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Polydiacetylene-Polymethylmethacrylate/Graphene Composites as One-Shot, Visually Observable, and Semiquantative Electrical Current Sensing Materials

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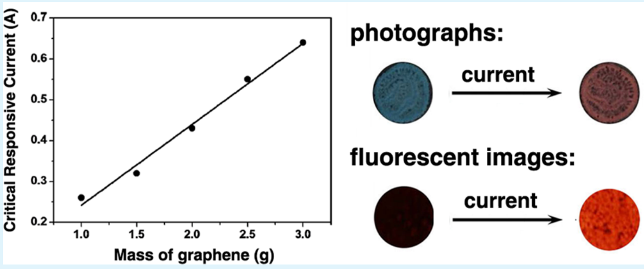
Ⓢ *Supporting Information*

ABSTRACT: Aiming to develop pH-paper-like current sensing materials, we prepared irreversible electrochromic PDA-PMMA/graphene composites. The composites exhibited an excellent linear relationship between critical responsive currents and the amount of graphene in the system. In these composites, PDA acted as the electrochromic material and graphene as the conductive matrix. The presence of PMMA not only ensured mechanical performance but also made the color change more obvious to be observed by the naked eye.



KEYWORDS: *polydiacetylene, graphene, electrochromic material, sensing, semiquantative*

1. INTRODUCTION

Electrical current sensing is a very important and fundamental requirement in many electronic systems. The current sensors have been developed in great variety because of the diverse applications, such as overcurrent indication for the protection of circuits, monitoring the supply current of the battery, and detecting the ever-existing current shock, circuit short, or electric leakage. The employment of current sensors can also avoid certain malfunctions that might hurt the performance of motor-controlled apparatus. The conventional current sensor detects the electrical current and then generates another measurable signal proportional to the original current, which usually requires the integration of the sensing material and several different apparatus into one device.[1−4] Developing materials that can detect the current and give out a directly observable response, such as color change, would be desirable for saving space and reducing cost on some occasions. The most successful analog in other sensing application is pH test strips. Compared to small molecular inorganic and organic electrochromic materials, conjugated polymers, including polypyrrole, polyaniline, polythiophene, etc., have been demonstrated to have advantages in many aspects, such as processability, color tailorability, and environmental stability. These electrochromic compounds which were used as display, smart, or protective materials in most applications have been incorporated into certain devices.[5−9] However, they were rarely used as visually observable and quantitative, or at least semiquantitative sensing materials, such as pH paper.

Polydiacetylene (PDA) materials have attracted great research interest because of their unique structural, electronic, and optical properties, such as facile synthesis (Scheme 1), high sensitivity toward external stimuli, and outstanding nonlinear optical properties. The blue-red change of PDA, which was attributed to the switch between different polymer conformations, has been widely reported in the literature.[10−14] In most cases, the color change was induced by pH value,[10] temperature variation,[11] organic solvent,[12] or inorganic ions.[13,14] To the best of our knowledge, though very few reports have used electrical current as the stimulus, the adjustability of the responsive current has not been discussed in those systems.[15,16]

Aiming to develop one kind of pH-paper-like current sensing materials, we prepared PDA-PMMA/graphene composites, which irreversibly respond to electrical current with the color change as the read-out (Figure 1). In the composites PDA acts as the electrochromic material, and the role of graphene is to provide the conductivity. Polymethylmethacrylate (PMMA) was originally introduced into the PDA as the inert polymer matrix to improve the mechanical properties. Interestingly, the presence of PMMA in the composites also enhanced the colorimetric phenomenon, as the blue-red phase transition can be more easily captured by the naked eye in PDA-PMMA/graphene, compared to PDA/graphene without PMMA. The critical current for the irreversible blue-red transition can be adjusted by varying the amount of graphene used during the preparative process.

2. RESULTS AND DISCUSSION

Graphene was synthesized, according to the literature, by a modification of Hummers and Offeman's method, followed by reduction treatment with ascorbic acid.[17,18] A typical sharp

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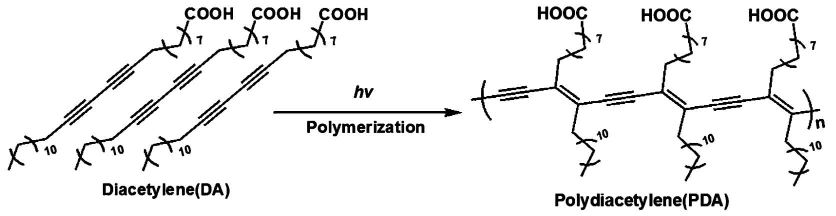
Scheme 1. Synthetic Strategy of PDA



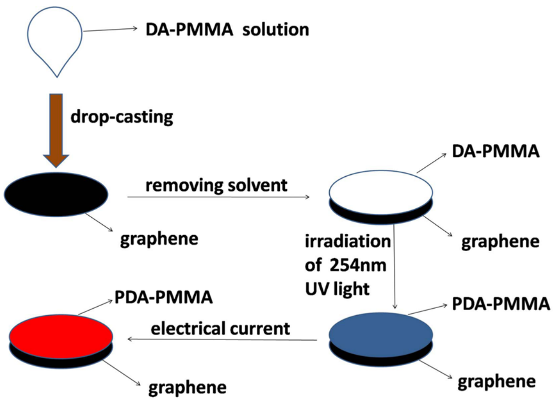


Figure 1. Schematic diagram for the preparation of PDA-PMMA/graphene composites followed by the electrochromic process.

increase at D line and decrease at G line was found and crumpled-silk-like layer structure was obtained (see Figures S3 and S4 in the Supporting Information), consistent with literature reports.[19] Among many diacetylene (DA) monomers with different substituents, 10,12-pentacosadiynoicacid was selected for our system, as shown in Scheme 1, based on the consideration that it has been widely studied and demonstrated to have typical properties of polydiacetylene after polymerization.[20,21] A predetermined amount of graphene was pressed into a disk. Then DA and PMMA mixture in THF solution was drop-cast onto that disk. After solvent evaporation, the disk was irradiated under 254 nm UV-light for 10 min, to form PDA-PMMA/graphene composites. The mass ratio between DA and PMMA was strictly controlled to be 1:3. A series of PDA-PMMA/graphene composites were prepared by varying the mass of graphene content. Then the composite was incorporated into a homemade circuit, with direct current as electrical stimulus. The electrical current passing through the circuit started from zero with an increasing rate of 0.01 A every 2 s. The circuit was removed after the whole disk turned red. The red color has always been retained, as least it has been there for more than one year since the first experiment.

The PDA-PMMA/graphene disks were prepared at five compositions. The mass of PDA was fixed at 45 mg and the mass ratios among PDA: PMMA and graphene were 9:27:200, 9:27:300, 9:27:400, 9:27:500, and 9:27:600, respectively. The critical responsive current (CRC) was recorded as the current applied on the disk at the first sight of red color. It is to be noted that the experiments were demonstrated to have very good repeatability and reliability. Almost negligible difference in the CRC values was obtained from five disks with the same composition (see Table S1 in the Supporting Information), because the smallest measurable change in the apparatus employed is 0.01 A. To further investigate whether the mass ratio between DA and PMMA influence the CRC, control samples with the mass ratio of 1:2 and 1:4 between DA and PMMA were also prepared. It turned out that the mass ratios of DA and PMMA had negligible effect on the responsive current. Interestingly, the CRC (average value from five measurements) exhibited an excellent linear relationship with the graphene content, as shown in Figure 2. This linear relationship suggested that the CRC can be easily tuned through varying the amount of graphene added into the composites.

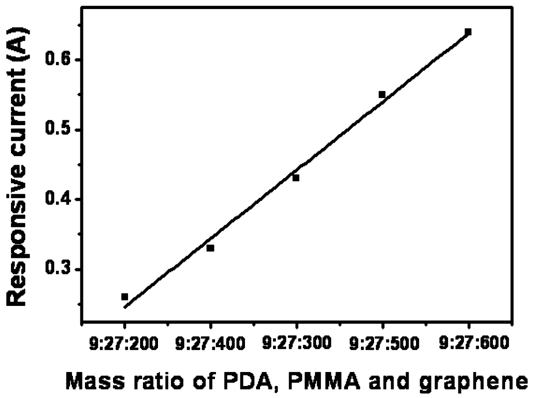


Figure 2. Relationship between the critical responsive current (CRC) and the graphene content by fixing the mass of PDA and PMMA at 45 and 135 mg, respectively.

The initial consideration for the addition of PMMA was that pure PDA powder can be easily wiped out of the surface of graphene, but becomes much more stable when dispersed in PMMA. Moreover, the PMMA is transparent within the UV—vis light region. For comparison, PDA/graphene composites were prepared with the same procedure. The critical current vs graphene content relationship for PDA/graphene composites was almost the same as the one for PDA-PMMA/graphene composites (see Table S2 and Figure S5 in the Supporting Information). Conclusions can be made that the presence/absence of PMMA or varying the amount of PMMA in the composite, had negligible effect on blue-red phase-switching of the PDA. However, the blue and red color themselves, and the color change process was more evident in the presence of PMMA (Figure 3). It is reasonable because the color of a small amount of PDA would not be clear on the top of black graphene, and mixing PDA with PMMA will reduced the color cover-up by graphene. The conclusion that PMMA had negligible influence on the blue-red phase transition of PDA can be further confirmed by the fluorescence images for the blue and red phases for PDA/graphene and PDA-PMMA/graphene, as also shown in Figure 3.

The absorption and fluorescence spectra (shown in Figure S6 in the Supporting Information) of the composites were consistent with the colors observed above. The red phase PDA had an absorption peak around 520 nm that is due to the absorption of the cyan-green light. The blue-phase PDA

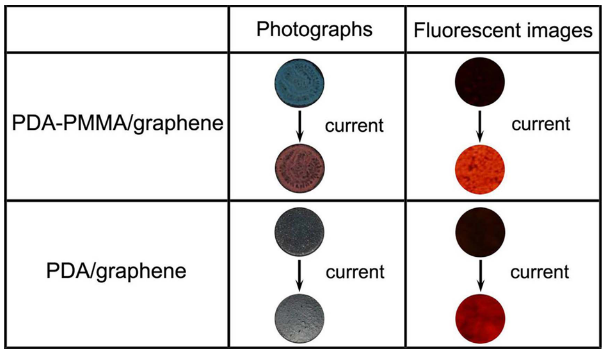


Figure 3. Photographs under ambient light (the whole image of the original disk with a diameter of 13 mm) and images from fluorescent microscope (part of the original disk, the actual diameter for the shown disk is about 5 μm), for PDA-PMMA/graphene and PDA/graphene composites before and after current stimulus. The composites with the mass ratios of 9:27:200 (PDA:PMMA:graphene) and 9:200 (PDA:graphene) was shown in this figure as the representatives. Other composites displayed similar phenomena.

absorbed light around 642 nm, thus displayed the bluish color. Under 510 nm excitation, negligible emission can be found for the blue- phase PDA, whereas the red phase has two emission peaks around 564 and 633 nm.

The widely accepted mechanism for the blue-red color transition of PDA was that the reduction of effective conjugation length caused by the conformation change of PDA backbone upon external stimuli.[11] It is reported in the literature that the color change of 10,12-pentacosadiynoicaci can only be realized with a temperature above 56 °C, if there is no any other stimulus. Thus, the possible thermally induced color change of PDA in this study can be ruled out because the highest temperature reached during the whole color change process was 31 °C, as measured by an infrared thermometer. Consequently, the origin of color change of PDA composites can be solely attributed to the applied electrical stimulus, which might affect the PDA backbone conformation. By drop-casting DA solution onto the surface of graphene disks, DA monomer, and then PDA, after UV irradiation, it can be easily attached onto graphene disks via hydrogen-bond interaction between the carboxylic group within PDA, with a small amount of hydroxyl group remaining on the graphene sheet.[17,18] This bread-and-butter-like tightly coupled double layer structure made the polarization of the −COOH groups possible when the electric current passing the graphene disk and thus the conformation of the PDA backbone changed. Due to the facts that the PDA layer was very thin and had strong interaction with the graphene, the conformation change required the current stimulus to reach a critical value. And the initial conformation was not easy to get recovered after removal of the applied stimulus.

This visually observable irreversible electrochromic phenomenon with adjustable critical responsive currents demonstrated by PDA-PMMA/graphene composites has not been reported previously, to the best of our knowledge. The reversibility of PDA conformation change under low electrical currents was reported in forms of PDA/carbon nanotube or PDA/graphene.[15,16] Though irreversibility was also observed under high electrical currents in certain cases, no tunability of the CRC was mentioned. In fact, this irreversibility is favorable in using this composite as one-shot sensing materials, because the color change can be observed afterward, even after the external stimulus is no longer present. Several scenarios can be envisioned in utilizing these PDA-PMMA/graphene composites in certain applications. This material can be used as an indication for safety-critical decision-making in certain overcurrent protection circuits, and composition of the tag can be regulated according to the defined value of the overcurrent; In addition, a series of composites with different critical currents can be incorporated into one system. This allows the visually observable and relatively accurate, or at least semiquantitative, determination of particular currents that passed through certain apparatus, without the aid of any other bulky data acquisition and transformation devices.

3. CONCLUSION

In conclusion, we have demonstrated the successful preparation of PDA-PMMA/graphene composites, which have distinguished irreversible electrochromic properties. The critical responsive currents were found to have an excellent linear relationship with the graphene content, when we fixed the mass ratio between PDA and PMMA. Different critical responsive currents can be obtained by varying the mass ratio of PDA and graphene. With PDA as the electrochromic material and graphene as the conductive layer, the introduction of PMMA into the PDA layer had negligible effect on the electrochromic response, but stabilized the composite and made the color change more obvious to the naked eyes. Ultimately, the desirable features possessed by the PDA-PMMA/graphene composites make them very promising materials in the electric current sensing application.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The details for the material preparation and characterizations, the instruments and setup for the measurements, the method for the data acquisition, pictures for the composites during the color change process, all the critical responsive current data obtained, and the relationship between the current and voltage applied on the disk. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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