Fabrication of Graphene/PDMS Nanocomposites for Optical Heating on Microfluidic Chips

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ABSTRACT

Graphene, a two-dimensional monoatomic thick carbon layer, is proposed as a novel nano-scale optical heater by uniformly dispersing it in PDMS matrix and subsequently a simple, fast and localized heating method on the microfluidic chips made out of the nanocomposites is domonstrated. The dodecylamine-modified graphene (C12-rGO) was well-dispersed in PDMS suspension to form uniform C12-rGO/PDMS nanocomposite due to the presence of the long dodecyl chain. Microfluidic channels can readily be fabricated by standard soft lithography out of the composite. The prepared chips with low graphene contents exhibit pronounced temperature increase in few minutes at very low power illumination. Our studies illustrated that Graphene/PDMS nanocomposite can serve as a practical optical heating platform for microfluidic chips with the advantages of simple, low-cost and high efficiency.

Keywords: graphene, composite, optical heating, microfluidic chips

1 INTRODUCTION

Microfluidic chips, on which fluids can be controlled and analyzed within microscale channels, have attracted extensive attention from both industrial and academic communities. Heating is of vital importance for the overall chip performance. So far on-chip heating has been generated mainly by resistive[1, 2] and optical means[3-5]. The resistive means have the limits in the spatial resolution of localized heating, and the required resistance wiring increases the complexity of microchip fabrication. In contrast, the optical means are much simpler due to the needlessness of electric connections, and the heating locations are more controllable owing to the elimination of resistive electrodes. Even so, the optical means often need strongly light-absorbing materials (microsized patterned surfaces[5] or gold nanoparticles[6]) for a better heating efficiency. The use of these materials not only introduces additional fabrication steps but also often interferes with on-chip optical analyses.[6]

Graphene, which is one atom thick and two-dimensional (2D) single carbon layer, is emerging as a rising star in the field of carbon materials due to its high specific surface area and superlate mechanical, electrical, and thermal properties. Especially, it has drawn significant interest in recent years for polymer nanocomposites. [7-9] The perfect sp^2 carbon-network structures of the graphene ensure them to have the great ability to efficiently absorb and transform IR light into thermal energy. Furthermore, it has the similar light absorption over a very wide range (from ultraviolet to infrared). [10] It can be conceived that introducing graphene into PDMS will finally lead to the invention of a simple, cost-effective, high efficient and wide-range optical heating method for microfluidic chips.

In this work, we describe the employment of graphene as a novel nanoscale optical heater for microfluidic chips by uniformly dispersing it in PDMS matrix.

2 RESULTS AND DISCUSSION

2.1 Characterization of C12-rGO

The dodecylamine-modified graphene was prepared by modification and reduction of GO simultaneously with DOA in solvothermal process and characterized in detail(Figure 1). The absorption peak of C12-rGO red-shifts to 261 nm in UV spectrum, which indicates the restoration of C=C bonds in C12-rGO sheet.[11] The most significant change in FTIR spectrum of C12-rGO is the large intensity increase for peaks at 2846, 2920 cm^{-1} and 1454, 720 cm^{-1}, corresponding to the C-H stretching and deformation. This is due to the introduction of long hydrocarbon chain into GO sheets. All these results confirm the intercalation and chemical reaction of DOA with GO. in our work, I_D/I_G of C12-rGO samples(1.16) are found to be obviously larger than that of corresponding GOs(0.83). In XRD pattern, the (001) peak for C12-rGO is shifted to 4.6°, correspongding to an intra-gallery spacing of 1.90 nm. The enlarged interlayer space of C12-rGO confirms the intercalation of DOA. This value is very comparable to the calculated value of ~1.86 nm using the equation derived by Bourlinos[12].
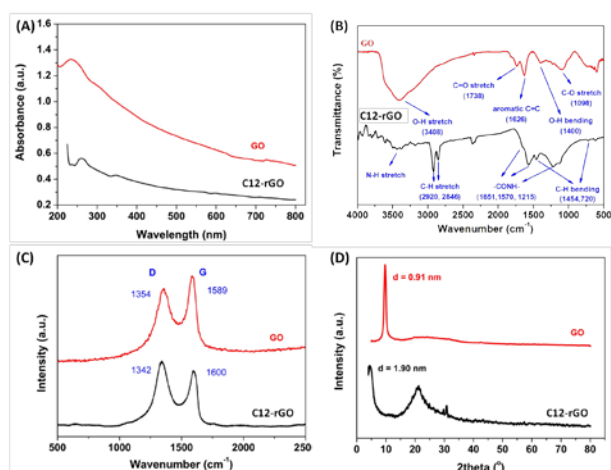
Figure 1: (A) UV/Vis absorption spectra, (B) IR spectra, (C) Raman spectra and (D) XRD patterns of GO and dodecylamine-modified graphene(denoted as C12-rGO).

2.2 Characterization of C12-rGO /PDMS composite

The C12-rGO were suspended in toluene and mixed with the PDMS prepolymer component A and the crosslinker component B, followed by thorough mixing and polymerization in oven to obtain the C12-rGO /PDMS composite. Figure 3 shows photographs of neat PDMS and its nanocomposites with different C12-rGO contents. The neat PDMS is entirely transparent, thus the image under the neat PDMS block can be seen clearly (Figure 2A). While the PDMS nanocomposite become dark, and the more C12-rGO the nanocomposite contains, the darker the it will be (Figiure 2B and 2C). Figure 2D displays the UV-vis transmission spectra of neat PDMS and its nanocomposites. In the spectra region with wavelengths longer than 350nm, the transmittance of neat PDMS is about 80%, while the transmittance of nanocomposite with 0.05wt% C12-rGO decreased sharply to less than 20%. When added more C12-rGO to the composites (about 0.1wt %), the transmittance further decreased to only about 1%.

2.3 Photothermal conversion properties of the graphene/PDMS composites

The photothermal conversion properties of the graphene/PDMS composites were examined via measuring the temperature rise of each PDMS block that was immersed in a cuvette containing 2 mL of water.[13] Figure 3A shows the temperature rises of only water, water with neat PDMS block, PDMS with 0.05 wt% C12-rGO block and PDMS with 0.1 wt% C12-rGO block under red laser illumination. After 30 min, the temperature elevates 5 °C for the nanocomposite with 0.05wt% C12-rGO. When the C12-rGO content increases to 0.1wt%, the optical heating performance further improves. For comparison, the water
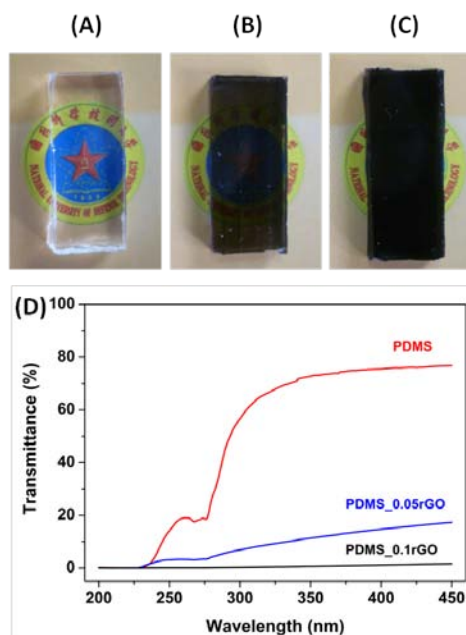

Figure 2: Photographs of (A) PDMS, (B) PDMS with 0.05wt% C12-rGO and (C) PDMS with 0.1wt% C12-rGO. (D) UV/Vis transmission spectra of PDMS with 0.05wt% C12-rGO, 0.1wt% C12-rGO and blank PDMS.

with or without blank PDMS blocks in it under the laser illumination results both only in a temperature increase less than 1 °C. Figure 3B showed the temperature rises of PDMS with 0.1 wt% C12-rGO block under lasers with different powers. Certainly, the temperature would rise more quickly under the higher power laser irradiation. At a high illumination laser power (180 mW), the temperature increased over 8°C from room temperature within ∼30 min. At a low laser power (100 mW), the temperature rises only about 2°C within ∼30 min. In addition, we investigated the optical heating effect under different wavelength, as shown in Figure 3C. The red light (650 nm) has the highest photo-thermal efficiency, while the green one (532nm) showed nearly no effect. There was still evident photo-thermal effect for the wavelength as short as 405nm. The finally reached temperature is determined by the interplay among the energy input rate, the heat capacity of the system, and the heat dissipation rate.[14] Therefore, the temperature of sample can be controlled simply by varying the illumination laser power, wavelength, or the illumination time.

Moreover, the photothermal conversion capabilities of the graphene/PDMS composite were examined by measuring the temperature rise of water confined in a microfluidic channel made out of the nanocomposite blocks. A temperature-sensitive dye, rhodamine B was chosen as the temperature probe.[5,13,15] Its temperature dependence has been found to be described by $\ln[I(T)/I(T_{ref})] = \beta(1/T -1/T_{ref})$, where $I(T)$ and $I(T_{ref})$ are the integral emission intensities at temperatures T and T_{ref}, respectively. β is a proportional constant, 2787 ± 222 K.[13] A green laser (532nm) was chosen to serve as the excitation light for RhB

dye, because the photothermal effect of the laser at this wavelength can be ignored according to above results. The temperature of the fluid in the channel under the 650-nm heating laser illumination was determined by measuring the fluorescence emission. Figure 3D shows the temperature rise traces of the fluid in the channel made of the graphene/PDMS nanocomposite, with the corresponding fluorescence spectra. At a low illumination laser power of 0.18W (650nm), the temperature at the illumination spot on the PDMS nanocomposite with 0.1wt% C12-rGO chip rises evidently and quickly. While the fluid heating in the channel fabricated from blank PDMS under the same laser illumination results almost no temperature increase, even illuminated for 20min. The photobleaching is insignificant in our experiments, because the heating laser wavelength is far away from the dye absorption band and the power of the fluorescence excitation laser is very low. It was also verified by the fact that the fluorescence intensity of the dye returns to its initial value after the fluid in the channel was cooled down naturally to room temperature.
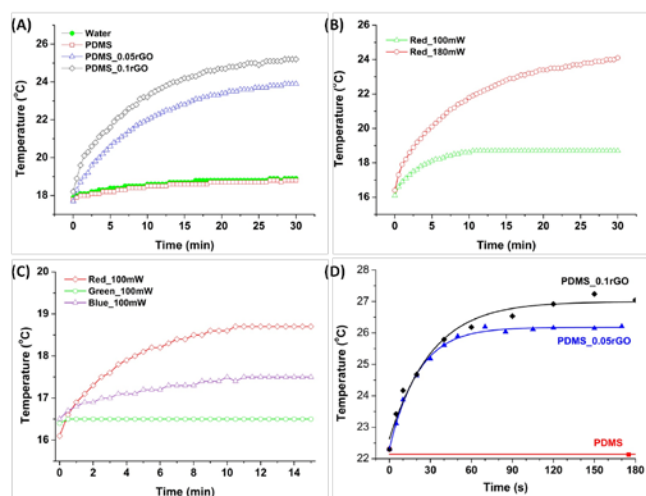

Figure 3: Photothermal conversion properties of the C12-rGO/PDMS composite blocks in water: (A) with varied C12-rGO contents under 100mW 650nm laser; (B) with 0.1wt% C12-rGO contents under 100mW laser at different wavelength; (C) with 0.1wt% C12-rGO contents under 650nm laser with different power. (D) Optical heating performance of the Graphene/PDMS composite chip. Temperature rise traces of the fluid inside the channel made of either the C12-rGO/PDMS composite or blank PDMS.

3 CONCLUSIONS

We have introduced graphene as a novel nanoscale optical heater for microfluidic chips by uniformly dispersing it in PDMS matrix and showed fast and localized heating on the microfluidic chips made out of the nanocomposites. Graphene oxide is modified and reduced simultaneously with dodecylamine under solvothermal condition. The resultant dodecylamine-modified graphene

can be well dispersed in PDMS suspension, and the exfoliation of modified graphene in PDMS is observed for the first time. The C12-rGO/PDMS nanocomposite blocks become dark and can be made into microfluidic channels by using standard soft lithography techniques. The prepared chips with low C12-rGO contents have exhibited obvious and rapid temperature increase under weak illumination. We have provided a first example that the optical heating effects are achieved not only under red laser irradiation, but also under short violet light. The proposed optical heating method provide a simple, cost-effective, and efficient approach for the optical heating on microfluidic devices and will lead to a wide range of applications in many fields, especially those where visible light heating is required.

4 EXPERIMENTAL SECTION

Tables and illustrations can appear within columns or span both columns. If two column figures or tables are required, place them at the top or at the bottom a page. They should have a self-contained caption and be center justified. Figures must be 600 dpi resolution or equivalent. All lettering should be 10-point type or larger. Figures must not extend into the margins.

Synthesis of GO: Graphene oxide was synthesized from graphite powder (<30 μm) by a modified Hummer's method.[16,17] 1.0 g of graphite powder was dispersed in a mixture of concentrated H_2SO_4/H_3PO_4 (117:17 mL) under ice-water bath. Next 6.0 g of $KMnO_4$ was slowly added to this mixture and keep the temperature was less than 20 °C. After thoroughly blend, the mixture was mixed well and transferred to a 50°C water bath and stirred for 12 h. Then, the reaction was cooled to room temperature and poured onto ice with sufficient 30% H_2O_2. The mixture was centrifugated and washed with distilled water repeatedly for 3 times. Finally, the resulting GO aqueous dispersion was further purified by dialysis for two weeks to remove the remaining metal species.

Synthesis of Dodecylamine-modified graphene (C12-rGO): The GO (10mg) was dispersed in 15mL of DMF through vortex mixing and mild sonication to form a colloidal suspension of single layer GO sheets. Dodecylamine (0.2g) was added to the dispersion and was left for 1h in an ultrasonic bath. Then the dispersion was transferred to a stainless steel autoclave and sealed and heated in oven at 120℃ for 3h. The product obtained after solvothermal treatment was washed with ethanol by centrifugation-redispersion for 3 times.

Preparation of C12-rGO/PDMS nanocomposites: Dodecylamine-modified graphene (C12-rGO) was dispersed in toluene by a solvent exchange method and diluted to 10 mg/mL. [18] The resultant C12-rGO/toluene dispersion was then mixed with the PDMS prepolymer component A (3.0 g, Silicone Elastomer SYLGARD 184) under ultrasonication at room temperature for 1 h. Subsequently, the crosslinker, component B (0.3 g, Silicone Elastomer SYLGARD Curing Agent), was added, followed

by ultrasonication for another 5 min. The C12-rGO/prepolymer mixture was thereafter cast on a mould and subjected to polymerization at 65 °C for 3 h.

Temperture measurement: The photothermal conversion properties of the composite blocks was measured first as follows:[19] A composite block (~1.0 × 2.2× 0.25 cm) was placed vertically in a standard quartz cuvette with an optical path length of 1 cm. The cuvette contained 2 mL of water. A continuous semiconductor diode laser at a wavelength of 650/532/405 nm was employed for the optical heating, and a thermocouple digital thermometer was utilized to monitor the temperature. In order to reduce the heat loss, the cuvette was covered by a lid of foam, and its each wall was coated with a piece of foam, except the wall which the laser radiated on. Furthermore, optical heating performance of the Graphene/PDMS composite chip was determined by employing the temperture-sensitive dye rhodamine B. One microchannel of the Graphene/PDMS chip was filled with of 0.1 mM rhodamine B aqueous solution. The chip was put on the object stage of an Olympus BX51 binocular microscope. A 532nm semiconductor diode laser (5mW, Local compony) was employed for the fluorescence excitation. The fluorescence spectra of the dye solution inside the channel were recorded using an Ocean Optics USB4000 fiber-optic diode-array dual-channel spectrometer interfaced with an ocular tube of the microscope by fiber optics and a 10_working-distance objective (Olympus 10X/0.30). A semiconductor diode laser (150mW, Local compony) at 650 nm was used for the optical heating. The fluorescence excitation laser and the heating laser were adjusted to illuminate the same region on the microfluidic chip, which is just under the object lens.

Characterization: UV/Vis absorption spectra of the grapheme oxide (GO) and C12-rGO were recorded by using a UV-1201 UV/Vis spectrophotometer (China). IR spectra(500-4000 cm^{-1}) were recorded on Brucker Tensor 27 spectrometer, the GO/CCG powder was abraded with KBr and pressed to prepare the pellet, while the spectra of the PDMS and C12-rGO/PDMS composite were taken with a single reflection attenuated-total-reflectance (ATR) sample accessory. The Raman spectra were recorded from 500 to 2500cm^{-1} using a FT Raman spectrometer (Senterra&Veate X70, Bruker, Germany) with an argon ion laser excitation of 514nm. X-ray Diffraction (XRD) measurements were performed by a Ttr III type X-ray diffractometer (Rigaku, Japan) between 4° and 80° equipped with a conventional Cu K_α X-ray radiation (λ=1.54 Å) source.

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