The formation of a carbon nanotube-graphene oxide core-shell structure and its possible applications

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Abstract

A stable aqueous dispersion of hydrophobic single-walled carbon nanotubes (SWCNTs) and amphiphilic graphene oxide (GO) nano-sheets was produced by sonication mixing without assistance of any surfactant. Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, and electrical characterization suggest that SWCNTs are completely wrapped by GO nano-sheets. The spontaneous formation of such a core-shell structure is due to the strong pi-pi stacking interaction between the two materials. The electronic coupling between them is evidenced by time-resolved fluorescence

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measurement. The potential of such a nanocarbon hybrid in optical limiting and supercapacitor applications is discussed.

1. Introduction

Single-walled carbon nanotube (SWCNT) and graphene is one-dimensional and two-dimensional carbon materials, respectively. Owing to their extraordinary electrical, mechanical, physical, and structural properties, both nanocarbon materials have attracted tremendous attention for fundamental research and applications in nanoelectronics [1-5], supercapacitors [6-7], biosensors [8-11], solar cells [12-13], and transparent electrodes [14-16]. SWCNT and graphene share many similar properties, while, on the other hand, differ in other aspects because of the structural difference. Attempts have recently been made to integrate these two novel materials in order to utilize the merits of both [17-22].

The wide-spread applications of carbon nanotubes (CNTs) are largely limited by the fact that they are insoluble in water. Dispersion of CNTs by surfactants or polymers usually compromises nanotube properties. In contrast, graphene oxide (GO, the chemically derived graphene) is an amphiphile with hydrophilic edges and hydrophobic basal plane [23-24]. It has recently been demonstrated that GO can be used as surfactant to disperse CNTs due to its high solubility and adhesion of CNTs onto the flat GO sheets through strong pi-pi stacking interaction [25-27].

Here, we studied the interaction between SWCNTs and GO nano-sheets. In contrast to the relatively large GO sheets (a few μm) used in the previous studies, GO nano-sheets (a few 100 nm) were used in this work. Raman spectroscopy, scanning and transmission electron microscopy, optical and electrical characterizations suggest that GO nano-sheets intimately wrap onto the small SWCNT bundle to form a core-shell structure. Furthermore, the possible applications of such a nanocarbon hybrid for optical limiting and supercapacitor are discussed.

2. Experimental

2.1 Hybridizing SWCNTs and GO nano-sheets

Graphene oxide was synthesised from natural graphite flakes (NGS, Germany) by a modified Hummers method, as described elsewhere [28]. To decrease the size of GO sheets, the obtained GO solution was ultrasonicated for 3 hours in ice bath followed by 30 min centrifugation at 18800g and collection of the supernatant. Subsequently, 0.2 mg SWCNT (HiPCo) was added into 1 ml GO solution (0.5 mg/ml) followed by 2 h ultrasonication in ice bath. After 10 min centrifugation at 2500g and removal of the precipitates, stable SWCNT/GO aqueous dispersion was obtained.

2.2 Characterizations

The UV-vis absorption (UV-2501, Shimadzu), Raman spectroscopy using the laser wavelength of 488 nm (CRM200 confocal Raman spectrometer, WITec), scanning electron microscopy (SEM, Sirion 200, JEOL), transmission electron microscopy (TEM, JEM-2010, JEOL), and atomic force microscopy (AFM, Dimension 3100, Veeco, CA, USA) were used to characterize the samples.

2.3 Fluorescence measurement

Time-resolved fluorescence spectra were excited with 400 nm and 150 fs laser pulses at 1 KHz repetition rate. The emission was collected to an Options Optoscope^{TM} streak camera system which has a temporal resolution of 30 ps in the scanning range. The optical-limiting properties of the SWCNT/GO solution, GO solution, and SWCNT dispersed with sodium dodecyl benzene sulfonate (SDBS) as surfactant, were examined by fluence-dependent transmittance measurements with 532 nm and 7 ns laser pulses at 10 Hz repetition rate. The laser pulses were divided into two parts with a beam splitter. One part was taken as the reference while the other was focused onto the sample with a concave mirror (f = 25 cm). The beam radius at the focus was 35 ± 4 μm. The incident and transmitted pulse energies were simultaneously measured with two energy detectors (Laser Probe RjP-735). The GO and SWCNT aqueous dispersions were measured under the same experimental conditions as references.

2.4 Electrical and electrochemical measurements

GO or SWCNT/GO films were fabricated by spray-coating. Subsequently, GO sheets were chemically reduced to reduced graphene oxides (rGO) by hydrazine vapor at 80 ^{o}C overnight. The electrical properties of SWCNT/rGO, SWCNT and rGO films were characterized in ambient condition using a Keithley semiconductor parameter analyzer (model 4200-SCS). Electrochemical characterizations of SWCNT/rGO, SWCNT, rGO films as supercapacitors were performed in a three-electrode half-cell system in 1M KOH solution (Model 1470E, Solartron).

3. Results and Discussion

Fig. 1a shows a typical AFM image of GO nano-sheets on SiO_2/Si surface. The dimension of the exfoliated GO sheets is about 100 – 400 nm with uniform thickness (~1.0 nm). The thickness appeared to be larger than the single-layer pristine graphene sheet due to the presence of oxygen containing functional groups. This is in agreement with the previously reported values [29]. As GO is an amphiphile with hydrophilic edges to render its solubility and hydrophobic basal plane to interact with CNTs, it can be used to disperse CNTs [30-32]. Smaller GO sheets are more hydrophilic due to increased edge-to-area ratio [30]. Therefore, GO nano-sheets are presumably better dispersing agents. As shown in Fig. 1b, water-insoluble SWCNTs can be stably dispersed by GO nano-sheets. The resulted SWCNT/GO dispersion can remain homogeneous without precipitation for months.

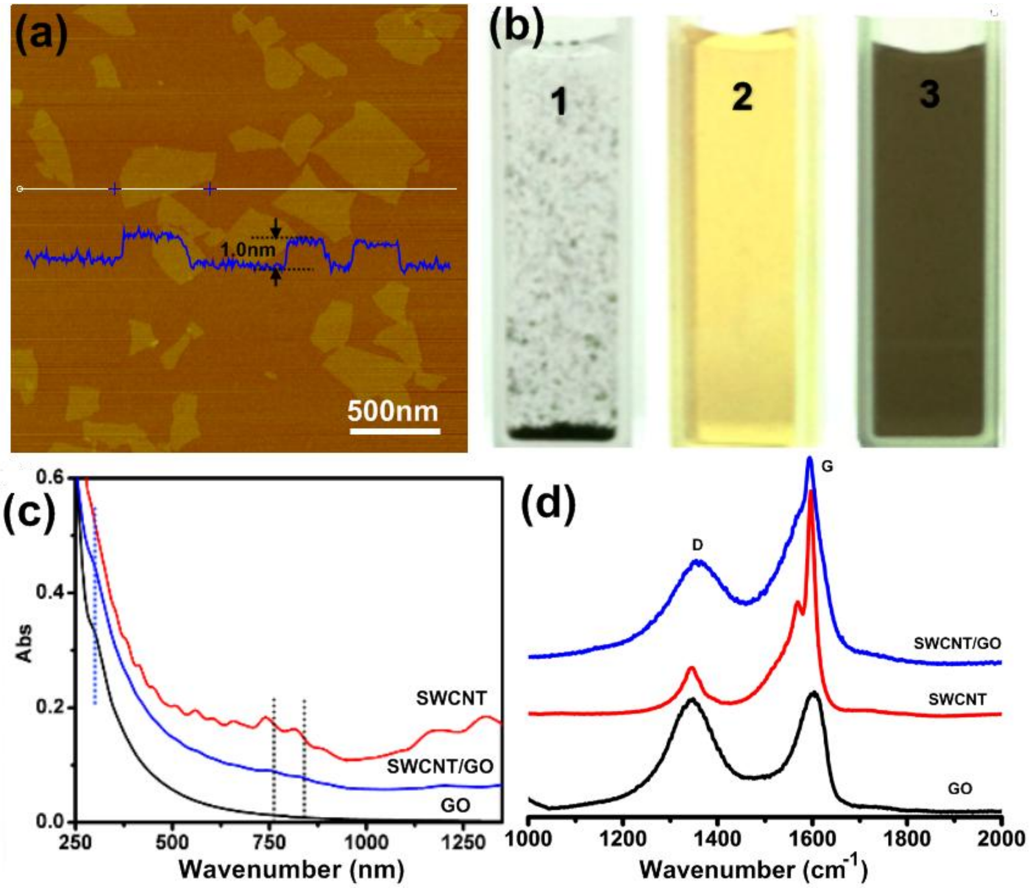

Fig. 1. (a) AFM image of the GO nano-sheets. The height profile (blue trace) across the white line is shown. (b) Photos of SWCNT (1), GO nano-sheets (2) and SWCNT/GO (3) aqueous solution. The photo of SWCNT/GO dispersion was taken three days after the preparation. (c) UV-vis spectra of SWCNT (dispersed by SDBS), GO and SWCNT/GO solutions. (d) Raman spectra of SWCNT, GO and SWCNT/GO film drop-casted on SiO_2/Si substrate.

UV-vis spectrum of SWCNT/GO aqueous solution (Fig. 1c) exhibits three characteristic peaks around 290, 760, and 835 nm, respectively. The first peak comes from GO [33] while the second and the third are due to SWCNT [34]. As compared to the absorption spectrum of SWCNT, it is noteworthy that some characteristic peaks of SWCNT disappeared and the peaks at 740 and 820 nm had obvious red-shift, due to the intimate interaction between SWCNT and GO. SWCNT, GO nano-sheet, and SWCNT/GO were further characterized by Raman spectroscopy. As demonstrated in Fig. 1d, the Raman spectrum of SWCNT/GO hybrid appears to be superposition of the spectra of GO and SWCNT, except that the G band split in SWCNT spectrum vanishes as a result of SWCNT-GO interaction. The UV-vis and Raman spectroscopy clearly suggest the hybridization between SWCNTs and GO nano-sheets.

To investigate the morphology and structure of SWCNT/GO hybrid, SEM and TEM characterizations were carried out. Heavily entangled SWCNT bundles with diameter about 20-30 nm are observed with SEM (Fig. 2a). Fig. 2b is a SEM image of SWCNT/GO hybrids, which, as compared to SWCNTs, are disentangled and have a larger diameter (~50-80 nm). It is possible that GO nano-sheets have wrapped onto the SWCNT bundle to form a core-shell structure through pi-pi stacking. To verify this, SWCNT/GO hybrids were observed under TEM. As seen from Fig. 2c, in addition to some flat GO nano-sheets, the core-shell structures are evident. Furthermore, under high-resolution TEM (Fig. 2d), the lattice fringes of the graphitic structure of SWCNT bundle can be clearly resolved in the core of the hybrid. The observed coverage on SWCNT bundles is not amorphous carbon resulted from the CNT growth process, as shown in the TEM images of bare single CNT and CNT bundle (Fig. S1 in Supplementary Material).

To confirm that SWCNTs are completely covered by GO nano-sheets, electrical characterizations of the core-shell structures were conducted.

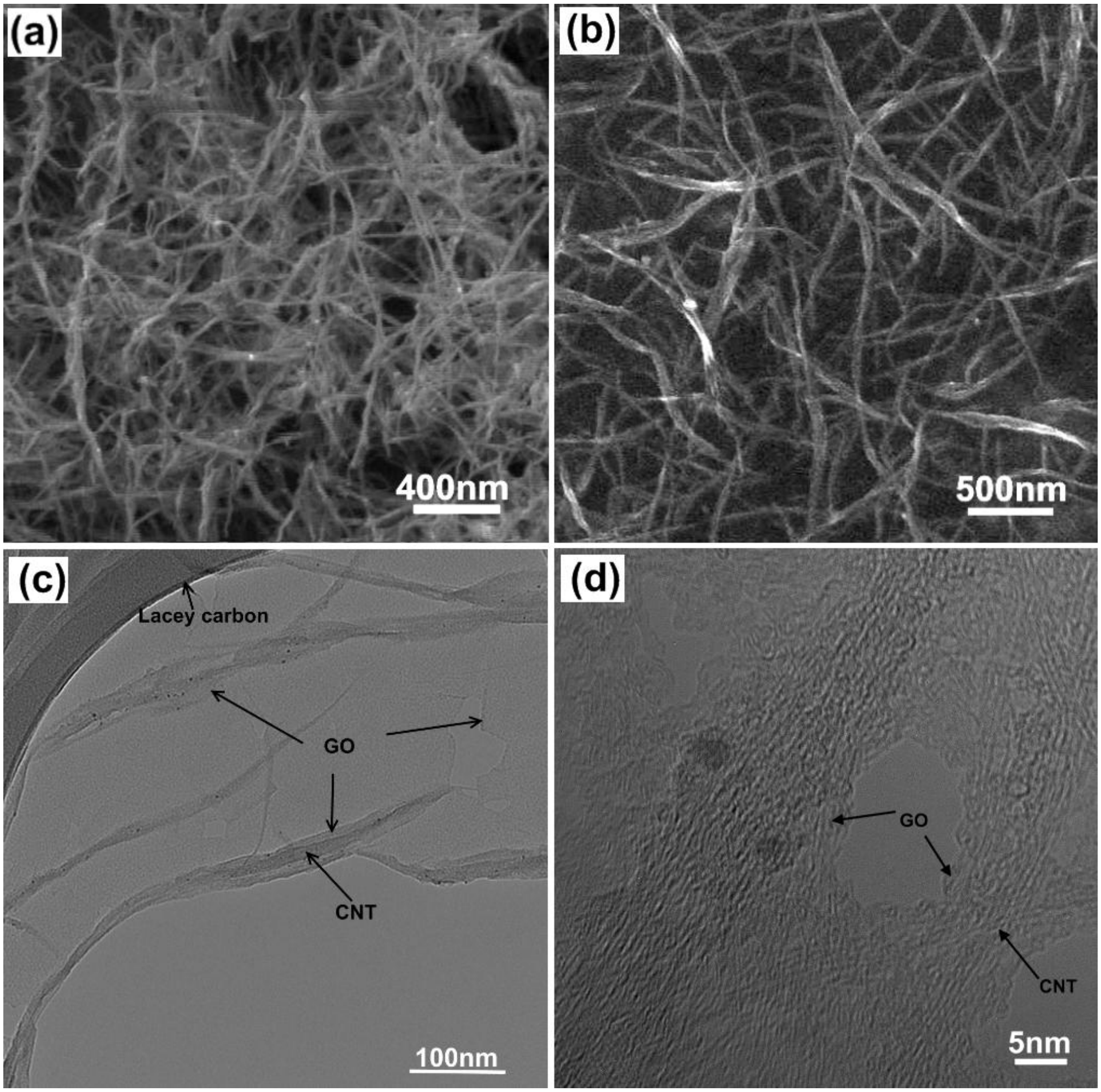

Fig. 2. (a) SEM image of SWCNTs. (b) SEM image of SWCNT/GO. (c) TEM image of SWCNT/GO. (d) High resolution TEM image of SWCNT/GO.

Thin-films of SWCNT/GO were made using spray coating. It was found that the SWCNT/GO thin-films (~80% transmittance at 550 nm) are not conductive. This observation strongly suggests that the highly conductive SWCNTs are completely wrapped by the insulating GO nano-sheets. In support of this notion, we also observed that SWCNT/GO hybrids could not be moved by electrophoresis or dielectrophoresis, indicating again their insulating property. Furthermore, GO nanosheets in the SWCNT/GO film were chemically reduced in-situ to reduced GO (rGO). The resulting SWCNT/rGO thin-films give a sheet resistance of ~6000Ω/sq, which is similar to that of pure rGO thin-films similarly prepared. The electrical properties of SWCNT/rGO thin-films were further examined using liquid-gated field-effect transistor configuration (Fig. 3a). As shown in Fig. 3b, the SWCNT/rGO thin-film manifests the ambipolar field-effect characteristics, with a Dirac point at ~0.4 V and an on-off ratio < 2. This is similar to the characteristics of rGO thin-film made by spray-coating (Fig. 3c) or by microfluidic patterning [35], and also similar to the chemical vapour deposition grown graphene [8, 10] and the mechanically exfoliated graphene [36, 37]. In contrast, the SWCNT thin-film exhibits an obvious p-type characteristics with a much higher on-off ratio (~30-40) (Fig. 3d). All these observations unambiguously suggest that the electrical properties of the nanocarbon hybrid thin-film are essentially dominated by GO or rGO, and that SWCNTs are completely wrapped. But, it should be pointed out that our results are different from the previous reports [26, 27, 30]. These studies showed that CNTs adhere onto (instead of being wrapped by) the flat of GO sheet and the CNT/GO thin-films are still highly conductive (~4000Ω/sq). The discrepancy may be attributable to the difference in the preparation processes and nanotubes used. More likely, our nanosized GO sheets may favour wrapping over adhesion, as compared to the microsized GO sheets used in the previous studies. Consistent with the previous studies, we confirmed that carbon nanotubes adhere to the surface of large GO sheets, instead of being wrapped (Fig. S2 and S3 in Supplementary Material).

Molecular dynamics simulations have demonstrated that graphene sheets can fully self-scroll onto CNTs, forming a stable core-shell structures [38]. Interestingly the authors suggested that *van der* Waals force plays an important role in the formation of core-shell structure, and that large size graphene sheets result in multilayered carbon nanoscroll shells with a tubular structure similar to multi-walled carbon nanotubes (MWCNTs). However, large rGO sheets which bares abundant surface charges is unlikely to scroll into multi-layers, due to electrostatic self-repulsion. A recently study showed that microsized GO can only scroll onto MWCNTs through convalent bond formation between complementarily functionalized MWCNTs and GOs [39]. In contrast, we showed here that GO-nanosheets can spontaneously wrap onto SWCNT bundles. This is probably because that the size of our GO-nanosheets is comparable to the circumference of SWCNT bundles, which ensures sufficient and intimate interaction between the two components to overcome the deformation energy.

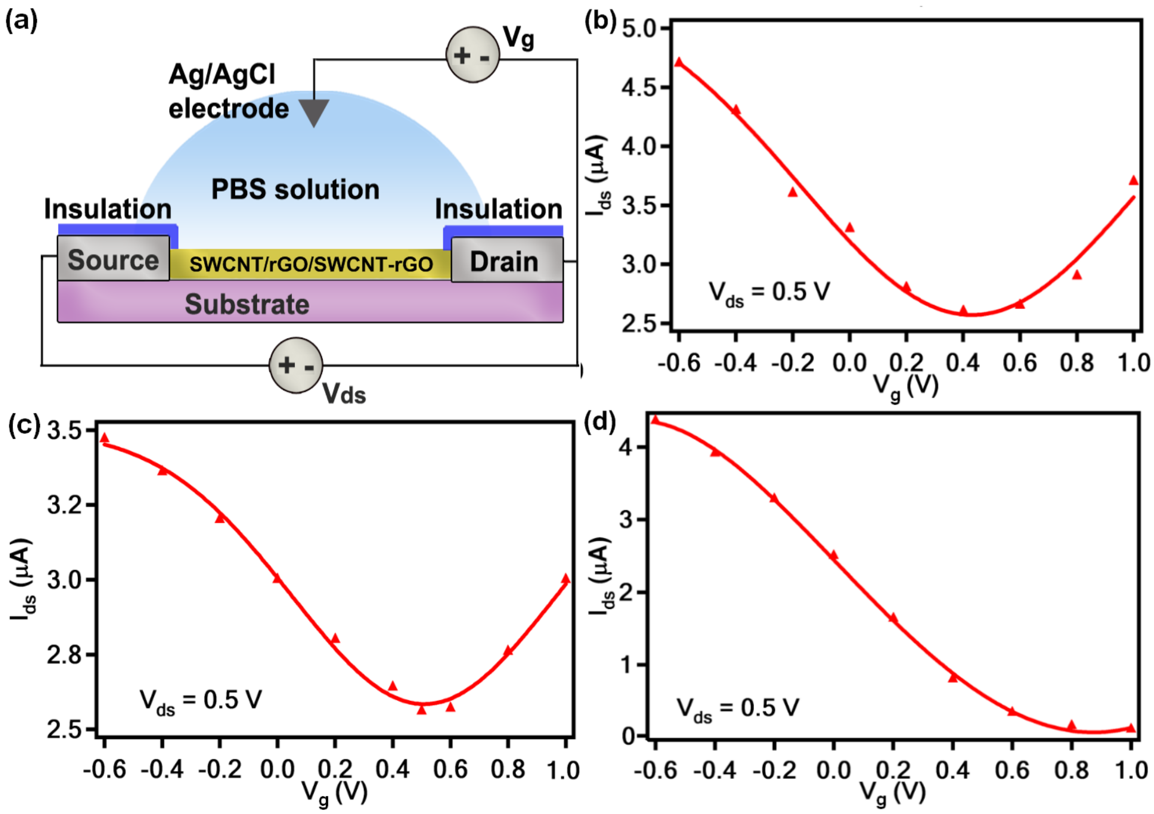

Fig. 3 (a) Schematic drawing of liquid-gated field-effect transistor based on the thin-film of SWCNT, rGO or SWCNT/rGO. An Ag/AgCl electrode was immersed in the phosphate buffer solution (PBS) to apply gate voltage. (b) I_d-V_g curve of SWCNT/rGO film. (c) I_d-V_g curve of rGO film. (d) I_d-V_g curve of SWCNT film.

In order to examine whether the SWCNTs are electronically coupled with the GO nano-sheets instead of mere physical attachment, fluorescence spectra of SWCNT/GO and pure GO nano-sheets in water were measured and compared in Fig. 4a. Both solutions have similar GO weight concentration. Upon photon excitation at 400 nm, the GO nano-sheets exhibit a broad visible light photon emission. This is believed to arise from the radiative recombination of the localized e-h pairs in sp^2 bonded carbon nanoclusters surrounded by oxygenated sp^3 carbon matrix in the GO nano-sheet [40]. However, when the GO nano-sheets are coupled with SWCNTs, the emission from the GO nano-sheets is quenched. Quenching could be due to the re-absorption of the emitted photons from GOs by the nearby SWCNTs or due to an electron and/or energy transfer from GO to SWCNTs because the latter are excellent electron acceptors [41]. To elucidate the mechanism, the time-resolved fluorescence from the samples following a 150 fs laser pulse perturbation (at 400 nm wavelength) was measured (Fig. 4b). The lifetime of the radiative recombination in GO nano-sheets is greatly shortened upon SWCNT hybridization, as indicated by the rapidly decaying fluorescence intensity. This observation confirms the existence of an electron and/or energy transfer, and therefore, an electronic coupling between the two nanocarbon materials. In contrast, the re-absorption of the emitted photons from GO by the SWCNTs in the vicinity would not have given rise to any lifetime shortening. The rate of transfer is in the order of 10 ps because the effective lifetime of the radiative recombination (i.e., the time to decay to 1/e of the maximum) is reduced from 1.2 ns to less than 30 ps by SWCNT, which is comparable to the reported values for the transfer rate between CNT and some semiconducting nanostructures [42]. The fast electron and/or energy transfer between SWCNT and GO nano-sheets holds great promise for potential developments of all carbon based optoelectronic devices. As an illustration, we investigated the possible application of SWCNT/GO hybrid in optical limiting.

Fig. 4c shows that all the samples (SWCNT, GO, and SWCNT/GO) exhibit a reduction in transmittance with increasing input fluence. This is the clear indication of their optical limiting property. The optical limiting performance of SWCNT/GO is apparently better than either that of SWCNT or GO individually. Specifically, the limiting threshold

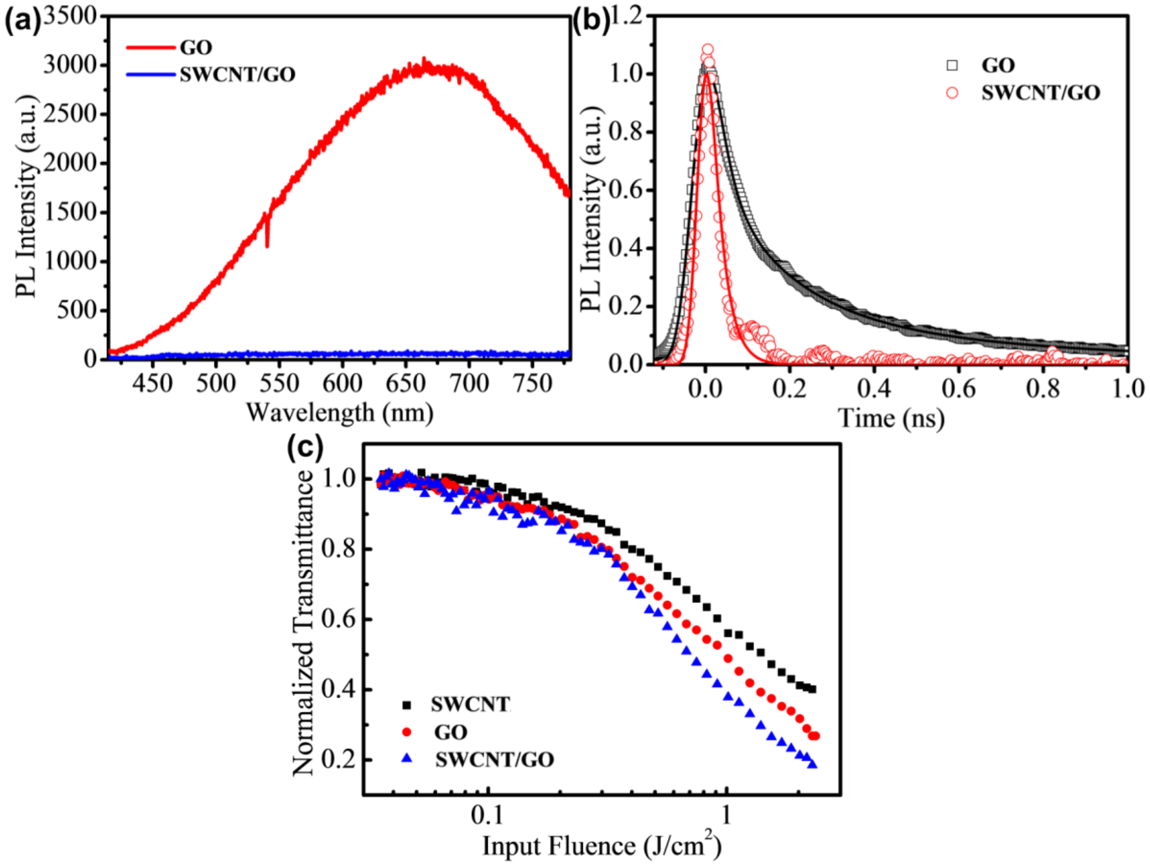

Fig. 4. (a) Fluorescence spectra of GO and SWCNT/GO aqueous dispersions excited at 400 nm. (b) Time-resolved fluorescence decays (± 5 nm around the emission peaks) of the GO nano-sheets and SWCNT/GO hybrids. (c) Optical-limiting responses of SWCNT, GO and SWCNT/GO solutions. SWCNTs were dispersed by SDBS. The linear transmittance of all the samples was adjusted to 75%.

(defined as the incident fluence at which the transmittance falls to 50% of the normalized linear transmittance) of SWCNT/GO was 0.7 J/cm^{-2}, which is superior to that of GO nano-sheet (1.0 J/cm^{-2}) and SWCNT (1.4 J/cm^{-2}). The optical limiting performance of our GO nano-sheets is better than the previously reported value for large GO sheets [43]. In the nanosecond time regime, the main optical-limiting mechanism of SWCNT is nonlinear scattering. In contrast, for GO, both the nonlinear absorption and nonlinear scattering can contribute significantly to the optical limiting performance [43, 44]. The outstanding optical limiting performance of SWCNT/GO is likely due to a consequence of the ultrafast electron and/or energy transfer between the two components upon photon excitation which suppresses dissipation of the absorbed energy through photo emission. In addition, the generation of light-scattering microplasmas may be synergistically facilitated by the ionization of both GO nano-sheets and SWCNTs upon rapid absorption of laser energy.

Both carbon nanotube and graphene have been widely explored for supercapacitance applications [6, 7]. Therefore, we tested the ability of SWCNT/rGO hybrid in this regard. Fig. 5a shows the electrochemical performance of the thin-film electrodes made from SWCNT/rGO, rGO and SWCNT, respectively. The cyclic voltammogram (CV) curves of all the samples display a quasi-rectangular shape at the scan rate of 50 mV/s, indicating excellent charge propagation within these electrodes. It is noteworthy that the current response of SWCNT/rGO is much larger than that of SWCNT and rGO at the same scan rate. It suggests that SWCNT/rGO electrode has a higher specific capacitance. Fig. 5b depicts the charge-discharge curves of SWCNT/rGO, SWCNT, rGO thin-film electrodes at a current density of 0.8 A/g. Based on the galvanostatic discharge curves, the calculated specific capacitances of SWCNT/rGO, rGO, SWCNT films are 194, 155 and 127 F/g, respectively. It is consistent with the CV results. The superior performance demonstrated by SWCNT/rGO may be arisen from its unique core-shell structure and the unusual quantum coupling between the two nanocarbon materials [45]. The underlying mechanism requires further investigation.

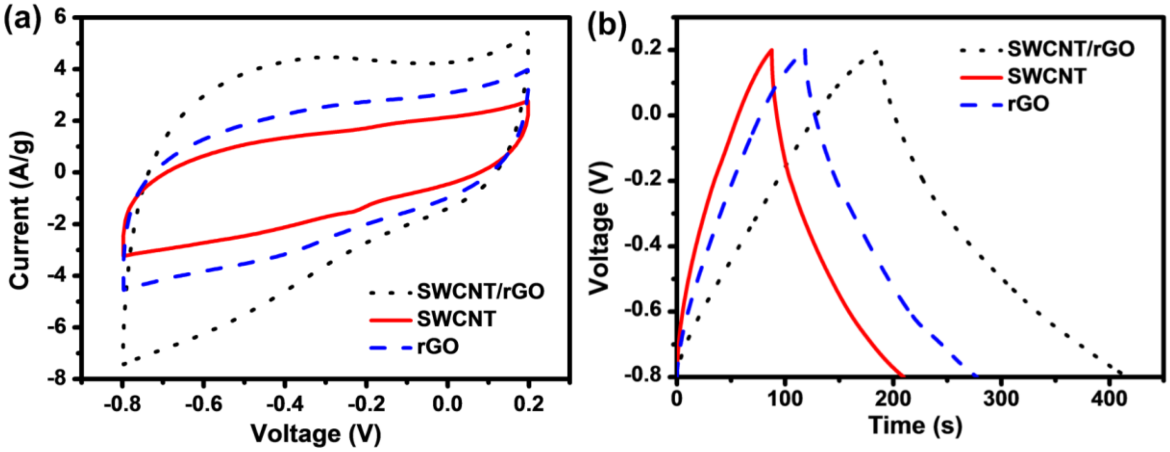

Fig. 5. Cyclic voltammogram curves of SWCNT/rGO, SWCNT and rGO at a scan rate of 50 mV/s in 1M KOH solution. (b) Galvanostatic charge/discharge curves of SWCNT/rGO, SWCNT and rGO in 1M KOH at 0.8 g/A.

4. Conclusions

Stable SWCNT aqueous dispersion has been prepared using GO nano-sheets as surfactant. Raman, UV-vis, SEM, TEM, and electrical characterization indicate that SWCNTs are completely wrapped by GO nano-sheets to form a core-shell structure. This is the first time to experimentally demonstrate the spontaneous formation of SWCNT/GO nanoscrolls and its applications. SWCNT/GO or SWCNT/rGO hybrids exhibit superior performance in optical limiting and supercapacitance as compared to individual components, suggesting their potentials in optoelectronic devices and energy storage. The unique core-shell structure and quantum coupling between the two nanocarbon materials promise many more applications. For example, such core-shell structured nanowires could be useful for nanoelectronics. They may serve as insulated nano-interconnections or building blocks of field-effect nano-transistors where the SWCNT core acts as the active channel and GO shell serves as the ultra-thin dielectric gate.

Acknowledgement

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