Supporting Information to:

Enhanced Photothermal Effect of Graphene/Conjugated Polymer Composites: Photoinduced Energy Transfer and Applications in Photocontrolled Switches

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S1. Synthetic protocols





Dispersible RGO

The RGO-g-P3HT and dispersible RGO were synthesized using an amidation according to our previous work (Scheme S1).¹ A typical procedure is as follows: GO (10 mg) was dispersed in anhydrous DMF (1.5 mL) with the aid of sonication for 3 hours. To the GO suspension, SOCl₂ (20 mL) was added slowly and the resulting mixture was refluxed at 70 °C for ca. 24 h. The chlorinated RGO was isolated by centrifugation, and further purified by 5 cycles of washing with anhydrous THF and centrifugation. The chlorinated RGO dispersed in anhydrous THF (10 mL) was added to an amino-terminated P3HT-NH₂ (200 mg, Mn ca. 6500 Da) solution in anhydrous THF (60 mL). Afterward, the

reaction mixture was cooled to 0 °C, and anhydrous triethylamine (2 mL) was added dropwise into the reaction flask. The reaction was allowed to proceed at 50 °C for 24 h. Finally, the product was obtained by centrifugation at 17000 rpm for ca. 2 h, followed by 5 cycles of washing with anhydrous THF and centrifugation. A same process was employed to synthesize dispersible RGO by using excess 1-hexylamine (3 mL) during the amidation reaction.²

S2: Characterization methods

UV-visible spectra were recorded on a Cary 5000 UV-Vis-NIR spectrometer. Photoluminescence (PL) spectra were recorded with a Hitachi F-4600 spectrophotometer. Thermogravimetric analysis (TGA) was carried out with a Q50 TGA at a scanning rate of 5 °C min⁻¹ under an atmosphere of N₂. Atomic force microscope (AFM) images were recorded on a Bruker Multimode 8 atomic force microscope by means of ScanAsyst mode. AFM samples were prepared by coating the RGO-g-P3HT suspension in tetrahydrofuran (THF) onto a newly cleaved mica substrate. Transmission electron microscope (TEM) observations were performed on a JEOL JEM-2100F TEM operated at 200 kV. TEM samples were prepared by dropping the RGO-g-P3HT suspension in THF on 400 mesh Cu grids with supporting carbon film. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 scanning electron microscope. SEM samples were prepared by dropping the suspensions of RGO-g-P3HT, RGO, and GO in THF on copper foil. The photothermal effect of the solution/suspensions was measured as following: the solution/suspensions (1 mL) were loaded in a quartz cell and illuminated with a continuouswave beam (532 nm, 0.78 W cm⁻²) generated by a MGL-FN laser (Changchun institute of Optics, Fine mechanics and Physics, CAS, China). For the photo-controlled electrical switch described in the manuscript, a laser beam with power density of 2.38 W cm⁻² was used to shine on the photothermal layers.

The temperature of the solution/suspensions was measured by using a PT100 thermal resistor immersed into the solution/suspensions. The resistance of the PT100 thermal resistor changed with temperature; i.e. with a constant potential applied to the PT100 thermal resistor (0.05 V), the current changed with temperature. The I-V curve of the PT100 thermal resistor was recorded with an electrochemical station (Zennium 40088). The instantaneous resistance of the PT100 thermal resistor was obtained from the I-V curve.

Basically, the resistance of a PT100 thermal resistor (R_T) as function of temperature (T) follows the formula shown below when T is higher than 0 °C:

$$R_T = R_0 \cdot (1 + A \cdot T + B \cdot T^2)$$

where, $A = 39083 \times 10^{-3} \text{ °C}^{-1}$, $B = -5775 \times 10^{-7} \text{ °C}^{-2}$, and $R_0 = 100 \Omega$. Thus, the temperature of the solution/suspensions was obtained by solving the equation. Likewise, the temperature change of the solution/suspensions was obtained from the difference between the final temperature and the initial temperature.



Figure S1. Electrical current of the PT100 thermal resistor recorded as the water bath cooled from 35.2 to 35.0 °C (with 0.05 V potential applied, the black line), and the calculated temperature (the red line).

The sensitivity of the measuring and recording system was evaluated. A small temperature change (ca. 0.2 °C) was obtained by cooling a thermostat water bath of ca. 35.2 °C. Figure S1 shows that the current passing through the PT100 thermal resistor increased as the water bath cooled down (with 0.05 V applied, the black line). Thus, the temperature was obtained through the calculation as shown above (the red line). It may be seen that the noise of the recorded current is smaller than the current change caused by the temperature change of 0.1 °C. As a result, the noise of the calculated temperature is smaller than 0.1 °C. Therefore, the sensitivity of this measuring and recording system is smaller than 0.1 °C. Thus, the accuracy of the measuring and recording system appears to depend on how the thermal resistor responds to small changes in temperature and how he recording equipment responds to small changes in current.

Energy conversion efficiency (η) was used to quantitatively evaluate the capability of converting the incident light into thermal energy and calculated using equation 1:³

$$\eta = \frac{Q}{E} = \frac{Cm\Delta T}{PSt} = \frac{C\rho V\Delta T}{PSt}$$
(1)

where Q is the generated thermal energy, determined by the ΔT over a period of irradiation, and the heat capacity (C), mass (m), density (ρ), and volume (V) of the solution/suspensions; E is the total energy of the incident light, determined by the power of the incident light (P), irradiation area (S), and irradiation time (t). Considering that the graphene-based materials and P3HT only accounted for a very small fraction in the solution/suspensions, the C (1.96 J g⁻¹ K⁻¹) and ρ (0.899 g cm⁻³) of the solvent (THF) were used for the calculation. It may be gleaned from Figure 1a that the temperature of the solution/suspensions increased rapidly during the initial period of the irradiation, followed by a saturated maximum temperature with continued irradiation. The phenomenon may be due to a balance between the generated heat and the heat dissipated to the environment. Regardless, the heat generated initially surpassed the dissipation of heat. Thus, to obtain a nvalue that approaches the real value for the materials studied, the ΔT obtained over 1 min of irradiation was used for the calculation, and V, P, and S were measured to be 1 mL, 0.78 W cm⁻², and 1 cm², respectively.

S3: Characterization of the RGO-g-P3HT composite

S3-1. NMR characterization



Figure S2. Solid state ¹³C CP/MAS NMR spectra of P3HT, GO, and RGO-g-P3HT.

Figure S2 displays the solid state ¹³C CP/MAS NMR spectra of P3HT, GO, and RGOg-P3HT. The spectrum of P3HT contains two groups that feature diagnostic resonances: the resonances from 10 to 35 ppm correspond to the carbons of hexyl groups and the resonances from 120 and 140 ppm correspond to the carbons of thiophene rings. The spectrum of GO contains three groups that feature diagnostic resonances: the resonances from 50 to 85 ppm represent the carbons in the epoxide and hydroxyl groups; the resonances from 120 to 145 ppm may be assigned to the unoxidized sp² carbons of the graphene network; and the resonances from 150 to 175 ppm arise from the carbonyl groups.⁴ As expected, the spectrum of RGO-g-P3HT contains features that reflect RGO as well as P3HT. Furthermore, the carbons of amide groups slightly shifted to higher fields compared to those in the spectrum recorded for the GO. This result is in agreement with a previous report.⁴ Collectively, the NMR data support that the P3HT chains have been covalently bonded to RGO sheets in the RGO-g-P3HT.





Figure S3. TGA curves of (a) RGO-g-P3HT and (b) dispersible RGO.

The thermal stabilities of the RGO-g-P3HT and the RGO materials were estimated using TGA (Figure S3). The grafting density of the RGO-g-P3HT was obtained from the mass loss corresponding to the P3HT component in the TGA curves and measured to be 17.81%.

S3-3. Raman spectra



Figure S4. Raman spectra of P3HT, GO, and RGO-g-P3HT.

Figure S4 displays the Raman spectra of P3HT, GO, and RGO-g-P3HT. The spectrum of P3HT features two sharp peaks at 1379 and 1448 cm⁻¹, which were assigned to the C=C skeletal stretching vibration mode and the C-C skeletal stretching vibration mode, respectively.⁴⁻⁵ The spectrum of GO contains an intensive G band at 1599 cm⁻¹ and an intensive D band at 1349 cm⁻¹. As expected, the RGO-g-P3HT shows both the feature peaks of RGO and P3HT. However, the Raman peaks corresponding to P3HT are stronger than that of RGO because of the stronger capability of P3HT for providing Raman signals.





Figure S5. C 1s XPS of (a) GO, (b) the RGO-g-P3HT, and (c) the dispersible RGO.

Figure S5 summarizes the C 1s XPS of GO, the RGO-g-P3HT, and the dispersible RGO. The spectrum of GO contains two dominant peaks at 284.7 and 286.7 eV corresponding to the C-C and C-O species, as well as two weak signals at 287.5 and 288.8 eV due to the C=O and O-C=O species (Figure S5a). The peaks at 286.7, 287.5, and 288.8 eV confirm the presence of oxygen-containing groups, such as hydroxyl, epoxide, carbonyl, and carboxylic acid groups, on the GO sheets. In the contrast, the peaks corresponding to the RGO-g-P3HT and the dispersible RGO (Figure S5b and S5c), supporting the transformation of GO into RGO during the amidation process through dehydration.⁶ In addition, two new peaks corresponding to C-N and N-C=O species, which are contributed to the carbons in the amide bonds, appears at 285.7 and 288.9 eV in the C1s XPS of RGO-g-P3HT. This result indicates that P3HT chains have been covalently linked to RGO sheets.



S4: Concentration dependence and reproducibility of the photothermal effect

Figure S6. Photothermal heating curves of the suspensions of (a) the RGO-g-P3HT, (b) the RGO, and (c) GO at various concentrations.



Figure S7. the η as function of concentration for the suspensions of RGO-g-P3HT, RGO, and GO when irradiated for 1 min.



Figure S8. reproducibility of the photothermal effect for the suspensions of RGO-g-P3HT, RGO, GO (1 mg mL⁻¹), with each cycle comprising irradiation for 3 min followed by removal of the light stimulus for 8 min.

The influence of concentration of the suspended graphene materials on their respective photothermal effects was also investigated. The photothermal heating curves for the suspensions of RGO-g-P3HT, RGO, and GO at various concentrations are shown in Figure S6. As summarized in Figure S7, the η (calculated after irradiation for 1 min) for the suspensions of RGO-g-P3HT, RGO, and GO increased with their concentrations (from 0.2 to 0.5 and to 1 mg mL⁻¹), with the RGO-g-P3HT showing the highest calculated η . These results suggested to us that the photothermal effect of the RGO materials dominated the temperature elevation of their suspensions. The reproducibility of the photothermal effect for the RGO-containing materials was evaluated after irradiation for 3 min followed by removal from the light stimulus for 8 min. Figure S8 shows the periodic changes of the ΔT for the suspensions of RGO-g-P3HT, RGO, and GO in THF (1 mg mL⁻¹). First, the materials studied all displayed repeatable response to the light irradiation.





Figure S9. PL spectra of the solution/suspensions of P3HT, RGO@P3HT, RGO-g-P3HT in THF (λ_{ex} = 450 nm). In the RGO@P3HT suspension, the two components have the same ratio as in the RGO-g-P3HT. In the P3HT solution, P3HT has the same concentration as the P3HT component in the RGO-g-P3HT.

S6: Morphology analysis of the RGO-g-P3HT composite



Figure S10. AFM images of RGO-g-P3HT composite: (a) large-sized sheets and small particles, (b) small particles.



Figure S11. TEM images of RGO-g-P3HT: (a) large-sized sheets and small particles, (b) small particles, and (c) size distribution of the RGO-g-P3HT particles. The statistical analysis was conducted on the base of 110 particles of TEM observation.

Since size dependent photothermal effect has been reported for graphene based materials,⁷ subsequent efforts were directed towards characterizing the morphology of the RGO-g-P3HT composite. The morphology of the RGO-g-P3HT composite was observed via atomic force microscope (AFM) (Figure S10), which indicated that the RGO-g-P3HT composite comprises sheets of hundreds nanometers in size as well as particles of ca. 12 nm in diameter and ca. 4 nm in thickness. The small particles were RGO-g-P3HT monolayers since they had the similar thickness to that of monolayered RGO-g-P3HT sheets.¹ It has been reported that the RGO-g-P3HT particles were formed by the sonication during the amidation process.⁷ In addition, the AFM images indicated the thickness of the RGO-g-P3HT sheets varied from less than 10 nm to more than 20 nm depending on the grafting density of P3HT

and the wrapping of the composite sheets (Figure S10a), and the thickness of the RGO-g-P3HT particles was measured to be ca. 4 nm (Figure S10b). The RGO-g-P3HT composite was also evaluated using transmission electron microscope (TEM) (Figure S11). In agreement with the AFM results, the TEM data further confirmed that the RGO-g-P3HT was comprised of sheets of hundreds nanometers in size and particles of ca. 14 nm in diameter. Statistical analysis indicated that the RGO-g-P3HT particles have a diameter distribution from 6 to 30 nm, with 10-14 nm being the dominant size (Figure S11c). Abundant TEM observation also indicated that there were on average 3-4 RGO-g-P3HT sheets in one hole of the TEM grid ($38 \times 38 \mu m^2$). Considering the distribution density of the RGO-g-P3HT particles from Figure S11b, the ratio between the RGO-g-P3HT sheets and the RGO-g-P3HT particles can be calculated to be ca. 1:9.5 according to their areas.

Morphology of the dispersible RGO was also conducted. We found that the dispersible RGO had a similar size distribution to the RGO-g-P3HT composite. This finding may derive from the similar synthetic procedures used to prepare the aforementioned materials. Statistical analyses of the particles of the dispersible RGO indicated that the dispersible RGO particles were slightly smaller than the RGO-g-P3HT particles. This result could be attributed to the fact that the hexyl groups are shorter than the P3HT chains. Therefore, the enhanced photothermal effect of RGO-g-P3HT composite compared with the dispersible RGO was not due to the size dependent photothermal effect,⁷ but due to the photoinduced electron transfer from P3HT to RGO sheets in the RGO-g-P3HT composite.

S7: SEM characterization of the films of RGO-g-P3HT, RGO and GO

The suspensions of RGO-g-P3HT, RGO, and GO in THF were cast on copper foils, and dried at room temperature. The morphologies of the resultant films were characterized using SEM. It may be seen from the SEM images that the RGO-g-P3HT yielded the smoothest film among the three samples studied (Figure S12, S13, and S14), revealing an intrinsic advantage in morphology of the RGO-g-P3HT material when used as a photothermal layer.



Figure S12. SEM images of the RGO-g-P3HT film: (a) at low magnification and (b) at high magnification.



Figure S13. SEM images of the RGO film: (a) at low magnification and (b) at high magnification.



Figure S14. SEM images of the GO film: (a) at low magnification and (b) at high magnification.

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