Preparation of Composited Graphene/PEDOT:PSS Film for Its Possible Application in Graphene-based Organic Solar Cells

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Abstract: The interface between graphene and organic layers is a key factor responsible for the performance of graphene-based organic solar cells (OSCs). In this paper, we focus on coating PEDOT:PSS onto the surface of graphene. We demonstrate two approaches, applying UV/Ozone treatment on graphene and modifying PEDOT:PSS with Zonyl, to get a PEDOT:PSS well-coated graphene film . Our results prove that both methods can be effective to solve the interface issue between graphene and PEDOT: PSS. Thereby it shows a positive application of the composited graphene/PEDOT:PSS film on graphene-based OSCs.

Key words: graphene; PEDOT:PSS; composite materials; coating

1 Introduction

Nowadays, organic solar cells attract much research attention due to their overwhelming advantages such as light mass, low lost, easy to prepare, and so on.[1-2] Organic solar cells usually consist of three parts, anode, active layer, and cathode. Normally, indium tin oxide (ITO) is hired as the anode; however, the limit storage of tin on earth leads to the high cost of ITO based OSCs.[3] Thus, it is of great point to replace ITO with another material which shows excellent electric and optical properties.

Considering of graphene's high transparency, good electric conductivity and mechanical robustness, it can be a satisfying replacement for ITO in OSCs.[4] However, the performance of graphene-based OSCs is worse than that of ITO-based devices in general. One important reason is the interface between graphene and organic active layer. In ITO-based OSCs, ITO is usually coated with a layer of conducting polymer, poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) in order to improve overall device performance by facilitating the injection/extraction of holes.[5] However, due to the hydrophobic nature of graphene surface, it is difficult to directly coat PEDOT:PSS onto graphene. Previous efforts indicate that UV/Ozone treatment is an efficient way to convey graphene surface from hydrophobic to hydrophilic, which can be one potential method to address this issue. Moreover, according to Park *et al.*,[6] adding fluorosurfactant to PEDOT:PSS is also possible to solve this problem

In this work, we applied two facile and effective methods to get a PEDOT:PSS well-coated graphene film. On one hand, we convert graphene surface from hydrophobic to hydrophilic *via* UV/Ozone treatment. On the other hand, we improved the wetting property of PEDOT:PSS solution with fluorosurfactant treat-

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ment, which made it possible to facilely deposit PEDOT:PSS onto graphene film. Based on the results we got, the effect of the two approaches and the possible application of the achieved PEDOT:PSS coated graphene in solar cells are discussed.

2 Experiments

In this study, graphene is prepared by chemical vapor deposition (CVD). PEDOT:PSS and fluorosurfactant (Zonyl FS-300) were purchased from Sigma Aldrich. For the first method, after graphene is grown on copper foil, it is transferred onto PET substrate. Then the sample is exposed in UV/Ozone environment for 2 min, after that, a layer of PEDOT:PSS is spin-coated onto graphene at the speed of 4 000 r/s for 60 s. As for the second method, graphene sample on PET substrate is prepared as before. Afterward, different amount of Zonyl are added in PEDOT:PSS solution, then the modified PEDOT:PSS with various percentages of Zonyl are separately coated on graphene at the speed of 4 000 r/s for 60 s. Moreover, multi-layer graphene is also prepared though layer by layer method. Then these two approaches are repeated as described above.

3 Results and discussion

In this work, in order to get an uniform coverage of PEDOT:PSS on graphene, we employed two methods. Firstly, we use UV/Ozone under appropriate condition to improve the wetting property of graphene with remaining its good conductivity; then we also try to modify PEDOT:PSS with a kind of surfactant called Zonyl and then cover this modified PEDOT:PSS onto graphene.

3.1 UV/Ozone treatment

Firstly, we use UV/Ozone treatment under appropriate condition to improve the wetting property of graphene. Due to the hydrophilic nature of PEDOT: PSS, this treatment is expected to effectively improve the coating effect.

UV/Ozone treatment is a common measure employed to convey graphene surface from hydrophobic to hydrophilic.[7] We tested the contact angle between two different liquid (DI water and diiodomethane) and

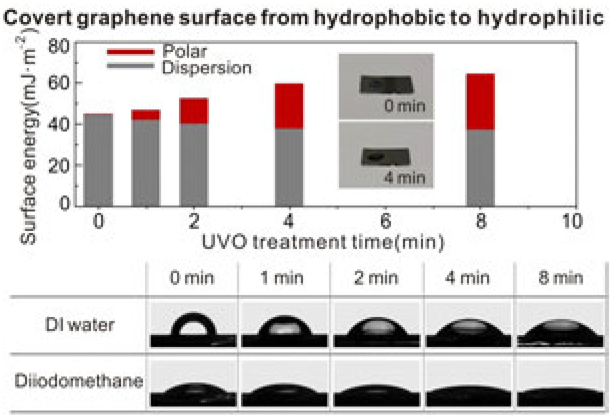

Fig.1 Surface energy of graphene and contact angle between liquid and graphene

graphene to calculate the surface energy of graphene, the results are shown in the Fig.1 below. After the treatment to graphene, the polar group on the surface increases, so that the polar component of surface energy gradually increases over time. The more the surface energy is, the better the surface wetting property is.

But it is widely recognized that UV/Ozone treatment to graphene will greatly reduce the electric conductivity of graphene.[8] According to Yuan *et al.*[9], however, electric resistance of CVD-grown graphene films won't change too much over time at ozone treatment temperature of 20 ℃. Hence, we tested the sheet resistivity of graphene with various layers which is exposed in the UV/Ozone environment under room temperature (around 20℃) for 2 min. The result is shown in Fig.2. It clearly shows that, within 2min' exposure in UV/Ozone environment at room temperature, the electric conductivity of graphene has demonstrated slight decrease.

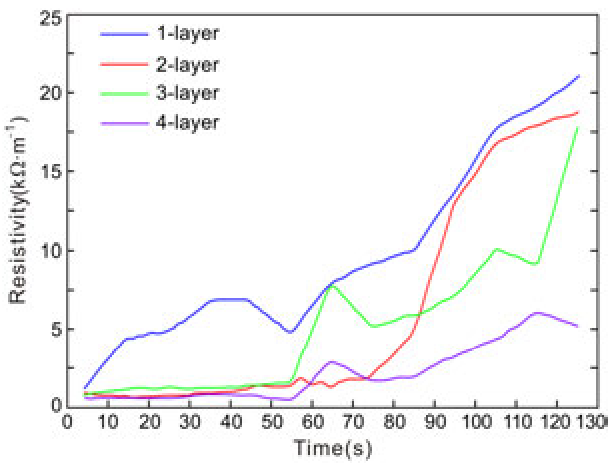

Fig.2 Electric resistivity change of graphene over time in UV/ Ozone environment at room temperature

Based on this survey, a layer of PEDOT:PSS is coated onto single layer CVD-grown graphene which is treated by UV/Ozone for 2 min under room temperature. As shown in Fig.3, compared to the coating sample without any treatment, UV/Ozone treatment to graphene shows a positive effect on achieving an uniform coverage of PEDOT:PSS on graphene.

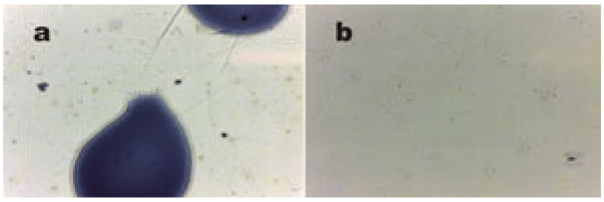

Fig.3 **a**: without treatment, graphene coated with PEDOT:PSS; **b**: after 2 mins' UV/Ozone treatment to graphene, graphene coated with PEDOT:PSS

Overall, it proves that UV/Ozone treatment is an efficient method to enhance the wetting property of graphene without significantly damage its conductivity, which enables the replacement of ITO with graphene in OSCs.

3.2 Modifying PEDOT:PSS with surfactants

Besides the UV/Ozone treatment to graphene, we also try to modify PEDOT:PSS with a kind of surfactant called Zonyl and then cover this modified PEDOT:PSS onto graphene.

Several reports demonstrate that modifying PEDOT:PSS with surfactants can make it possible to achieve uniform coverage of PEDOT:PSS on hydrophobic substrates, yet, it has not been applied in graphene electrodes.[10-13] In our work, we choose a surfactant called Zonyl which is composed of both a hydrophobic (fluorinated) and hydrophilic (ethylene glycol) segment enabling it to interact with the corresponding parts in PEDOT:PSS. Due to the amphiphilic nature of the Zonyl molecule,[14] PEDOT:PSS solution distinctly increases its wettability on hydrophobic surfaces. Here we prepare four PEDOT:PSS solutions with different amounts of Zonyl (0.5wt.%, 2wt.%, 5wt.%, and 10wt.%, respectively), and separately coat them on single layer CVD-grown graphene. The results are shown in Fig. 4, which indicate that all the four samples present a well coating result.

Nevertheless, as Zonyl is an insulating material and remains in PEDOT:PSS, it begins to interfere with the

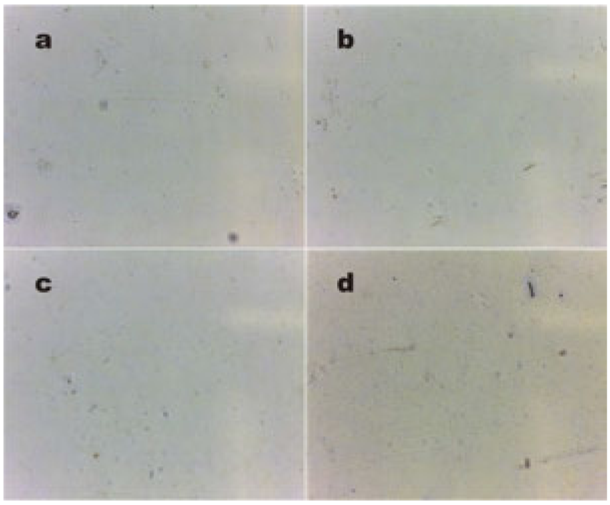

Fig.4 From **a** to **b**: four PEDOT:PSS solutions with different amounts of Zonyl (0.5wt.%, 2wt.%, 5wt.%, and 10wt.%) coated on single layer CVD-grown graphene

conductive PEDOT pathways at high concentrations[15]. Thereupon, we compare the conductivity of four different samples, CVD-grown graphene, graphene coated with PEDOT:PSS (0.1wt.%zonyl), graphene coated with PEDOT:PSS (0.5wt.%zonyl), graphene coated with PEDOT:PSS (2wt.%zonyl). As a result (Table 1), graphene coated with PEDOT:PSS (0.5wt.%zonyl) exhibits the most satisfying electric property. Thereby, PEDOT:PSS with 0.5wt.%zonyl is defined as the optimum concentration, and is applied on bilayer and triple-layer graphene. As expected, a uniform coverage can also be achieved as demonstrated in Fig.5.

The above result ensures that modified PEDOT:PSS with Zonyl can be an effective approach to solve the interface issue between graphene and PEDOT:PSS.

Table 1 Conductivity of four different samples,

Graphene	Graphene coated with PEDOT:PSS		
	0.1wt.%zonyl	0.5wt.%zonyl	2wt.%zonyl
8 kΩ	100 kΩ	20 kΩ	100 kΩ

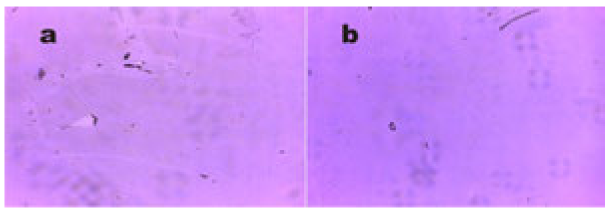

Fig.5 **a**: 0.5wt.%zonyl applied on bilayer graphene; **b**: 0.5wt.%zonyl applied on triple-layer graphene

4 Conclusions

In this paper, we propose two simple and effective methods, UV/Ozone treatment to graphene and modified PEDOT:PSS with Zonyl, to get a PEDOT:PSS well-coated graphene film. Our results prove that UV/Ozone treatment is an efficient method to enhance the wetting property of graphene without significantly damage its conductivity, and that modified PEDOT: PSS with Zonyl can be an effective approach to solve the interface issue between graphene and PEDOT: PSS. Both methods can result in a coverage uni-formity of PEDOT:PSS onto graphene. Therefore, it shows a positive application on graphene-based OSCs. As a result, our work provides a further confirmation about the promising development of graphene-based optic-electronic applications.

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