Nonlinear optical properties of covalently linked graphene-metal porphyrin composite materials

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The nonlinear optical (NLO) and optical limiting (OL) properties of covalently linked graphene-porphyrin composite materials were investigated using Z-scan technique in nanosecond regime. We observed enhanced NLO and OL properties of graphene-porphyrin composites in comparison to the individual graphene and porphyrins. The improved OL property of composites is attributed to energy transfer between porphyrin and graphene, which improved excited state absorption and nonlinear scattering. Nonlinear optical susceptibilities $\chi(3)$ of graphene and graphene-porphyrin composites were, in the order of 10^{-12} esu, measured using degenerate four wave mixing technique in nanosecond regime. High values of excited state absorption and two-photon absorption were observed for the composites. © *2011 American Institute of Physics*. [doi:10.1063/1.3553500]

Graphene is an emerging star in world of materials. Its atoms are arranged in a honeycomb network and exhibit remarkable electronic and mechanical properties usually justified by citing high mobility of its charge carriers, extremely high thermal conductivity, and high intrinsic breaking strength. Graphene, a one-atom-thick crystal of carbon, was isolated in 2004 using adhesive tape applied to graphite[1] and forms a basic building block for graphitic materials of all other dimensionalities such as zero-dimensional fullerenes, one-dimensional nanotubes, and three-dimensional graphite.[2] Now graphene is the only material which can compete with silicon based technology and may even overtake it in next coming years. The applications of graphene have been hindered by its poor solubility which is mainly caused by the high interlayer attraction energies. This problem can be overcome by the functionalization on the sheet surface by either a covalent or noncovalent method which opens new directions to introduce various organic molecules into graphene sheets.[3] Graphene sheets are extended conjugated systems that are 100–1000 times larger than the size of typical organic molecules; thus, the functionalization of these extended frameworks allows an entirely new library of organic-graphene composites to be created. Organic molecules with extensive π-electron delocalization show good nonlinear optical (NLO) properties.[4,5] Among many organic molecules, porphyrin is one of the most studied classes of compounds because of their importance and abundance in nature. Also porphyrins are attractive materials for many applications in nonlinear optics,[6] harvesters in solar cells,[7] photodynamic therapy,[8] etc. Porphyrins are very flexible and fine tune their optical properties through proper substituents such as metal and nonmetals. Earlier studies reveal that fullerenes and carbon nanotubes can efficiently be attached to the porphyrin molecules. Studies on porphyrin linked fullerene hybrid materials[9] reveal that covalent or noncovalent combinations of NLO materials may be a better approach to improve NLO properties than those of the blended samples or individual components. It is well documented in the literature that large complex delocalized π-electron systems show good nonlinearities. Unlike synthesis and electronic applications of graphene materials, the linear and nonlinear optical and optoelectronic properties remain largely unexplored. There are a few research articles that have explored NLO properties: recently, Liu *et al.* studied graphene oxide in nanosecond and picosecond regimes,[10] Wang *et al.* showed broadband nonlinear optical response of graphene dispersions,[11] and Dean and van Driel showed second harmonic generation in graphene and graphitic films.[12] Graphene and porphyrins having large π-electron conjugation are ideal to fulfill the requirement of a perfect nonlinear material. If it is possible to enhance the large optical nonlinearities through conjugation of delocalized π-electron systems such as graphene with porphyrin, it can open a new window for nonlinear optical applications.

High power laser sources have motivated an extensive research for designs of optical limiting (OL) systems for protection of sensors and eye. An ideal optical limiter should have linear transmittance at low incident light fluencies and should become opaque at high light levels. Large nonlinear response, low losses at wavelength of interest, good optical quality, and mechanical stability are essential characteristics of potential optical limiters. Strong optical power limiting properties have been observed in various materials such as carbon nanotubes,[13] C_{60}, carbon-black suspension, porphyrins, metallophthalocyanines, glasses,[14] quantum dots, dendrimer molecules, oligothiophene-functionlized graphene,[15] and metal nanoparticles.[16] It has been shown that high nonlinearity induced scattering along with two photon absorption (TPA) and excited state absorption (ESA) can make a material an ideal optical limiter. This has prompted us to study a system that can provide large π-electron conjugation and hence large nonlinearity, can induce good nonlinear scattering, and can have strong TPA and excited state absorption. Such an ideal system has been realized by covalently linking porphyrin with graphene. In this paper, we report the nonlinear optical and optical limiting properties of pure graphene,

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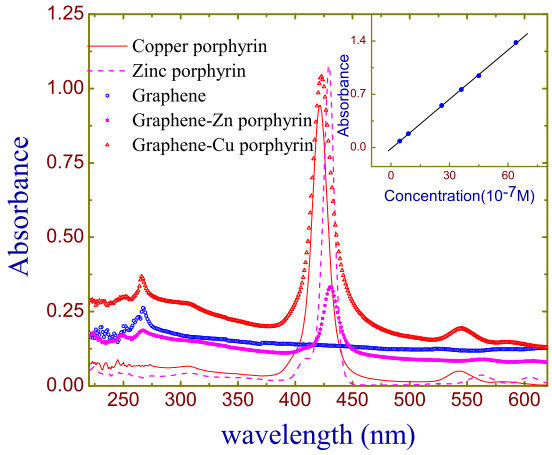

FIG. 1. (Color online) UV-visible absorption spectra of copper porphyrin ($4.5\times10^{-6}M$), zinc porphyrin ($4.5\times10^{-6}M$), graphene (0.018 mg/ml), graphene-zinc porphyrin (0.018 mg/ml), and graphene-copper porphyrin (0.018 mg/ml) composites in DMF. The inset shows the variation of copper porphyrin absorbance with concentration at 421 nm peak wavelength. The straight line is a linear fit to the experimental data.

zinc porphyrin, copper porphyrin, and their composites—graphene-zinc porphyrin and graphene-copper porphyrin.

The absorption spectra were studied by UV-visible spectrometer (JASCO V-670) and the nonlinear absorption and optical limiting properties through the standard through the standard open aperture Z-scan technique.[17] The NLO and OL properties of graphene and its composites with porphyrin were studied using 6 ns, 532 nm, and 10 Hz Nd:YAG laser (model-INDI40, Spectra Physics). Figure 1 shows UV-visible absorption spectra of composite materials, individual porphyrins, and graphene. Graphene absorption peak at 268 nm agrees well with the literature value.[15] Copper porphyrin has absorption peak at 421 nm and graphene-copper porphyrin composite has absorption peaks at 266 and 423 nm. Zn porphyrin has absorption peak at 429 nm and graphene-zinc porphyrin composite has absorption peaks at 267 and 431 nm. Absorption peaks at 267 and 431 nm in graphene-zinc porphyrin composite were suppressed while these peaks get enhanced in graphene-copper porphyrin composite indicating the tunability of optical properties though different substituents in porphyrin molecules. For the present studies graphene

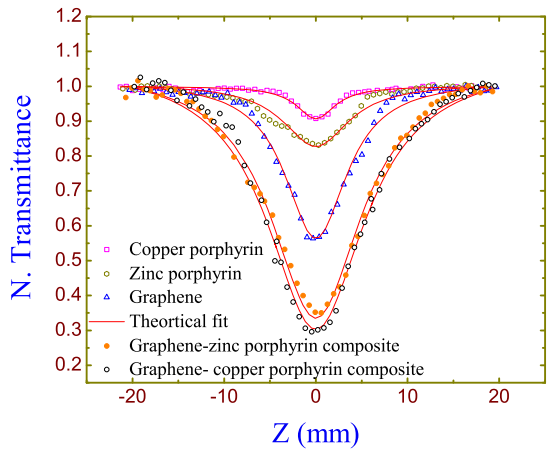

FIG. 2. (Color online) Open aperture Z-scan curves of copper porphyrin, zinc porphyrin, graphene, graphene-zinc porphyrin, and graphene-copper porphyrin composites in DMF with input intensity of 0.3 GW/cm^2 at 532 nm in nanosecond regime. Red lines represent theoretical fittings.

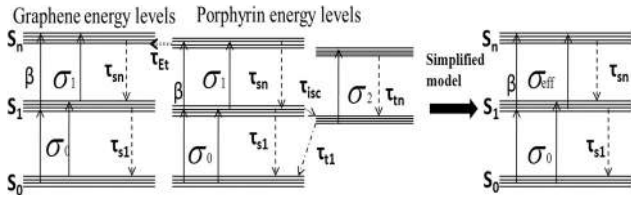

FIG. 3. Schematic energy-level diagram of graphene-porphyrin composite and its simplified model.

and graphene-porphyrin composite suspensions were prepared in dimethylformamide (DMF). To find out the concentration of graphene and porphyrins in the composite materials, we recorded absorption spectra for porphyrins and graphene separately at various concentrations and draw the absorbance versus concentration calibration curves. Matching the absorbance value with that of graphene-porphyrin composite, we estimated the porphyrin and graphene contents in the composite as 0.037 mg/ml ($5\times10^{-5}M$) and 0.163 mg/ml, respectively.

Third order optical nonlinear susceptibilities of pure porphyrins, graphene, and composite materials were studied by standard DFWM in the boxcar geometry.[18] We have taken 0.2 mg/ml of composite material for all nonlinear optical experiments. The sample was filled in 1 mm cuvette. The beam waist is about 27 μm. Linear transmittances of graphene, copper porphyrin, zinc porphyrin, graphene-copper porphyrin, and graphene-zinc porphyrin composites were 84.9%, 97.1%, 86.8%, 74.7%, and 79.5%, respectively. Figure 2 shows the open aperture nanosecond Z-scan results of pure graphene, copper and zinc porphyrins, and graphene-copper and zinc porphyrin in DMF with concentration of 0.2 mg/ml at an input intensity of 0.3 GW/cm^2. The normalized transmission curves of the pure and composites show ESA and TPA, leading to reverse saturable absorption behavior in the nanosecond time scales. In order to determine the linear and nonlinear absorption parameters and excited state lifetime, we have assumed a three level model for the graphene because of its metallic behavior as shown in Fig. 3. As normally done for the porphyrin molecules, we have taken a five level model with $1/\tau_{isc}$, intersystem crossing rate, to include the contribution of triplet states T_1 and T_n. For the composite

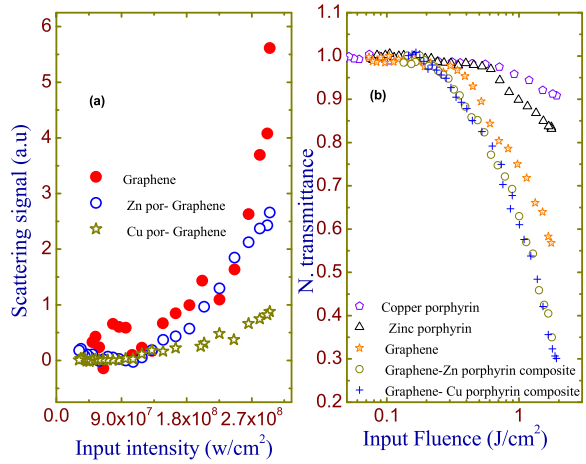

FIG. 4. (Color online) (a) Scattering signal with input intensity of graphene and graphene-porphyrin composites. (b) Optical limiting curves of copper porphyrin, zinc porphyrin, graphene, graphene-zinc porphyrin, and graphene-copper porphyrin composites in DMF at 532 nm in nanosecond.

TABLE I. Excited state and ground state parameters σ_{eff}^{ex}, β, $\sigma_{eff}^{ex}/\sigma_0$, τ_{s1}, τ_{sn}, and σ_0 for copper porphyrin, zinc porphyrin, pure graphene, and graphene-porphyrin composites at 532 nm in nanosecond time scales.

Samples	σ_0 (10^{-19}) (cm^2)	σ_{eff}^{ex} (10^{-19}) (cm^2)	β (cm/GW)	FOM ($\sigma_{eff}^{ex}/\sigma_0$)	τ_{sl} (ns)	τ_{sn} (ps)
Copper porphyrin	4	79	132	19.75	0.9	6
Zinc porphyrin	4.4	113	366	25.68	0.78	5
Pure graphene	5.3	30.1	900	5.68	0.009	0.009
Graphene-copper porphyrin	8.3	380	4720	45.78	0.5	7
Graphene-zinc porphyrin	4.9	214	3570	43.67	0.68	9

molecules, we have reduced it to a simplified model of three level system, where σ_{eff}^{ex} is taken as the effective excited state absorption cross section—which includes the $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ of the porphyrin molecules and $S_1 \rightarrow S_n$ of graphene molecules—and β_{eff} is taken as the effective TPA coefficient for both graphene and porphyrin molecules. This is quite reasonable as the absorption levels $S_1(T_1)$ and $S_n(T_n)$ of porphyrins closely match in energy of graphene molecules. As there is a strong TPA in the composites and the energy levels of the S_n states of porphyrin materials match with the graphene S_n states, there will be an energy transfer from the excited states of porphyrins to graphene and then graphene's S_n states relax to the ground state nonradiatively. The composite molecule comes to the ground state through subnanosecond relaxation times. Because of the strong excited state absorption and cumulative TPA of porphyrin as well as the graphene and immediate energy transfer to the graphene, the role of triplet state lifetimes does not appear to influence the fittings of the nanosecond data though it does influence the excited state absorption cross section σ_{eff}^{ex}. Optical nonlinear susceptibilities of graphene, graphene-zinc porphyrin, and graphene-copper porphyrin measured through the DFWM in the boxcar geometry are found to be 4.2×10^{-12}, 7.1×10^{-12}, and 8.5×10^{-12} esu, respectively, estimated with reference to CS_2 value of 6.8×10^{-13} esu.

We also observed nonlinear scattering from the graphene and composite materials as shown in Fig. 4(a), while the pure porphyrin samples do not show any nonlinear scattering. The experimental procedure to determine the nonlinear scattering is discussed in detail in our earlier article.[19] The optical limiting curves are plotted and shown in Fig. 4(b) for pure porphyrins, pure graphene, and composite materials in nanosecond time scales. Compared to individual porphyrins and graphene, composite materials show good limiting behavior. We estimated the figure of merit (FOM) for the pure graphene, copper porphyrin, zinc porphyrin, graphene-zinc porphyrin, and graphene-copper porphyrin composites and it is shown in Table I. Capability of a material for optical limiting can be described by FOM ($=\sigma_{ex}/\sigma_0$), where σ_{ex} and σ_0 are excited state and ground state absorption cross sections. FOM for composite materials goes as twice of their individual porphyrins. We estimated the limiting thresholds of copper porphyrin, zinc porphyrin, graphene, graphene-zinc porphyrin, and graphene-copper porphyrin composites to be 1.7, 1.3, 0.8, 0.2, and 0.1 J/cm^2, respectively. Both graphene-copper porphyrin and graphene-zinc porphyrin composites exhibit enhanced optical limiting behavior which arises from ESA, TPA, and nonlinear scattering.

In summary, from our observations, we conclude that graphene-porphyrin composite helps in achieving stronger nonlinear absorption, TPA, and nonlinear scattering, leading to a better optical limiting material. The ratio of excited state to ground state absorption cross sections was found be around 45 and TPA coefficient was found to be around 4720 cm/GW, which are quite high compared to many other compounds reported in the literature for achieving a good optical limiting device. In the nanosecond time scales, enhanced TPA, which arises due to the energy transfer from porphyrin to graphene, and ESA are dominant mechanisms. Because of the strong optical nonlinearities, the graphene-porphyrin composites exhibit a nonlinear scattering, which we strongly believe helps in increasing the damage threshold of the material.

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