Accepted Manuscript

Graphene oxide covalently functionalized with zinc phthalocyanine for broadband optical limiting

Jinhui Zhu, Yongxi Li, Yu Chen, Jun Wang, Bin Zhang, Jinjuan Zhang, Werner J. Blau

PII: S0008-6223(11)00030-3
DOI: 10.1016/j.carbon.2011.01.014
Reference: CARBON 6330

To appear in: *Carbon*

Received Date: 26 September 2010
Accepted Date: 7 January 2011

Please cite this article as: Zhu, J., Li, Y., Chen, Y., Wang, J., Zhang, B., Zhang, J., Blau, W.J., Graphene oxide covalently functionalized with zinc phthalocyanine for broadband optical limiting, *Carbon* (2011), doi: 10.1016/j.carbon.2011.01.014

Revised version-CARBON-D-10-02398

Graphene oxide covalently functionalized with zinc phthalocyanine for broadband optical limiting

Jinhui Zhu[a],Yongxi Li[a], Yu Chen*[a], Jun Wang[b]*, Bin Zhang[a], Jinjuan Zhang[a], Werner J. Blau[b]

[a] *Key Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.*

[b]*Materials Ireland Polymer Research,School of Physics and the Centre for Research on Adaptative Nanostructures and Nanodevices(CRANN),Trinity College Dublin, Dublin 2, Ireland.*

Abstract

A soluble graphene oxide (GO) covalently functionalized with zinc phthalocyanine (PcZn), GO-PcZn, was synthesized by an amidation reaction. The formation of an amido bond between PcZn and GO has been confirmed by x-ray photoelectron and Fourier transform infrared spectroscopy. At the same level of linear extinction coefficient, GO-PcZn exhibited much larger nonlinear optcial extinction coefficients and broadband optical limiting performance than GO at both 532 and 1064 nm, indicating a remarkable accumulation effect as a result of the covalent link between GO and PcZn.

---

1. Introduction

All kinds of light sources interfere with electro-optical sensors and the eye. A laser beam generally possesses much higher intensity (the focused laser intensity is 350 times greater than sun) and can therefore damage the retina before the blink reflex is activated. For this reason, significant research effort has been invested into optical limiting (OL) materials and

*Corresponding author. Fax: +86-21-64252485;
E-mail addresses: chentangyu@yahoo.com(Chen), jwangsci@gmail.com (Wang)

processes in an attempt to achieve some measure of protection from such laser beams.[1-5] A successful optical limiter should strongly attenuate intense, potentially dangerous laser beams, while exhibiting high transmittance for low intensity ambient light. However, the preparation of the nonlinear and optically active materials required for such practical applications still represents a significant challenge so far.

Graphene discovered most recently has attracted considerable interest owing to their long-range π-conjugation yielding extraordinary thermal, mechanical, and electrical properties.[6-14] The ultrafast carrier dynamics and large absorption of incident light per layer make graphene a fast saturable absorber over a wide spectral range.[15] We observed a significant nonlinear optical (NLO) response of graphene dispersions to nanosecond laser pulses at 532 and 1064 nm, implying a potential broadband OL application.[16] NLS arising from the formations of solvent bubbles and microplasmas is the principle mechanism for OL. The surface tension of solvents has strong influence on the OL performance of graphene dispersions. We also observed the NLO and OL properties of graphene families, including graphene oxide (GO) nanosheets, graphene nanosheets (GNSs), GO nanoribbons (GONRS), and graphene nanoribbins (GNRs) at 532 and 1064 nm.[17] GNSs, GONRs, and GNRs exhibited broadband NLO and OL properties. Reduced graphene samples displayed stronger NLO and OL responses than their GO precursors because of their increased crystallinity and conjugation. Nonlinear scattering (NLS) and two-photon or multiphoton absorption (TPA) were found to have strong effects on the NLO and OL responses of the graphene nanostructures. The implantation and growth of metal nanoparticles on GNS led directly to severe damage to the regular structure of the graphene sheets, which disrupts the extended π

conjugation, resulting in an impaired device performance. To address this problem, we developed an easy approach for achieving the lossless formation of graphene composite decorated with tiny cadmium sulfide quantum dots (QDs) with excellent nonlinear optical properties by using benzyl mercaptan as the interlinker.[18] Using this strategy, CdS QDs with an average diameter of 3 nm are uniformly dispersed over the surface of graphene, and the resulting QD–graphene hybrid material exhibits excellent optical limiting properties, mainly contributed by NLS and nonlinear absorption (NLA), upon both 532 and 1064 nm excitations, in the nanosecond laser pulse regime.

It has long been recognized that to protect against both pulsed and continuous wave (CW) or quasi-CW lasers simultaneously with one material is problematic. It would thus be very interesting to combine together the outstanding properties of the graphenes and Pcs to form new broadband OL chromophores. Among the nonlinear optical applications of phthalocyanines (Pcs) with extensive two-dimensional 18 π-electron system, optical limiting has emerged as a particularly promising one due to strong excited-state absorption, high triplet yields, and long excited-state lifetimes. The nonlinear optical absorption mechanism of Pcs in the optical region comprised between Q- and B-bands involves the population of excited states which absorb more effectively than the ground state. This gives rise to the phenomenon of Reverse Saturable Absorption (RSA) as a consequence of multiphoton absorption.[1,5] As phthalocyanine analogues, the structurally similar and biologically important porphyrins are also effective optical limiters. In contrast to porphyrins, like hemoglobin, chlorophyll and vitamin B_{12}, however, phthalocyanines (Pcs) do not occur in nature. Xu et al reported the synthesis and OL properties of a graphene hybrid material

covalently functionalized with metal-free porphyrin.[19] In their work they only simply described the open-aperture Z-scan results measured at 532 nm. They did not give the data concerning the NLO coefficients (including nonlinear extinction coefficient and the imaginary third-order susceptibility), or show the open-aperture Z-scan figures with scattered signal observed at both 532 and 1064 nm.

In this study, we designed and synthesized a new soluble graphene oxide covalently functionalized with unsymmetrically substituted zinc phthalocyanine (GO-PcZn, **Figure 1**) via an amidation reaction that was widely used to prepare GO- and carbon nanotubes-based functional materials. As a result, at the same level of linear extinction coefficient, GO-PcZn exhibited much larger NLO extinction coefficients than GO at both 532 and 1064 nm, indicating a remarkable accumulation effect via the covalently link of GO and PcZn.

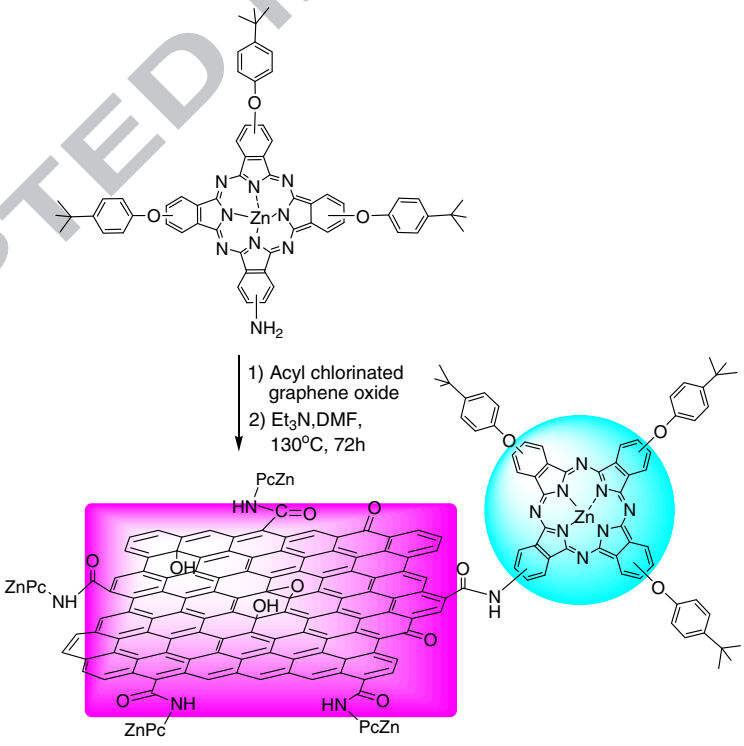


Figure 1. Synthesis of GO-PcZn.

2. Experimental

2.1 Materials and Methods: All chemicals were purchased from Aldrich and used without further purification. Organic solvents were purified, dried and distilled under dry nitrogen. Purified natural graphite was purchased from Shanghai Yifan's Graphite CO. Ltd. The tri(*p-tert*-butylphenoxyl)aminophthalocyanine zinc (PcZn-NH_2) was synthesized according to a method reported by Kudrevich et al.[20] In a typical reaction, a mixed condensation of the 4-*tert*-butylphenoxyl phthalonitrile (3 equiv) and 4-nitrophthalonitrile (1 equiv) in the presence of $Zn(OAc)_2$ at 190^0C give a mixture of mono- through to *tetra*-nitrophthalocyanine derivatives which were further treated with $Na_2S.9H_2O$ in DMF at 65^0C to yield a mixture of mono- and poly-aminophthalocyanines. In contrast to the nitrophthalocyanines, the more polar amino derivatives could be easily separated on a silica gel column, and gave the pure PcZn-NH_2.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. The ultraviolet /visible (UV/Vis) absorption spectral measurements were carried out with a Shimadzu UV-2450 spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluoro-photometer equipped with a photomultiplier tube having high sensitivity in the 700 - 800 nm region. The sample for the fluorescence measurement was dissolved in dry toluene, filtered, transferred to a long quartz cell, and then capped and bubbled with high pure argon(without O_2 and moisture) for at least 15 minutes before measurement. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Thermo ESCALAB 250 spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of

100ms and a pass energy of 20 eV. Raman spectra were taken at room temperature with a MicroRaman System RM3000 spectrometer and an argon ion laser operating at a wavelength of 514.5 nm as the excitation source.

The NLO and OL properties of the samples were investigated using open aperture Z-scan, which is widely adopted to investigate third-order NLO processes, including nonlinear absorption, scattering and refraction. This measures the total transmittance through the sample as a function of incident laser intensity, while the sample is gradually moved through the focus of a lens (along the z-axis). Effective extinction (absorption and/or scattering) coefficients are calculated by the theory reported previously.[21] The normalized transmittance as a function of position z, $T_{Norm}(z)$, is given by $T_{Norm}(z)=Log[1+ q_0(z)]/q_0(z)$, where $q_0(z)=q_{00}/[1+(z/z_0)^2]$, z_0 is the diffraction length of the beam. $q_{00}=\beta_{eff}I_0L_{eff}$. β_{eff} is the effective intensity-dependent nonlinear extinction (NLE) coefficient and I_0 is the intensity of the light at focus. L_{eff} is known as the effective length of the sample defined in terms of the linear absorption coefficient, α_0, and the true optical path length through the sample, L, $L_{eff}=[1-exp(-\alpha_0 L)]/\alpha_0$.

In this work, the Z-scan was carried out by employing a Q-switched Nd:YAG laser of 6 ns pulses, operated at the fundamental 1064 nm and its second harmonic, 532 nm, with a repetition rate of 10 Hz. The laser beam was tightly focused with a 9 cm focus lens, after spatially removing higher-order modes. Meanwhile, another focusing lens was setup at ~35^o to the direct incident beam to monitor the scattered light from the dispersions. All samples were examined in 0.1 cm quartz cells.

2.2 Preparation of Graphene oxide (GO): Twelve grams of graphite were suspended in 500

mL of concentrated H_2SO_4 in a 1 L round-bottom flask under vigorous stirring. Six grams of $KMnO_4$ was then added gradually with stirring and cooling so that the temperature was maintained below 10 °C. The stirring was then continued for 2 h at 35 °C, followed by the addition of 300 mL of de-ionized water and stirring for another 15 min. Finally the content of the flask was poured into 1 L of de-ionized water and a sufficient amount of H_2O_2 (50 mL of a 30% aqueous solution) was added to destroy the excess permanganate. Graphene oxide was isolated by centrifugation or filtration through a sintered glass filter, washed with dilute HCl until no sulfates were detected, and then dried for 10 days over P_2O_5 in a vacuum oven before use. 21 g of purified GO was obtained.

2.3 Preparation of GO-COCl: The COOH-containing GO (500 mg) were reacted with a large excess of $SOCl_2$ containing a catalytic amount of *N*,*N*′-dimethylformamide (DMF) under reflux for 24h. The residual thionyl chloride and solvent were removed by distillation.

2.4 Preparation of GO-PcZn: To a suspension of GO-COCl (50mg) in anhydrous DMF (70 mL) was added to PcZn (60mg) and Et_3N (15 mL) under purified nitrogen. The reaction mixture was sonicated 1h at 40 °C first and then refluxed at 130°C for 3 days. It should be noted that light must be strictly excluded during this step in order to avoid possible photodegradation of phthalocyanine. After cooling to room temperature and removing the solvents by centrifugation, a large amount of water was added to the solid residue to remove the triethylammonium salts formed during the reaction. A total of 200 mL of tetrahydrofuran (THF) was then added to the above reaction mixture under stirring. The obtained blue-green solution was vacuum-filtered through a single layer Nylon film (φ0.22 μm) until the filtrate became colorless. The black solid on the Nylon film was collected and then was

well-dispersed in THF under the ultrasofnic irradiation (40kHz), followed by filtering through a five-layer filter paper (this procedure was repeated at least five times until the filtration became colorless). The crude product collected after evaporation of the solvent was subjected to recrystallization from a mixture of CH_2Cl_2/MeOH (v/v 1:1) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40-60 °C under slightly reduced pressure. The resultant product, a bluish-black solid, was collected by filtration, washed twice with methanol, and dried at 60 °C in vacuo for 10 h. Yield: 62 mg.

3. Results and Discussion

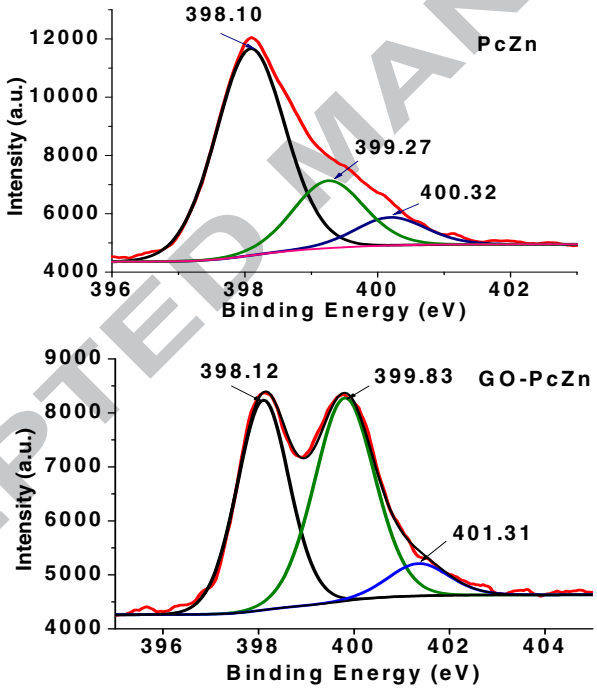


Figure 2. The N1s XPS spectra of the samples.

A knowledge of GO's chemistry provides valuable insight into its reactivity and ultimately its properties, as well as those of graphenes that are derived therefrom.[22-24] A wide range of reactions utilizing the carboxylic and/or hydroxyl functional groups of GO have

been developed. The condensation of PcZn-NH_2 and GO-COCl give a bluish-black GO-PcZn hybrid material. As shown in **Figure 2**, the XPS spectrum provides essential and useful information for the covalent attachment of the PcZn moieties onto the surface of GO. The N1s XPS spectrum of PcZn clearly indicated that the peaks of nitrogen functionalities appeared at 398.12(the N in C-N bonds), 399.27(the N in -NH_2) and 400.32 eV (the N in C=N bonds). In contrast to PcZn, peripherally grafting of GO onto the macrocycle of PcZn led to a red-shift of 0.56 eV and a considerable intensity enhancement of the peak at 399.27eV due to the electron-withdrawing effect of GO.

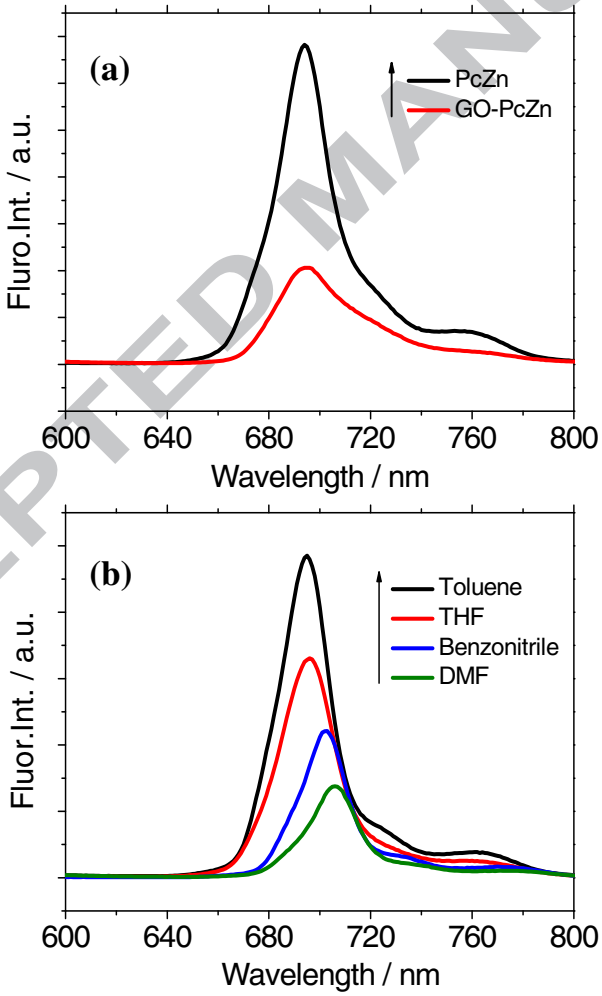


Figure 3. (a) Photoluminescence spectra of GO-PcZn and PcZn in toluene, and (b) Photoluminescence spectra of GO-PcZn in different solvents. λ_{ex}=400 nm.

The electronic absorption spectra of phthalocyanines are characterized by an intense Q-band in the red end of the visible spectrum of light between 600-700 nm, and a B-band at 300-400 nm in the blue end of the visible spectrum. The Q-band of GO-PcZn are slightly shifted to the red when compared to that of PcZn in toluene. Given that the studied GO-PcZn contains electron donor (PcZn) and acceptor (GO) units, we started to study the photoinduced intramolecular events by measuring the steady-state fluorescence spectra with λ = 400 nm excitation light. From **Figure 3a**, it can be clearly seen that the emission spectrum of the GO-PcZn in toluene shows a maxmum emission band at 695 nm, followed by the significant decrease of the fluorescence intensity. With increasing the polarity of the organic solvents, the emission band of the GO-PcZn exhibited red-shifted, 696 nm (THF), 702 nm (benzonitrile) and 707 nm (DMF) (Figure 3b). The finding that the fluorescence intensity decreased with increasing the solvent polarity suggests that the quenching process is likely due to the electron transfer process from the PcZn to the ^{1}GO*.

The main characteristic absorption bands in the IR spectrum of GO are located at 1731($\nu_{C=O}$), 1412(δ_{O-H}), 1226(ν_{C-OH}) and 1053 (ν_{C-O}) cm^{-1}. After grafting of PcZn moieties onto the graphene, the bands at 1731 cm^{-1} disappeared, followed by the appearance of new band at 1658 cm^{-1} ($\nu_{NH-C=O}$). This result further confirmed the formation of an amido-bond between PcZn and GO. As shown in **Figure 4**, there are two prominent bands at about 1363 (D-band) and 1608 (G-band) cm^{-1} in the Raman spectrum of GO (514.5 nm excitation). In contrast to GO, both the D- and G-bands of GO-PcZn, which appear at 1355 and 1593 cm^{-1}, respectively, are found to be slightly shifted to the lower wavenumbers. The new band at 1514 cm^{-1} is assigned to pyrrol C=C stretching mode of PcZn. The D- to G-band intensity ratios

(I_D/I_G) increased from 0.79 for Go to 0.90 for GO-PcZn.

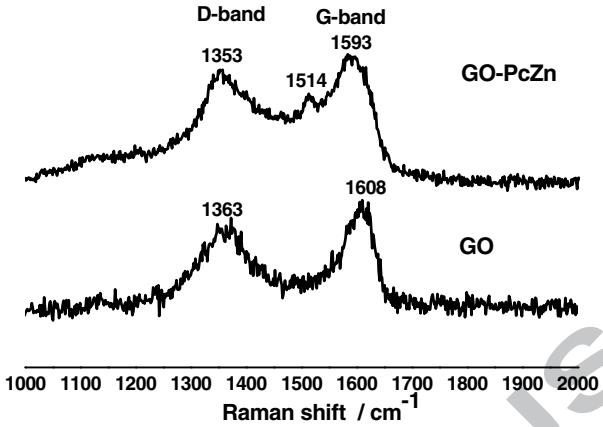


Figure 4. Raman spectra of GO-Pc and Graphene.

To test the NLO response, the GO-PcZn and GO compounds were dispersed in DMF at a concentration of 1.0 g/L, followed by 30 min ultrasonic processing. Both of the compounds exhibit very good dispersibility in DMF. The GO dispersions have a deep gray color, while the GO-PcZn dispersions possess a gray-green color, implying the existence of the Pc moieties. **Figure 5** shows the typical open-aperture Z-scan results for the GO and GO-PcZn dispersions. All *Z*-scans performed in this work exhibited a reduction in the transmission and a scattering accompanying on the focus of the lens, indicating a prominent broadband OL response. In contrast to the graphene dispersions, in which the thermally induced NLS dominates the OL for ns pulses at 532 and 1064 nm,[16] the GO dispersions possess OL for ns pulses at 532 nm due to a combination of TPA and NLS.[17] We argue that the NLS should play a major role in this case since the TPA is much more pronounced for ps pulses than ns pulses.[25] For the ns pulses at 1064 nm, the NLS dominates the OL of the GO dispersions similar as that of the pristine graphene dispersions. Compared with the zero-bandgap

graphene, there is a finite bandgap in GO, which depends on the functionalization by oxygen and hydroxyl groups.[26] Thus, we cannot rule out the possibility of nonlinear absorptions such as, multi-photon-absorption and/or excited state absorption of the GO at 1064 nm, but the contribution of the nonlinear absorptions to the OL should be minor in comparison with the NLS.

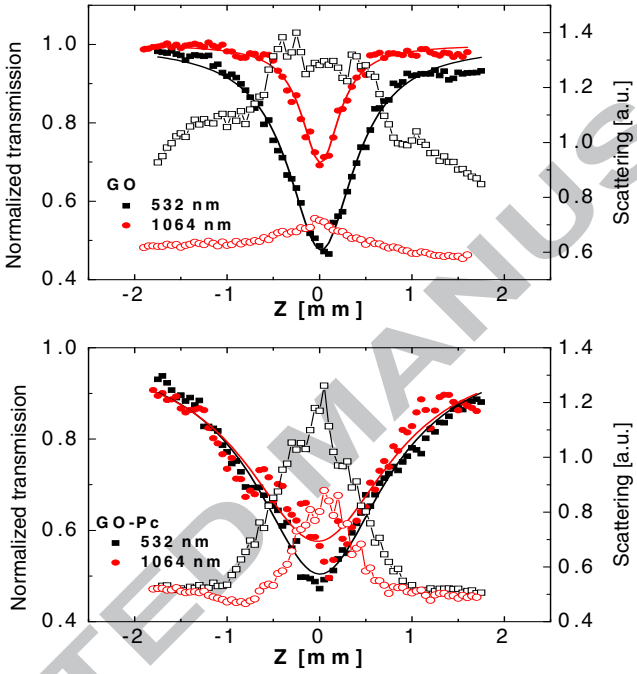


Figure 5. Open-aperture Z-scan results with normalized transmission (solid symbols) and scattered signal (open symbols) for the GO and GO-PcZn dispersions.

Compared with the GO dispersions, the Z-scans of the GO-PcZn dispersions have much broader reduction in transmission at the same level of incident fluence, implying a stronger NLO response. In addition to the contribution of GO moiety, the PcZn manifests its contribution in the enhanced NLO response at 532 nm due to RSA. At the same level of linear extinction coefficient (**Table 1**), the GO-PcZn exhibit much larger NLO extinction coefficients than the GO and PcZn at both 532 and 1064 nm, indicating a remarkable accumulation effect as a result of the covalent link between GO and PcZn.

Table 1. Linear and NLO coefficients of GO and GO-PcZn dispersions and PcZn solutions in DMF at a concentration of 1.0 g/L. α_0: linear extinction coefficients; βeff: nonlinear extinction coefficient; Im{χ(3)}:the imaginary third-order susceptibility.

Sample	λ [nm]	T [%]	α_0 [cm^{-1}]	β_{eff} [cm GW^{-1}]	Im $\{\chi^{(3)}\}$ [$x10^{-12}$, esu]
GO-PcZn	532	53.3	6.28	51.16±11.71	17.62±4.03
	1064	50.5	6.83	31.04±6.28	21.39±4.33
GO	532	51.9	6.55	30.22±2.78	10.41±0.96
	1064	59.9	5.13	6.19±0.99	4.27±0.68
PcZn	532	53.6	6.24	31.07±2.91	10.70±1.00

Figure 6, in which the normalized transmission and the corresponding scattering were plotted as functions of input energy density (J cm^{-2}), presents the OL behavior of the GO-PcZn, GO and PcZn. It can be clearly seen that at the same level of linear transmission, GO-PcZn dispersions present much better OL performance than both GO and PcZn. The enhanced OL response at 532 nm can be attributed to the effective combination of the different NLO mechanisms, *i.e.*, RSA of PcZn, and NLS and TPA of GO. It is likely that the significant scattering signal from the pure PcZn solution results from the formation of PcZn nanoparticles, as reported in [27]. Although PcZn did not make any significant contribution to the OL at 1064 nm,[28,29] it is surprising that the GO-PcZn dispersions have much greater OL response than GO. Coincidently, as shown in Figure 6(b), the scattered curve from the GO-PcZn dispersions is steeper than that from GO as well. Whereas the origin of such large

improvement of the OL at 1064 nm is not clear yet, it is undoubted that the GO-PcZn hybrid material has much better broadband NLO and OL performance than the GO alone.

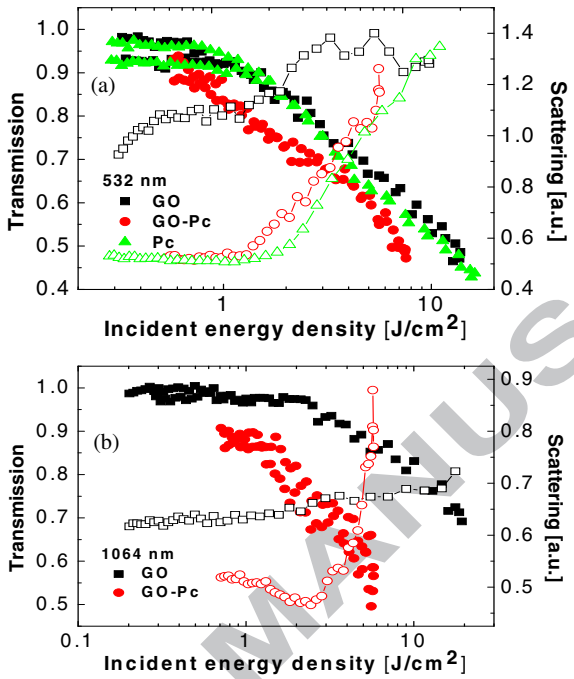


Figure 6. Nonlinear transmission (solid symbols) and scattering (open symbols) of the GO-PcZn and GO dispersions and PcZn solutions at (a) 532 nm and (b)1064 nm.

4 . Conclusions

A new soluble graphene oxide covalently functionalized with unsymmetrically substituted zinc phthalocyanine (GO-PcZn) was synthesized by an amidation reaction. A number of techniques are employed to characterize the resulting product, GO-PcZn. The XPS and FTIR results provided essential and useful information for the covalent attachment of the PcZn moieties onto the surface of GO. When compared to PcZn, an apparent fluorescence quenching was observed in the photoluminescence spectrum of GO-PcZn due to the possible electron-transfer process from PcZn to ^{1}GO*. As expected, GO-PcZn exhibited much larger NLO extinction coefficients and broadband OL performance than GO at both 532 and 1064

nm, indicating a remarkable accumulation effect via the covalently link of GO and PcZn.

Acknowledgements

The authors are grateful for the financial support of the National Natural Science Foundation of China (20676034, 20876046), the Ministry of Education of China (309013), the Fundamental Research Funds for the Central Universities, the Shanghai Municipal Educational Commission for the Shuguang fellowship (08GG10) and the Shanghai Eastern Scholarship.

REFERENCES

[1] ChenY, Hanack M, Araki Y, Ito O. Axially modified gallium phthalocyanines and naphthalocyanines for optical limiting. Chem Soc Rev 2005; 34: 517-29.

[2] Chen Y, Lin Y, Liu Y, Doyle J, He N, Zhuang X, et al. Carbon nanotube-based functional materials for optical limiting. J Nanosci Nanotechn 2007;7:1268-83.

[3] Spangler CW. Recent development in the design of organic materials for optical power limiting. J Mater Chem 1999; 9: 2013-20.

[4] Chen Y , Lin Y, He N. Carbon nanotubes enable laser protection applications. SPIE Newsroom 2007, DOI:10.1117/ 2.1200706.0750.

[5] Chen Y, EI-Khouly ME, Doyle JJ, Lin Y, Liu Y, et al. Phthalocyanines and related compounds: nonlinear optical response and photoinduced electron transfer process, in Handbook of Organic Electronics and Photonics, American Scientific Publishers, Stevenson Ranch, California, USA, 2008; 2: 151-81.

[6] Wu J, Pisula W, Muellen K. Graphene Molecules as Potential Material for Electronics. Chem Rev 2007;107:718-47.

[7] Chen F, Tao NJ. Electron transport in single molecules: from benzene to graphene. Acc Chem Res 2009; 42: 429-438.

[8] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The Chemistry of Graphene Oxide. Chem Soc Rev 2010; 39: 228-40.

[9] Park S, Ruoff RS. Chemical methods for the production of graphenes. Nature Nanotechn 2009; 4: 217-24.

[10] Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A. Graphene: The new-dimensional nanomaterials. Angew Chem Int Ed 2009; 48: 7752-77.

[11] Lee C, Wei X, Kysar JW, Hone J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science 2008; 321: 385–8.

[12] Chen F, Tao NJ. Electron transport in single molecules: from benzene to graphene. Acc Chem Res 2009; 42: 429-38.

[13] Stoller MD, Park S, Zhu Y, An J, Ruoff RS. Graphene-based ultracapacitors. Nano Lett 2008; 8: 3498–3502.

[14] Zhang Y, Tan YW, Stormer H L, Kim P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. Nature 2005; 438: 201–4.

[15] Sun Z, Hasan T, Torrisi F, Popa D, Privitera G, Wang F, et al. Graphene mode-locked ultrafast laser. ACS Nano 2010;4:803-10.

[16] Wang J, Hernandez Y, Lotya M, Coleman JN, Blau WJ. Broadband nonlinear optical response of graphene dispersions. Adv Mater 2009;21:2430-5.

[17] Feng M, Zhan H, Chen Y. Nonlinear optical and optical limiting properties of graphene families. Appl Phys Lett 2010; 96:033107/1-3.

[18] Feng M, Sun R, Zhan H, Chen Y. Lossless synthesis of graphene nanosheets decorated with tiny cadmium sulfide quantum dots with excellent nonlinear optical properties. Nanotechnology 2010;21:075601/1-7.

[19] Xu Y, Liu Z, Zhang X, Wang Y, Tian J, Huang Y, et al. A graphene hybrid material covalently functionalized with porphyrin:synthesis and optical limiting property. Adv Mater 2009; 21:1275-9.

[20] Kudrevich SV, Ali H, van Lier JE. Syntheses of monosulfonated phthalocyanines, benzonaphthoporphyrazines and porphyrins via the Meerwein reaction. J. Chem. Soc. Perkin Trans.1 1994; 2767-74.

[21] Sheik Bahae M, Said AA, Wei TH, Hagan DJ, Van Stryland EW. Sensitive measurement of optical nonlinearities using a single beam. IEEE J. Quantum Electronics 1990; 26: 760-9.

[22] Wu J, Pisula W, Muellen K. Graphenes as potential material for electronics. Chem Rev 2007; 107:718-47.

[23] Chen F, Tao NJ, Electron Transport in single molecules: from benzene to graphene. Acc Chem Res 2009;42: 429-438.

[24] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. Chem Soc Rev 2010; 39: 228-40.

[25] Wang J, Blau WJ. Inorganic and hybrid nanostructures for optical limiting. J. Opt. A: Pure Appl. Opt. 2009;11: 024001/1-16.

[26] Boukhvalov DW, Katsnelson MI. Modeling of graphite oxide. J Am Chem Soc 2008 ; 130:10697-701.

[27] Nitschke C, O'Flaherty SM, Kroll M, Blau WJ. Material investigations and optical properties of phthalocyanine nanoparticles. J Phys Chem B 2004; 108: 1287-95.

[28] O'Flaherty SM, Hold SV, Cook MJ, Torres T, Chen Y, Hanack M, Blau WJ. Molecular engineering of peripherally and axially modified phthalocyanines for optical limiting and nonlinear optics. Adv Mater 2003; 15: 19-32.

[29] de la Torre G, Vazquez P, Agullo-Lopez F, Torres T. Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds. Chem Rev 2004, 104, 3723.

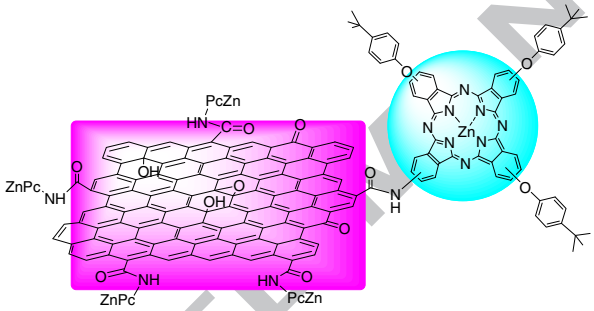
Graphical Abstract

Graphene oxide covalently functionalized with zinc phthalocyanine for broadband optical limiting

Jinhui Zhu[a],Yongxi Li[a], Yu Chen [a]*, Jun Wang[b]*, Bin Zhang[a] , Jinjuan Zhang[a], Werner J. Blau[b]

[a] *Key Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. Email: chentangyu@yahoo.com*

[b]*School of Physics and the Centre for Research on Adaptative Nanostructures and Nanodevices(CRANN),Trinity College Dublin, Dublin 2, Ireland. Email: wblau@tcd.ie*



GO-PcZn exhibits much larger nonlinear optcial extinction coefficients and better broadband optical limiting performance than GO at both 532 and 1064 nm due to the effective combination of the different NLO mechanisms.

Research highlights

Graphene oxide covalently functionalized with zinc phthalocyanine for broadband optical limiting

Jinhui Zhu[a],Yongxi Li[a], Yu Chen*[a], Jun Wang[b]*, Bin Zhang[a] , Jinjuan Zhang[a], Werner J. Blau[b]

[a] *Key Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. Email: chentangyu@yahoo.com*

[b]*School of Physics and the Centre for Research on Adaptative Nanostructures and Nanodevices(CRANN),Trinity College Dublin, Dublin 2, Ireland. Email:* jwangsci@gmail.com

Research highlights

- Graphene oxide (GO) is covalently functionalized with zinc phthalocyanine (PcZn)
- The formation of an amido bond between PcZn and GO is confirmed
- The hybrid material exhibits much larger NLO extinction coefficients than GO and PcZn
- Broadband optical limiting performance is due to a remarkable accumulation effect