Nanoscale

COMMUNICATION

Investigation of charge-transfer complexes formation between photoluminescent graphene oxide and organic molecules

Guoqing Xin,[a] Hongzhe Wang,[a] Namhun Kim,[a] Wontae Hwang,[a] Sung Min Cho[a] and Heeyeop Chae*[ab]

Charge-transfer complexes have formed between photoluminescent graphene oxide and organic electron-donating molecules. With the increase of electron-donating power of molecules, the colour of solutions containing complexes became darker; UV absorption was red-shifted to longer wavelength and a new charge-transfer complex emission was also enhanced.

Graphene, layers of carbon with monoatomic thickness, is a star material with unique electronic structure and fascinating properties.[1,2] As an oxidized derivative of graphene, graphene oxide (GO) contains a large fraction (0.5–0.6) of sp^3 hybridized carbon covalently bonded with oxygen in the form of epoxy and hydroxyl groups.[3] The conducting ordered small sp^2 domains isolated in the sp^3 C–O matrix with a large energy gap make GO an electronically hybrid material.[4–7] The π and π^* electronic levels of the sp^2 clusters lie within the band gap of σ and σ^* states of the sp^3 matrix and are strongly localized.[4–7] Therefore, unlike graphene sheets with zero band gap, GO has a finite electronic band gap.[4–7] GO has been reported to emit a broad PL in the visible and infrared regions, which is contributed to radiative recombination of electron–hole pairs in localized sp^2 domains.[4–7] Highly efficient photoluminescent GO has been applied in cell imaging successfully.[8] Further research is required to promote its application in various fields, such as light-emitting materials and biosensors.

Due to the high electron affinity, carbon materials such as 0D fullerenes, 1D carbon nanotubes (CNTs) and chemically modified 2D graphene are all good electron-withdrawing materials.[9–15] Charge-transfer can take place easily between electron-donating molecules and the above electron-accepting carbon materials.[9–15] When those electron acceptor materials are mixed together with conjugated polymers, a heterojunction will form and dissemble the photoexcited electron–hole pair to generate photocurrent in solar cells.[9–15] Charge-transfer complexes (CTCs) also can easily form between fullerenes and CNTs with small molecules. Photophysical properties of CTCs between various electron-donating molecules and fullerenes in the ground-state and excited-state are well examined by photoluminescence spectra.[16,17] The formation of a CTC between CNTs

and aniline was reported to enhance the quantum yield and solubility of CNTs.[18] Recent studies using Raman spectra suggest that graphene can be doped with electrons by charge-transfer with donor and acceptor molecules, resulting in modified electron and hole concentrations and changed electronic properties.[19–21] Meanwhile, electrons which transferred between the donor molecule (tetrathiafulvalene)/acceptor molecule (tetracyanoethylene) and graphene also gave rise to clear charge-transfer bands on the UV-vis absorption spectra.[20] Prompted by the precious results, we have investigated the formation of CTCs between photoluminescent GO and electron-donating molecules and the effect of the charge-transfer process on the photophysical properties of GO. Various molecules with different electron-donating power were tested and we found that the colour of the CTC containing solution became darker with molecules of increased electron-donating power, as well as longer red-shifted UV absorptions and enhanced CTC-related emissions. The effects of electron-donating molecules on the photophysical properties of GO provide a new possibility for potential applications such as GO-based electronics, biological fluorescence probe and molecular sensor.

GO sheets were prepared efficiently by microwave-irradiated expansion of graphite oxide followed by solution exfoliation. Pristine natural graphite flakes were mixed with concentrated sulfuric acid (98 wt%) and hydrogen peroxide (30 wt%). After washing with deionized (DI) water to neutral pH, the graphite oxide was expanded in a microwave oven at 750 W for 10 s. 5 mg expanded graphite oxide was dispersed in 50 ml DI water and sonicated by a tip sonication instrument at 500 W for 10 h. A well-dispersed GO solution was obtained after centrifugation at 13 000 rpm. To obtain nanoscaled GO, the centrifuged supernatant was filtered through a 0.2 μm microporous membrane. After lyophilization for 2 days, GO powder was obtained. The atomic composition obtained from the X-ray photoelectron spectrum (Fig. 1) shows a C : O ratio of 2.7 : 1, which is little higher than that of GO obtained from conventional methods.[22] As reported, a slight reduction can optimize the PL of GO.[5] A highly efficient PL peaked at 404 nm can be observed from GO when it was dispersed in tetrahydrofuran (THF) (Fig. 2(a)), which can be attributed to the recombination of electron–hole pairs in localized electronic states in GO sheets.[4–7]

However, when aniline was added to the GO/THF solution, the PL intensity of GO decreased immediately. Concurrently, a new PL band can be seen at longer wavelength and the corresponding intensity got higher with increasing aniline concentration, as shown in Fig. 2(a). This is a common phenomenon when charge-transfer

[a]School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon, 440-746, Republic of Korea. E-mail: hchae@skku.edu
[b]SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon, 440-746, Republic of Korea
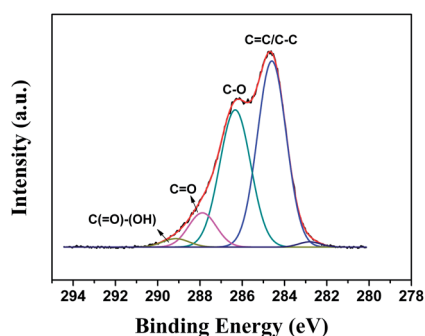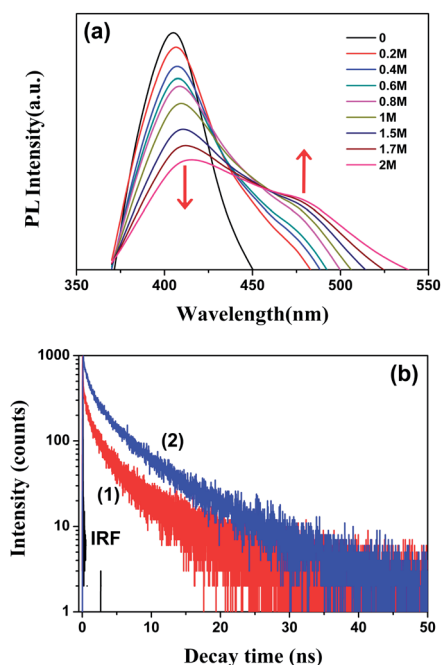
Fig. 1 XPS C 1s spectra of GO.

Fig. 2 (a) Effects of the addition of aniline on the PL spectrum of GO in THF at room temperature. (b) PL decay times measured at (1) 404 nm and (2) 475 nm when the concentration of aniline was 1 M in the GO/THF solution. All samples were excited at 340 nm.

happens among organic molecules.[23] Similar behaviour also has been observed when charge transferred from *N*,*N*-diethylaniline (DEA) to C_{70}.[17] A CTC emission emerged at longer wavelength and its intensity increased with elevated concentration of DEA.[17] The formation of a CTC between CNTs and aniline has been reported to induce a longer wavelength emission as well.[18] Photoluminescent GO in our experiment contains many sp^2 bonds, which has similar structure to that of fullerenes and CNTs. GO and aniline may form a CTC in THF solution since aniline is a fairly good electron donor.[18] With increased concentration of aniline, such charge-transfer processes formed a new pathway for the de-excitation of excitons and this would weaken the original emission. Accordingly, this new luminescence band was attributed to the excited state of the GO/aniline CTC and could be enhanced by the successive addition of aniline. At higher aniline concentrations, the peak of the luminescence band moved to longer wavelengths. This may be due to a solvent polarity effect and/or the formation of higher order complexes.

When the concentration of aniline was 1 M in the GO/THF solution, the time-resolved PL was carried out with a femtosecond pulsed Ti:sapphire laser at an excitation wavelength of 340 nm. Fig. 2 (b) shows the PL decay times at emission wavelengths of 404 nm and 475 nm at room temperature. The decay dynamics of 404 nm emission and 475 nm emission show different characteristics, reflecting the distinctive difference between localized excited electronic states of GO and CTC excited states.[24] The decays can be modelled with the sum of two-exponential functions, as to be expected with two excited species. The PL decay time (τ) and amplitude (A) of emissions are shown in Table 1. The major component associated with 404 nm has a decay time of 0.06 ns with 90.7%. However, 475 nm emission exhibited much longer decay times: 0.749 ns with 66% and 5.68 ns with 34%. The longer decay time for 475 nm emission accorded with the CTC formation in this solution.[24,25]

Encouraged by these results, we examined the effect of various molecules with different electron-donating power on the photophysical properties of GO. As is known, the electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital. The lower ionization potential indicates a stronger electron donating power. Aniline, phenetole, anisole, toluene and THF were used in this work and they have ionization potentials of 7.7 eV, 8.13 eV, 8.22 eV, 8.82 eV and 9.54 eV, respectively. Typically, CTC formation can be determined by the notable colour change and intense absorption at long wavelength.[26] In this case, with decreasing value of ionization potential, the colour of the solution containing the CTC became darker, as shown in Fig. 3. The GO/THF solution remained clear after adding toluene; however, when phenetole and anisole were added to the GO/THF solution, the colour changed to a bright green colour. An orange colour emerged when aniline was added to the GO/THF solution. The change of colour reflects the charge-transfer transition energy ($\Delta E = h\nu_{CT}$) which is determined by the difference between the donor's ionization potential (EI) and the acceptor's electron affinity (EA), adjusted by the dissociation energy of the excited state (J): $h\nu_{CT} = EI - EA + J$.[27,28] If a number of complexes are considered of the same acceptor with different electron donors, ΔE can be assumed to be determined only by the EI of the donors.[27,28] The strong electron-donating molecules with low ionization potential can form CTCs with low transition energy, which can be excited by absorbing low energy photons to show intense colours.[26] Meanwhile, the UV absorption spectra also showed a redshift with the decrease of ionization potential (Fig. 4(a)). Aniline showed the strongest donating power and the aniline–GO CTC broad absorption spectrum extended up to 760 nm. Absorptions of the phenetole–GO CTC and anisole–GO CTC shifted to 550 nm and 520 nm, while that of the toluene–GO CTC only shifted a little due to the low donating power of toluene.

By adding different electron donating molecules, the CTC-caused emission bands emerged at longer wavelength with different intensity. In Fig. 4(b), the CTC peaks have been separated by dashed lines.

Table 1 The PL decay time (τ_i) and amplitude (A_i) of 404 nm and 475 nm emissions

Emission	Amplitude A_1	Decay time τ_1/ns	Amplitude A_2	Decay time τ_2/ns
404 nm	0.907	0.06	0.093	2.51
475 nm	0.66	0.749	0.34	5.68

Fig. 3 Image of the GO/THF solution with 1 M external molecules: toluene, phenetole, anisole and aniline. Pure phenetole, anisole and aniline also shown to compare the colour change.
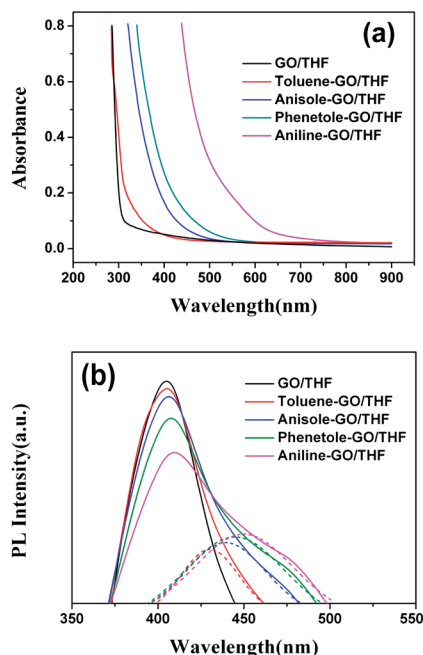

Fig. 4 (a) UV-vis absorption of GO in THF with various interacting molecules. (b) PL spectra (solid line) of GO in THF with various interacting molecules. Dashed lines represent the separated CTC emissions. All samples were excited at 340 nm.

Compared with UV absorption, CTC related emissions were enhanced and shifted to longer wavelengths with the increase of electron-donating power of molecules. It can be deduced that the charge-transfer interaction between GO and organic molecules becomes stronger and the equilibrium constant of CTCs becomes higher with the increase of electron-donating power of interacting organic molecules, which means the formation of higher concentration of CTCs.

Conclusions

In summary, well-resolved PL spectra of GO–aniline in THF have confirmed the CTC formation. The increase of aniline decreased the PL emitted from GO and enhances CTC-related emission. Meanwhile, the decay time for CTC emission has been found to be much longer than the localized electronic state emission of GO. Photophysical properties of CTCs between various electron-donating

molecules have been determined. With the increase of electron-donating power of molecules, the colours of solutions containing CTCs become darker; UV absorption is red-shifted to longer wavelength and CTC related emission is enhanced.

Acknowledgements

Notes and references

1 C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem., Int. Ed.*, 2009, **48**, 7752–7777.
2 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
3 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228–240.
4 K. P. Loh, Q. Bao, G. Eda and M. Chhowalla, *Nat. Chem.*, 2010, **2**, 1015–1024.
5 G. Eda, Y.-Y. Lin, C. Mattevi, H. Yamaguchi, H.-A. Chen, I. S. Chen, C.-W. Chen and M. Chhowalla, *Adv. Mater.*, 2010, **22**, 505–509.
6 T. Gokus, R. R. Nair, A. Bonetti, M. Böhmler, A. Lombardo, K. S. Novoselov, A. K. Geim, A. C. Ferrari and A. Hartschuh, *ACS Nano*, 2009, **3**, 3963–3968.
7 Q. Mei, K. Zhang, G. Guan, B. Liu, S. Wang and Z. Zhang, *Chem. Commun.*, 2010, **46**, 7319–7321.
8 X. Sun, Z. Liu, K. Welsher, J. Robinson, A. Goodwin, S. Zaric and H. Dai, *Nano Res.*, 2008, **1**, 203–212.
9 Z. Liu, Q. Liu, Y. Huang, Y. Ma, S. Yin, X. Zhang, W. Sun and Y. Chen, *Adv. Mater.*, 2008, **20**, 3924–3930.
10 Q. Liu, Z. Liu, X. Zhang, L. Yang, N. Zhang, G. Pan, S. Yin, Y. Chen and J. Wei, *Adv. Funct. Mater.*, 2009, **19**, 894–904.
11 V. Gupta, N. Chaudhary, R. Srivastava, G. D. Sharma, R. Bhardwaj and S. Chand, *J. Am. Chem. Soc.*, 2011, **133**, 9960–9963.
12 H. Ago, K. Petritsch, M. S. P. Shaffer, A. H. Windle and R. H. Friend, *Adv. Mater.*, 1999, **11**, 1281–1285.
13 R. A. Marsh, J. M. Hodgkiss, S. Albert-Seifried and R. H. Friend, *Nano Lett.*, 2010, **10**, 923–930.
14 J. Geng and T. Zeng, *J. Am. Chem. Soc.*, 2006, **128**, 16827–16833.
15 C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia and S. P. Williams, *Adv. Mater.*, 2010, **22**, 3839–3856.
16 J. W. Arbogast, C. S. Foote and M. Kao, *J. Am. Chem. Soc.*, 1992, **114**, 2277–2279.
17 Y. Wang, *J. Phys. Chem.*, 1992, **96**, 764–767.
18 Y. Sun, S. R. Wilson and D. I. Schuster, *J. Am. Chem. Soc.*, 2001, **123**, 5348–5349.
19 B. Das, R. Voggu, C. S. Rout and C. N. R. Rao, *Chem. Commun.*, 2008, 5155–5157.
20 R. Voggu, B. Das, C. S. Rout and C. N. R. Rao, *J. Phys.: Condens. Matter*, 2008, **20**, 472204.
21 N. Jung, N. Kim, S. Jockusch, N. J. Turro, P. Kim and L. Brus, *Nano Lett.*, 2009, **9**, 4133–4137.
22 V. C. Tung, M. J. Allen, Y. Yang and R. B. Kaner, *Nat. Nanotechnol.*, 2009, **4**, 25–29.
23 J. Wolleben and A. C. Testa, *J. Phys. Chem.*, 1975, **79**, 1137–1138.
24 J. A. Osaheni and S. A. Jenekhe, *Macromolecules*, 1994, **27**, 739–742.
25 W. E. B. Shepherd, A. D. Platt, M. J. Kendrick, M. A. Loth, J. E. Anthony and O. Ostroverkhova, *J. Phys. Chem. Lett.*, 2011, **2**, 362–366.
26 P. J. Atkins and D. F. Shriver, *Inorganic Chemistry*, W.H. Freeman and Company, New York, United States, 3rd edn, 1999.
27 D. Simov, L. Kamenov and S. Stoyanov, *Chem. Heterocycl. Compd.*, 1973, **9**, 458–461.
28 H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, 1953, **21**, 66–70.