

General Route toward Patterning of Graphene Oxide by a Combination of Wettability Modulation and Spin-Coating

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Graphene, a basic unit of graphite, fullerene, and carbon nanotubes, is atomically thin with stable two-dimensional hexagonal honeycomb structure and shows novel electronic and mechanical characteristics.^{1–17} From the discovery of graphene in 2004,¹⁴ great efforts and development have been made in the synthesis, characterization, and applications of graphene. In the case of graphene synthesis, chemical oxide methods attracted focusing attention compared with other approaches such as mechanical exfoliation of highly ordered pyrolytic graphite, extension growth,^{18,19} and chemical vapor deposition due to its unique advantages of easily forming a single layer, scalability, and low-cost.^{1–11,20–29} Further development of graphene oxide relies on effective reducing method and exploration of effective patterning approaches. Among these challenges, patterning of reduced graphene oxide sheets (RGOs) plays an important role in its practical applications. So far, a few approaches, such as polydimethylsiloxane stamps and electrostatic interactions, have been developed.^{7–9} However, effective, general, and low-cost patterning techniques are still highly desired along with rapid progress of RGOs. Therefore, patterning of solution-processable graphene, which meets the urgent requirement of graphene technologies, might boost rapid development of graphenes.^{7–11}

Surface science focuses on the investigations of physical and chemical phenomena that occur at the interface of two phases. The corresponding surface technologies have been widely applied in the patterning of carbon nanotubes and organic

ABSTRACT A general route was demonstrated to realize the patterning of reduced graphene oxide sheets (RGOs) on a variety of substrates by a combination of modulating the solution wettability of the substrates and spin-coating process. By virtue of usual surface treatment technique or application of mixed solvent, the GO solution wettability can be controlled precisely. The wettability modulation combined with spin-coating and reducing process brings on patterning of RGOs. This simple but effective, general, and low-cost approach holds great promise for numerous potential applications in organic electronics, flexible transparent conducting thin films, and flexible semi-transparent sensors.

KEYWORDS: patterning graphene oxide · wettability · spin-coating · organic transistor · sensors

crystals.^{30–33} Similarly, GOs as a good hydrophilic material might also be effectively patterned by surface engineering and lead to patterned RGOs. However, this challenge has proved difficult to be realized due to the lack of electrostatic interactions or other forces between substrates and GOs.^{4–11} Wang *et al.* and Wei *et al.* achieved solution graphene patterning by the construction of electrostatic interaction.^{7,8} If the patterning can be fulfilled without designed construction of certain forces between the graphene and the substrate, the whole process will be widely applicable and represent an important step forward. Here, we achieved effective patterning of RGOs by using a wettability modulation technique combined with spin-coating. More interestingly, the wettability modulation is achieved by a simple substrate treating technique or selection of a mixed solvent for graphene.

RESULTS AND DISCUSSION

Figure 1a,b shows the patterning process of GOs on SiO₂. The SiO₂ substrate is first modified by 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (PFS) to

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Received for review June 28, 2010 and accepted September 15, 2010.

Published online September 21, 2010.
10.1021/nn101463j

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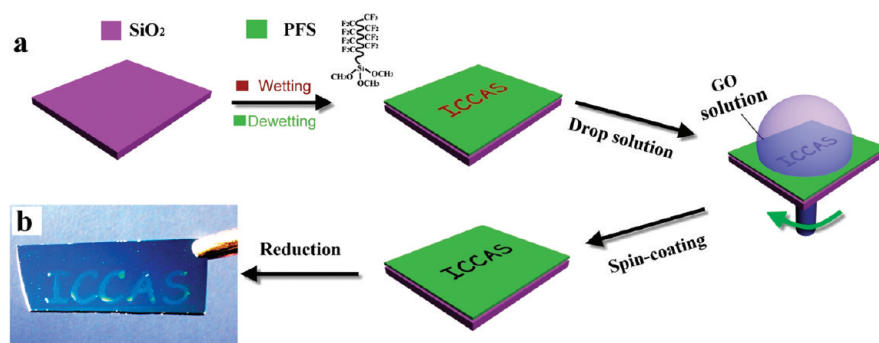


Figure 1. Schematic illustration of RGO patterning process. (a) Patterning process of GOs on SiO_2 , (b) optical microscope images of patterned RGOs (with ICCAS characters) on SiO_2 .

form dewetting surfaces for GO solutions.³⁴ The wetting region (with “ICCAS” characters) is fabricated by ultraviolet ozone (UVO) treatment with shadow mask on the silicon oxide (SiO_2) substrate. The following solution-dropping, spin-coating, and thermal reduction treatment (for details, see Materials and Methods) result in patterning of RGOs. Accordingly, the graphene can be patterned once the wetting and dewetting region are predefined. We also marinated the substrates in the GO solution to absorb the GOs on its surface by van der Waals force.³¹ However, patterning GO sheets cannot be achieved using this approach. The result is consistent with previous reports by other groups.^{7,8} It proved that the spin-coating is a key parameter in patterning GOs. We then performed an experiment to study the relationship between the spin-coating rate and the GOs’ coverage. We dropped enough GO solution on the wafer and made a spin-coating immediately, which excluded the effect of spread time.^{28c} The results demonstrated that spin-coating rate should be controlled higher than 3000 r/m to achieve a good uniformity and coverage. The detail relationship of spin-coating rate, uniformity, and coverage is shown in Figure S1 (see Supporting Information).

In the patterning process, the solution wettability on the substrate and the GO concentration determine the deposition position and GOs’ coverage on the substrates. We then investigate the relationship between the GOs’ coverage and the solution wettability on SiO_2 . The GO solution wettability is controlled by the different UVO treatment time. We can obtain substrates with different contact angles (CAs) (Figure 2a). Thereafter, GO solution (1.5 mg/mL) was dropped and spin-coated. As shown in Figure 2b–e, the GOs’ coverage is strongly related to the CA of the solution on the substrates. No obvious GO deposition is observed for the surface with CA above 90° when the PFS-modified SiO_2 was treated with UVO for less than 60 s. As a comparison, the following UVO treatment decreases the CA and increases GO coverage dramatically. When the treat time is longer than 100 s, both the CA and GO coverages do not change any more. Consequently, low CA contributes to the high GO coverage and $\text{CA} < 10^\circ$ is required to ensure continuous GO film. The concentration of the GO solution is another key factor. The GO solutions with different concentrations were spin-coated on these hydrophilic surfaces (UVO treated 180 s with $\text{CA} < 10^\circ$) (Figure S2, Supporting Information). The GO coverage

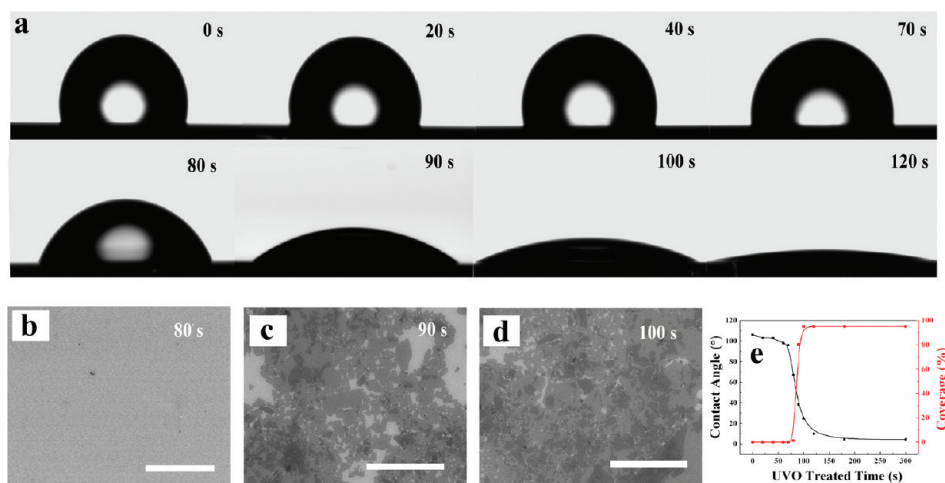


Figure 2. (a) Series of CA graphs on PFS surface with different UVO treatment time: 0, 20, 40, 70, 80, 90, 100, and 120 s. SEM images of GO (1.5 mg/mL) coverage on PFS surfaces with UVO treatment time of (b) 80 s, (c) 90 s, and (d) 100 s (the scale bar is 20 μm). (e) Plot of relationships between the GO solution CA and coverage of GOs on the PFS’s surface with different UVO treatment time.

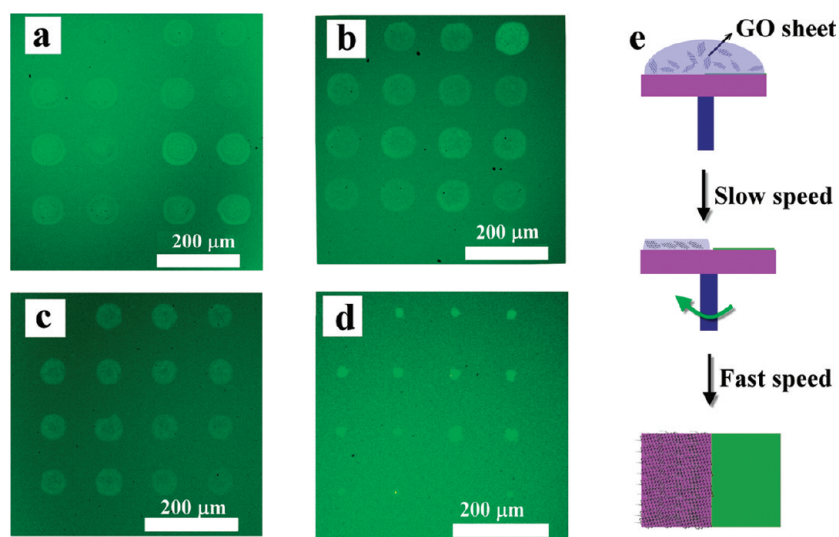


Figure 3. Optical images of patterned GOs with different sizes. Patterning areas with (a) 80, (b) 60, and (c) 30 μm GOs and almost with several single (d) 10–15 μm sheets. (e) Suggested mechanism of the patterning of the GO process.

increases gradually along with the increase of concentration of GO solution. The near 100% coverage was formed at a concentration above 1.5 mg/mL. Although the low GO solution concentration corresponds to low GO coverage, the high coverage can also be obtained by cycling spin-coating. For example, coverage higher than 80% is achieved with spin-coating of 0.7 mg/mL GO solution three times (Figure S3).

With optimized patterning condition (UVO treated for 180 s, GO concentration of 2 mg/mL, spin-coating rate >3000 r/m), we may easily pattern the GOs on a given position with designed shape. Figure 3 and Figure S4 (Supporting Information) show the optical microscope images and SEM images of patterned GOs, respectively. The patterning result is consistent with the shadow mask. Interestingly, we can get several GOs at the certain position by decreasing the diameter of wetting area (Figure 3d and Figure S4). These results indicate good resolution of the patterning technique.

According to the above-mentioned results, we suggest the following mechanism (Figure 3e). For the dewetting surfaces, the solution is easily spun out of the substrate during the spin-coating process, while a solution film would be formed on the wetting surface at the start-up spin-coating speed. In the following fast spin-coating process, the GOs in fastened solution are inclined to the wetting surface due to the tangential force and are deposited on the wetting region with the solvent drying. Therefore, the GOs are patterned on the predefined wetting surfaces. Since the solution wettability as well as the GO concentration affects the solution fastened on the substrate and GOs' number per volume, respectively, they influence the GOs' number on the substrates.

In the previous reports, GO deposition on normal metal surfaces such as Au, Ag, Cu, and Al is difficult to be realized due to the lack of electrostatic

interactions.^{7,8} Besides, the CA of GO solution on these metals' surface is still high for depositing GOs (in our experiment, $\text{CA} > 60^\circ$). As a result, the successful sample of GOs depositing on the metal surface is very limited.⁸ It is well-known that the solution wettability on the substrate is affected by the properties of both the solvent and the substrate. We then modulate the GO solution wettability on metals by using mixed solvent of ethanol and water. The relationship between coverage of GOs and ratios of water/ethanol is shown in Figure S5 and Figure S6. Small water/ethanol ratio favors increase of graphene coverage. The coverage can increase from 0 to 60% even for low concentration solution of 0.7 mg/mL. It is worth noting that this simple approach is applicable for many kind of metals such as Au, Ag, Cu, Al, etc.

Patterned graphene is an excellent source–drain electrode for organic field-effect transistors (OFETs) in previous studies.^{10,11} The graphene/metal composite electrodes possess good contact to organic semiconductors. However, the high-temperature processes make real application with them difficult. Here, our graphene patterning technique is a low temperature one and meets the requirement. We fabricated OFETs with a graphene/metal composite electrode by the following procedures (Figure 4a). The SiO_2 substrate was first treated with PFS to form hydrophobic surface. Then the metals are deposited through a shadow mask. The patterned graphene/metal electrodes are then constructed after the spin-coating of GO solutions (1.5 mg/mL, with solvent of water/ethanol = 1:2) and reducing process (0.1 Pa vacuum stage under argon atmosphere at 220 $^\circ\text{C}$ for an hour). Little graphene was deposited in the channel region since the solution CA on the surface is higher than 65° , which is unsuitable for graphene oxide deposition during the spin-coating process (Figure 4b). Finally, the organic layer was deposited. Figure

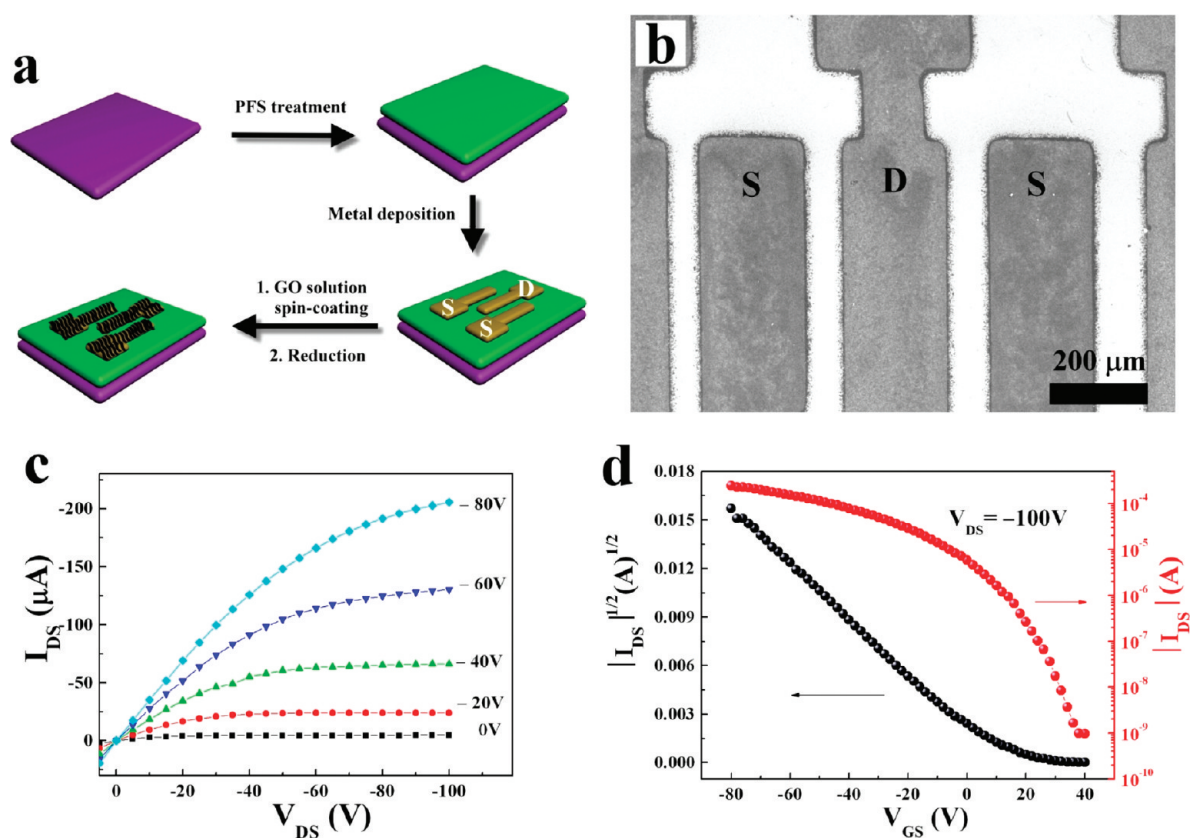


Figure 4. Fabrication processes of modified electrodes and the I – V characteristics of OFETs based on pentacene with Au + RGOs electrodes. (a) Schematic drawing of the electrode fabrication process and (b) the optical image of the Au electrode with deposited GOs. (c) Output characteristics and (d) transfer characteristics of the OFET. “S” represents “source electrode”; “D” represents “drain electrode”; I_{DS} is the drain electrode for collecting current.

4c,d shows the device characteristics of pentacene FETs with composite electrodes. The devices with Au + RGO electrodes show a mobility of 0.3 – 0.45 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is higher than that of a Au electrode with a mobility of 0.04 – 0.06 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Similarly, the pentacene FETs with Al + RGO electrodes show a much higher mobility than Al electrodes. The I – V characteristics of the devices based on Al + RGO electrodes are shown in Figure S7. For comparison, the pentacene FETs were also fabricated with pure RGO electrodes. The mobility is about 0.014 – 0.024 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which may be due to the bad conductivity of RGO electrodes (reduced at 220 °C) (see Figure S8). All of the performance details are shown in Table 1, which proved that the composite electrodes integrated the conductivity of metal and good contact surface of the RGOs to organic semiconductors.

TABLE 1. Pentacene Field Effect Transistors Performances Based on Different Source and Drain Electrodes with PFS Surfaces and Bottom Contact Structure

electrode material	mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	ON/OFF ratio	threshold voltage (V)
Au	0.04 – 0.06	$\sim 10^6$	20 – 26
Au + RGO (220 °C)	0.30 – 0.45	$\sim 10^6$	10 – 15
Al	$(1.2$ – $4.8) \times 10^{-4}$	$\sim 10^4$	-35 to -30
Al + RGO (220 °C)	0.10 – 0.20	$\sim 10^5$	-21 to -15
RGO (220 °C)	0.014 – 0.024	$\sim 10^4$	10 – 16

Polyethylene terephthalate (PET) is a widely applied substrate for flexible electronics. The graphene patterning on PET is thus of vital importance. It is known to all that the PET substrates have a hydrophobic surface. However, wettability modulation was also available to PET surfaces. We realized the GO patterning on PET by UVO treatment as demonstrated above. The patterning picture is shown in Figure S9. Importantly, the deposition of GOs on the PET surface can also be achieved directly by ethanol added in the GO solution and spin-coating (Figure 5). This process decreases energy cost dramatically for flexible conducting graphene films which possess potential application in transparent electrodes and sensors. The reduced process was made by hydrazine hydrate at 150 °C, for 2 h at vacuum stage of 0.1 Pa. The flexible reduced thin film shows resistance of 8×10^4 Ω/\square at 70% permeation of 550 nm. Figure 5d shows electrical properties of I_2 vapor sensors based on RGOs. The conductivity of graphene film increases obviously when the device is stored under I_2 atmosphere.

CONCLUSION

We demonstrated a facile way to pattern RGOs on a variety of substrates by a combination of wettability modulation and low-cost spin-coating process. By virtue of the above strategy, simple UVO treatment was

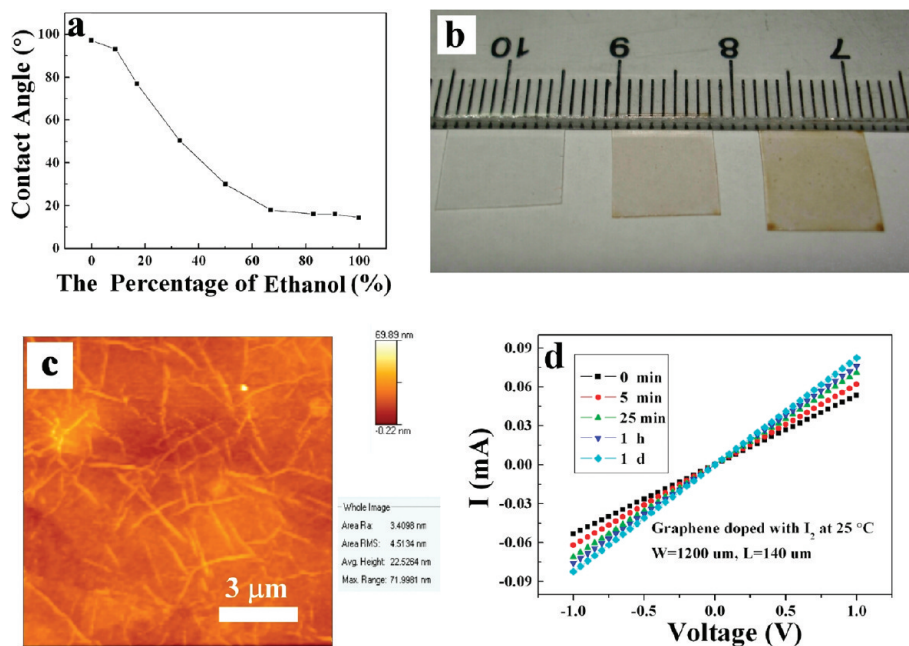


Figure 5. Characterizations of conducting films and sensors. (a) Different ratios of water/ethanol vs contact angle on the PET. (b) Photographs of the GO solution (1:2, 1.5 mg/mL) spin-coated on the PET (left is bare PET, middle is the once spin-coating, right is the three times spin-coating). (c) AFM image. (d) Electrical property of RGO sensors for I_2 vapor.

used to pattern the wettability of the SiO_2 surface and get the patterning of RGOs. Patterning of composite electrodes based on normal metals and RGOs exhibits excellent application in high-performance OFETs.

Flexible-transparent conducting graphene films and sensors on PET were also realized through this method. All of these achievements might boost further development of RGOs toward actual applications.

MATERIALS AND METHODS

Preparing GOs. Graphene oxide was prepared using Hummer's method (1). A mixture of 2 g of graphite (powered flake graphite, Alfa Aesar China) and 1.5 g of $NaNO_3$ was placed in a flask cooled by an ice bath. Then, 100 mL of H_2SO_4 (98%) was added to the mixture and stirred until homogenized. Five grams of $KMnO_4$ was gradually added to the solution over 1 h while stirring. The solution was removed from the ice bath after 1 h and was further stirred for 10 h at 40 °C. Then, the heating was stopped and maintained for 12 h. After that, deionized water was added in the flask over 1 h and continuously stirred. H_2O_2 (30 wt % aqueous solution) was then added to the mixture and stirred for a further 2 h. The product was changed to a brown-colored slurry. The slurry was washed by centrifugation at 9000 rpm/20 min 6–8 times with total of 1 L of HCl (5%). The same process of washing was performed with deionized water until to pH 7. At last, the product was dried in a vacuum oven for 3 days. The different concentration was made by dispersing a certain weight of dry GO product into the deionized water. The GO solution is very stable for several months.

Thermal Reduction. *In vacuum atmosphere:* The patterned GOs were reduced in a furnace backfilled with Ar gas and N_2 gas. At this time, the vacuum is still at about 0.1 Pa.

For the hydrazine hydrate reduction: First, patterned GOs were put into one stage of a two-zone furnace; second, a small glass bottle with 1 mL of hydrazine hydrate was put into the other part of the furnace; third, the furnace was vacuum pumped (about 0.1 Pa); at last, the patterned GO was heated to 150 °C for 2 h.

Devices Fabrication and Characterization. The OFET devices were fabricated with a bottom contact configuration. A heavily doped n-type Si wafer and a 500 nm thick layer of wet oxidized SiO_2 were used as a gate electrode and gate dielectric layer, respectively. The substrates were cleaned in water, deionized water, and ethanol and rinsed in acetone. Then, the substrates were modified by PFS in a vacuum oven (0.1 Pa) at 120 °C. The

source–drain (SD) gold contacts were thermally evaporated through a shadow mask. The pentacene was deposited onto the PFS-treated SiO_2 dielectric layer by high-vacuum evaporation at room temperature. The electrical characteristics of the OFETs were measured with a Keithley 4200 SCS semiconductor parameter analyzer under ambient conditions at room temperature.

Acknowledgment. This work is supported by the National Natural Science Foundation of China (60911130231, 60736004, 20825208, 20973184, 60901050, 20421101), the Major State Basic Research Development Program (2006CB806203, 2006CB932103, 209CB623603), and the Chinese Academy of Sciences.

Supporting Information Available: Additional experimental details and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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