Enhanced optical limiting of reduced graphene oxide covalently decorated with camphor sulphonic acid doped polyaniline

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The field of graphene is evolving exponentially with many potential applications [1] due to its fascinating properties like large surface to volume ratio, extraordinary high electron mobility, conductivity, stiffness, etc [2]. However, the practical applications of graphene are limited by the poor processability as a result of high cohesive van der Waals energy adhering the sheets one another [3]. Functionalization at the carbon basal planes and edge sites will overcome this limitation and recently graphene based hybrids of conjugated polymers with dramatic improvement in properties are reported [4,5]. Among conjugated polymers, polyaniline emerged as a widely studied group of NLO materials, because of its ultrafast response, high damage threshold architectural flexibility and relative ease of processing [6]. Although hybrids of polyaniline covalently grafted on graphene sheets are very recently studied aiming supercapacitor applications [7,8], its optical limiting applications are largely unexplored.
Encouraged by these considerations, we have covalently functionalized reduced graphene oxide with camphor sulphonic acid doped polyaniline and the hybrid was characterized by Fourier transform infrared spectroscopy , X-ray diffraction analysis, X-ray photoelectron spectroscopy, thermogravimetric analysis, UV-Visible spectroscopy and scanning electron microscopy. Graphite oxide synthesized by simplifying the modified Hummers method was first activated by acyl chlorination followed by amine functionalisation and subsequently polymerized along with aniline monomer and yielding the hybrid. The synthesis strategy is given in figure 1(A). Figure 1(B) shows the HRSEM images of GO, GO-NH_2 and the hybrid. GO exhibits typical flake like morphology in micrometer dimensions and after amine functionalization, it shows curled and wrinkled morphology. This change in morphology indicates the existence of phenyline diamine groups on reduced graphene oxide surfaces. The introduction of Pani is clearly visible in the HRSEM images of hybrid, which shows rice grain like morphology. During *insitu* polymerisation of aniline in presence of GO-NH_2, graphene sheets acts both as a support material and also participate in polymerisation by the formation of GO-NH_2 radical cation. Using the initiator $(NH_4)_2S_2O_8$, two types of cation radicals are formed, namely, GO-NH_2 radical cation covalently linked on graphene sheets and aniline radical cation adsorbed on GO-NH_2. The chains initiated by the former will covalently get grafted on the graphene sheets and those initiated by the adsorbed aniline radical cation will get entrapped in the graphene sheets by noncovalent interactions. Nonlinear optical properties of the hybrid, graphite oxide and the pristine polyaniline were investigated by Z-scan technique at 532 nm. Figure 2 shows the typical Z scan curves of GO, Pani and the hybrid. At the same linear transmittance, the hybrid exhibits better nonlinear response with nonlinear absorption coefficient 7 cm/GW, compared to GO (4.6 cm/GW) and Pani (4.5 cm/GW), indicating a remarkable effect of covalent grafting. Pani is well known to exhibit RSA, while GO exhibits NLS and two photon absorption (2PA) at 532 nm. . Enhanced nonlinear response of the hybrid can be attributed to the combination of NLS, 2PA and RSA. When using nanosecond pulses, NLS is observed to play the major role for the nonlinearity of GO, since 2PA is more pronounced for picosecond laser pulses.

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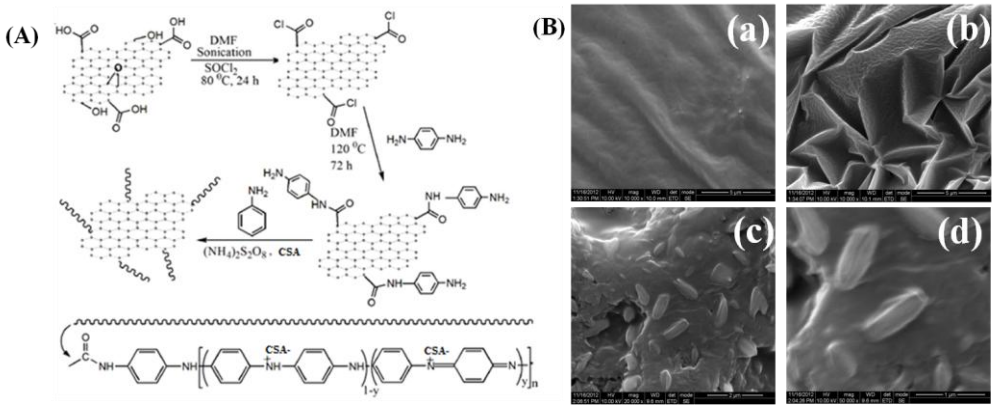

Figure 1. (A) Synthesis strategy for the grafting of polyaniline on graphene sheets. (B) HRSEM image of **(a)** GO **(b)** GO-NH_2 **(c), (d)** GO-NH_2-Pani hybrid

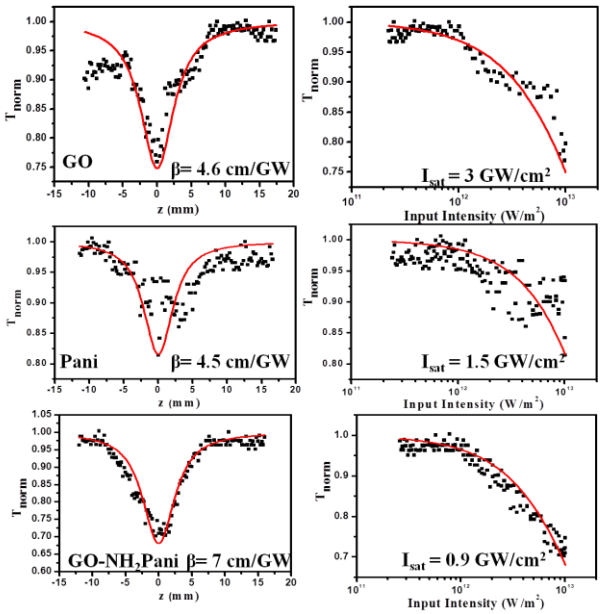

Figure 2. Open aperture Z scan curves and optical limiting plots of GO, Pani and the hybrid (GO-NH_2-Pani) at 35 μJ input laser energy