Preparing a Flexible Conductive Film Comprised of Well-dispersed Graphene and Silver Nanoparticles

Sheng-Yen Shen/ Rui-Xuan Dong/ Po-Ta Shih/ Jiang-Jen Lin*
Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan
E-mail: jianglin@ntu.edu.tw

Introduction

In literature, graphene has drawn much attention due to its electrical, thermal properties and its relevant potential applications. It is known that graphene sheets have high specific surface area which tended to form aggregation because of the van der Waals interaction. As a result, dispersion of graphene will be a key challenge for the use of its following applications with silver nanoparticles (AgNPs). AgNPs have the potentials for electric conductor uses besides their catalytic and antimicrobial properties. Traditionally, graphene oxide was formed first through acidification of grpahene, then $AgNO_3$ and reducing agent was added to form a conductive film. In this work, we first synthesized poly(oxyethylene)-segmented oligo(imide) with the poly(oxyethylene) $–(CH_2CH_2O)_x–$ moieties and imide –(CONCO)– linking functionalities for the homogeneous dispersion of grapheme and AgNPs. In the second step, a facile process of preparing Ag/graphene hybrid film with high conductivity by heating is developed.

Results and Discussion

Poly(oxyethylene)-segmented oligo(imide) (POE-imide) was prepared by the imidation of poly(oxyethylene)-diamine and 4, 4′-oxydiphthalic anhydride in a molar ratio of 6:5 at the temperature of 150 °C (Scheme 1). The polymeric dispersant consisted of alternating POE $–(CH_2CH_2O)_x–$ and aromatic imide –(CONCO)– segments that were allowed to exfoliate graphene aggregates into graphene nanosheet (Figure 1) and further interact homogeneously with the in-situ reduced AgNPs. It was observed that some AgNPs with a diameter distribution of 10–25 nm were deposited on the graphene surface through the non-covalent van der Waals force while other free AgNPs were remained in the solution (Figure 2). Afterwards, graphene/Ag solution was drop-casted on Polyimide film and annealed in high temperature oven with the heating program set as follows: 110, 150, 160, 300, and 350 °C for 1 h at each temperature. When the annealing temperature was increased from 150 °C to 160 °C, the appearance of the film was changed from red wine color into golden (Figure 2). Further increase of the temperature to 350 °C made it become milky white and reach a minimum resistance (2.4×10^{-2} Ω/sq), as shown in Table 1. From the FE-SEM micrographs (Figure 3), we observed the AgNPs migrated and aggregated at 160 °C, and melted at 350 °C. The result was attributed to the catalytic effect induced by AgNPs which accelerated the decomposition of POE-imide, on the other hand, graphene exhibiting good thermal conductivity and electric conductivity than CNT leads to good interconnection among graphene and AgNPs or AgNPs and AgNPs to form a conductive channel, as observed by thermal gravimetric analyzer (Figure 4). The conductive film was able to be applied in semi-conductor. In Figure 4, when the graphene/Ag mixture was heated at a temperature under 160 °C, the surface resistance was too high to illuminate the LED lamps (Figure 5a). In contrast, when the graphene/Ag mixture was annealed at a temperature above 160 °C, the surface resistance was sufficiently low to illuminate the LED bulbs (Figure 5b, c and d).

Conclusions

The POE-imide dispersant was essential for exfoliating graphene and homogeneously dispersing AgNPs in a DMF/water medium. The AgNPs were decorated on graphene and free AgNPs were uniformly dispersed in the solvent with a diameter distribution of 10–25 nm. After being drop-casted on a PI substrate and annealed, a flexible and conductive film was prepared and the film showed high surface conductivity up to 1×10^{-1} Ω/sq and 1×10^{-2} Ω/sq. In the presence of graphene, fine AgNPs migrated and aggregated to generate a surface resistance of 2.4×10^{-1} Ω/sq at 160 ℃, this result was better than those CNT/AgNP film showed. Furthermore, with a further increase in temperature to 350 ℃, the resistance decreased by another order of magnitude. Such resistance was low enough to show their potential as nanoconductors for electronic devices.

Reference

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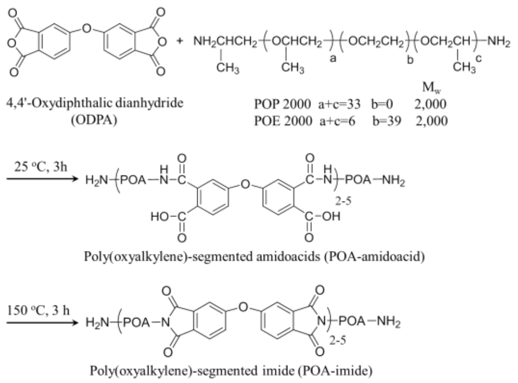

Scheme 1. Synthesis of the tic scheme for the poly(oxyethylenealkylene)-segmented amidoacid (POA-amidoacid) and imide dispersant (POA-imide).

Sample[a]	Weight fraction (w/w/w)	Resistance (Ohm/sq)[b]					
		130 °C	150 °C	160 °C	170 °C	300 °C	350 °C
Pristine CNT	1	1.7×10^1	1.7×10^1	1.7×10^1	1.7×10^1	1.7×10^1	1.7×10^1
CNT/POE-imide	1/10	1.2×10^6	3.3×10^4	4.2×10^3	1.8×10^3	1.3×10^3	4.7×10^2
	1/20	——[c]	——	2.1×10^6	1.7×10^6	8.2×10^5	6.2×10^2
CNT/$AgNO_3$/POE-imide	1/10/10	——	——	5.2×10^5	1.3×10^2	9.5×10^1	2.4×10^0
	1/20/20	——	——	2.1×10^5	2.0×10^{-1}	1.1×10^{-1}	1.0×10^{-2}
Ag/POE-imide	1/1	——	——	1.0×10^5	1.5×10^3	9.3×10^1	3.2×10^{-1}
Pristine Graphene(CPC)	1	1.4×10^3	1.4×10^3	1.4×10^3	1.4×10^3	1.4×10^3	1.4×10^3
Graphene/POE-imide	1/10	——	——	——	——	6.6×10^3	3.4×10^3
	1/20	——	——	——	——	8.1×10^3	5.7×10^3
Graphene /$AgNO_3$/POE-imide	1/10/10	——	0.6×10^5	4.3×10^0	1.1×10^0	8.4×10^{-1}	5.5×10^{-1}
	1/20/20	——	3.6×10^7	2.4×10^{-1}	1.2×10^{-1}	9.6×10^{-2}	2.4×10^{-2}

[a] solution drop coating on glass
[b] measured by four-point probe
[c] —— the resistance is too high to detect

Table 1. Sheet resistance of the films prepared from the Graphene/polymer/Ag and CNTs/polymer/Ag nanohybrids.

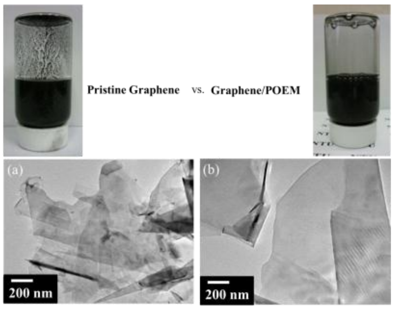

Figure 1. Comparison of TEM micrographs Graphene solution and Graphene/POE-imide solution.

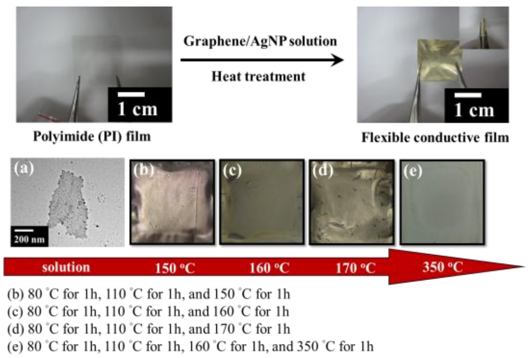

Figure 2. TEM of (a)AgNPs solution and photographs of melting AgNPs on the surface of polyimide film during the heating treatment. (b) 150 °C after 1h, (c) 160 °C after 1h, (d) 170 °C after 1h, and (d) 350 °C after 1h.

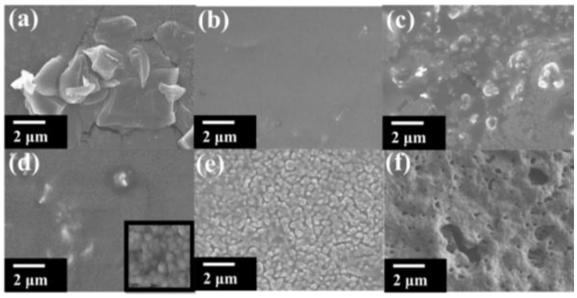

Figure 3. FE-SEM micrographs of (a) pristine Graphene; (b) Graphene:POE-imide hybrids with a weight ratio of 1:20, dried at 160 °C; (c) Graphene:$AgNO_3$:POE-imide hybrids with a weight ratio of 1:20:20, dried at 150 °C; (d) 160 °C; (e)170 °C and (f) 350 °C on polyimide substrate.

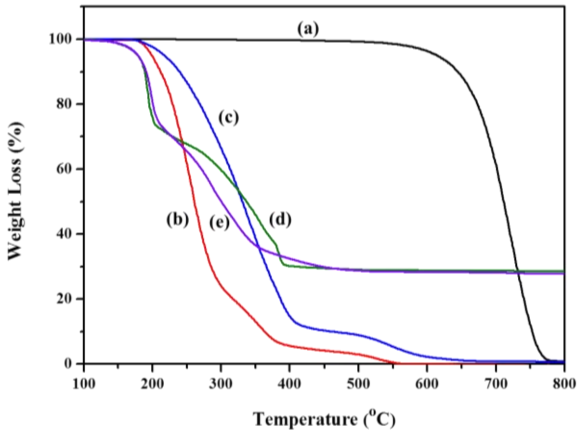

Figure 4. Relative thermo-oxidative stability by TGA in air: (a) pristine Graphene, (b) POE-imide (organic dispersant), (c) 5 wt% Graphene in POE-imide matrix, (d) POE-imide nanocomposite with AgNP/Graphene, and (e) AgNP/POE-imide.

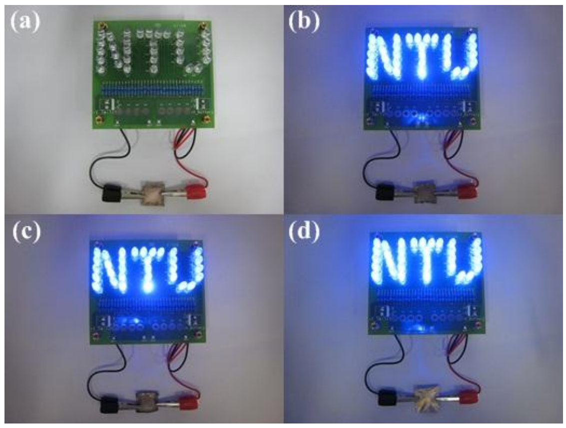

Figure 5. Demonstration of conductive application by heating Graphene/Ag films at (a) 150 °C, (b) 160 °C, (c) 170 °C and (d) 350 °C, respectively.