin-coating, dip-coating.

So it has been known that SWCNTs can be dispersed in solvents, for example Dimethylformamide (DMF). And graphite can be exfoliated defect-free graphene in DMF or amide solvents, recently. Because SWCNTs and graphene can both be dispersed in DMF, it is possible to prepare mixed dispersions graphene/SWCNTs hybrid films. In this study, we observe graphene and SWCNTs sheet resistance and transmittance and the suspended graphene which mass concentration is 1.000–0.001 mg/ml. The 60 % of supernatant was then carefully decanted. Graphene suspension, treated with DMF is defined DTG.

2.3 Prepare of DMF treated SWCNTs

SWCNTs powder (10 mg) was heated at 400°C for 30 mins. As the bundles were separated by the thermal effect, the SWCNTs were subjected to 30 mins of high power tip sonication in solvent DMF (300 ml). After that, centrifuge 7000 rpm and the top 60 % of supernatant was decanted. The SWCNTs concentration was 0.1–0.08 mg/ml.

2.4 Hybrid films preparation

Two carbon materials of graphene and SWCNTs were mixed various compositions such as 0 % SWCNTs solution (graphene-only), hybrid with 8, 50, 92 wt% graphene and 100 % SWCNTs suspension. All those samples were sonicated for 5 h at room temperature. Graphene/SWCNTs hybrid films were produced on cellulose mixed ester filter membranes with 0.2 μm pore size (ADVENTEC) using a vacuum filtration apparatus.

After the hybrid film which was attached to the cellulose mixed ester membrane, was wetted with water, it was placed on the substrate of interest and aligned as desired. The membrane was subsequently a flat plate, to keep the film flat as it dried in an oven at 90 °C for 60 min. The high surface tension of the water brings the film and the substrate into close contact as the assembly dries.
The film and substrate assembly was then transferred into fresh solvent baths to remove the cellulose mixed ester membrane leaving the thin hybrid film on the substrate.

3 Characterization

Samples for AFM imaging were prepared by spin coating colloidal suspensions of DTG on quartz substrates. Imaging was done in non-contact mode using XE-70 in Park systems’ AFM. FE-SEM images were obtained with a field emission gun scanning electron microscope (SUPRA 55VP, Carl Zeiss, Germany). HR-TEM images were obtained with a high resolution transmission electron microscope (JEM-30010, JEOL, Japan). Raman spectroscopy was performed on a T64000 (HORIBA Jobin Yvon, FRANCE) using an excitation wavelength of 514.5 nm in order to characterize properties of the graphenes. The transmittance of varying graphene was measured with UV-vis spectroscopy (Agilent 8453). Sheet resistance \( R_s \) measurements were made using a four-point probe (FPP-5000, Veeco, USA)

4 Results and Discussion

Figure. 1(A) shows that graphene/SWCNTs suspension with thermal treatment was stable for several months. Unlike, raphene/SWCNTs suspension without thermal treatment (B) was aggregated.

Raman spectroscopy shows that most graphene/SWCNTs hybrid film raman spectra peak is dominated by the SWCNTs component. For example, the G band \((-1650 \text{ cm}^{-1})\) becomes dominated by the SWCNTs component. And we should focus on the 2D band near 2700 \text{ cm}^{-1}. The 2D band for the graphene-only film (Figure. 2A) is obviously different with that of the mixture. For the graphene film only one peak appeared, but mixture has two peaks between 2600 and 2700 \text{ cm}^{-1}. The 2D band of the hybrid film is dominated by SWCNTs component. It proves that the hybrid mixture can keep exfoliating even after film formation. This shows that, during film formation, graphene does not re-aggregate to form graphite.

HR-TEM image given in figure. 3(A) confirms that the graphene produced in this method was 1–2 layers thick. It appears transparent and these observations prove the DMF-suspension graphene, a single exfoliated graphene better greatly than graphene sheet exfoliated from Hummer method.

Figure. 3(B) also shows a high resolution transmission electron microscope (HR-TEM) image of dispersed SWCNTs, where the sample was prepared by depositing droplets of the dispersed solution onto the carbon-coated copper grid and HR-TEM image indicates that thermal treatment can separated SWCNTs bundles in DMF.

Figure. 4(A) shows a film which contains only graphene sheets. As the SEM image, the film doesn’t have enough contacts between graphene. Moreover the flake size is near 1 micrometer, so conductivity is low. As these reasons, we fabricate films which mixed with graphene and SWCNTs. Figure. 4(B) ~ (D) shows various ratio hybrid films image such as 8, 50, and 92 wt% graphene. Comparison of SEM images shows that graphene and SWCNTs have clearly uniform network. Graphene in aqueous dispersion have sizes of 100–500 nm, thus electron can’t move well between graphene and graphene. However, adding proper amount of SWCNTs helps to make bridges which induce low resistance and high conductivity.

We described an easy method to deposit graphene/SWCNTs films from aqueous suspension to create a flexible transparent electrode in figure. 4. We have used the vacuum filtration method, which has been used widely to deposit highly uniform graphene/SWCNTs thin films. Vacuum filtration includes the filtration of a mixed graphene/SWCNTs suspension through a commercial mixed cellulose ester membrane with a pore size of 0.2 \( \mu \text{m} \). As the suspension is filtered through the ester membrane, the liquid is able to pass through the pores, but the graphene/SWCNTs become formation of hybrid thin sheets. After transfer the hybrid carbon materials from membrane, the yield of the process is almost 100 %, independent of the substrate, indicating that van der Waals interactions give rise to sufficiently strong cohesive forces within the film and also between the hybrid sheets and the substrate to obtain a well adhered uniform film.

Figure. 5 shows the sheet resistance of the 100 % SWCNTs film for 82% transmittance was 620 ohm/sq. And the sheet resistance for the 8 wt% graphene film decrease to a minimum of 540 ohm/sq for the 8 wt% graphene film. But a sheet resistance of others increased steady with increasing graphene content. We suggest this...
phenomenon that addition of proper graphene can improve the electrical properties of graphene/SWCNTs films. The reason is that the contact resistance graphene and SWCNTs is lower than the contact resistance between graphene and graphene. And the electron-scattering sites of graphene layer is higher than SWCNTs electron-scattering site.

5 Conclusions

We have fabricated easy graphene/SWCNTs hybrid composite films. The method to exfoliate and separate respectively graphene and SWCNTs is same as thermal treatment and the solvent also is same kind one, so the process can be progressed at one step. The network between graphene/SWCNTs shows better properties as a conducting film than use only graphene or SWCNTs. We believe that our results provide significant way for electronic applications.

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Fig. 1. Preparation of thermal treated graphene/SWCNTs suspension. (A) photographs of graphene and SWCNTs dissolved in DMF with thermal treat (A) and without heating at 800 °C (B), repectively. After 2 h, the solution without heating already aggregated.

Fig. 2. Raman spectra for various films (A) DTG and (B) mixture of graphene/SWCNTs.

Fig. 3. High resolution transmission electron microscope (HR-TEM) image of typical DTG over a micrometer in size. Fig. 3 (A). Separated SWCNTs in DMF shows Fig. 3 (B). Aqueous of SWCNTs complex are well dispersed.
Fig. 4. SEM images shows (A) graphene only, hybrid films with (B) 92, (C) 50 and (D) 8 wt% graphene. The scale bar is 300 nm.

Fig. 5. Transferred films on PET substrate.

Fig. 6. Electrical properties of graphene/SWCNTs hybrid films as a function of graphene content for washed films at 82 % transmittance.

4 References

