Giant broadband nonlinear optical absorption response in dispersed graphene single sheets

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Background

- ❖ manipulating the intensity and shape of laser pulses in a number of advanced optical technologies using nonlinear optical (NLO) materials.

- ❖ There are two main classes of such materials: (i) saturable absorbers, which give increased transmittance at high optical intensities or fluences, and are useful for pulse compression, Q-switching and mode locking; and (ii) optical limiters, which give decreased transmittance, and are useful not only for pulse shaping and mode locking, but also for the protection of eyes and sensor focal-plane arrays.

- ❖ optical limiters with large NLO responses, particularly in carbon-based materials. These include graphitic systems such as carbon black suspensions (CBS), single-walled and multiwalled carbon nanotubes (CNTs) and small π-electron systems such as fullerenes, porphyrins and phthalocyanines.

- ❖ These limit the transmission of optical energy by nonlinear scattering when solvent microbubbles and/or microplasmas are formed at high fluences.

❖ However, neither mechanism is effective against pulses shorter than a few nanoseconds because of the required breakdown time. They are also ineffective in solid films where there is no solvent and breakdown of the material leads instead to the formation of pinholes

❖ The small π-electron systems, on the other hand, can provide optical-limiting properties by means of excited-state absorption of long-lived triplet states formed in the sub-nanosecond timescale.

❖ This mechanism can provide highly effective optical limitation in liquid cells and solid films, but only over narrow wavelength bands because of the strong wavelength dependence of the ratio of excited-state to ground-state absorption cross-sections.

❖ Recently, suspensions of graphene and graphene oxides (GOx) have also been shown to give broadband optical-limiting characteristics in a variety of solvents

❖Their limiting thresholds and output clamping characteristics are, however, broadly similar to those of CBS and CNT suspensions, and the mechanism is also nonlinear scattering

❖This suggests that a number of graphitic nanostructures share similar NLO behaviour.

Present work

❖ graphene is functionalized dispersed as single sheets in heavy-atom solvents or in certain film matrices

❖ it exhibits a novel excited-state absorption mechanism that can provide highly effective optical limitation across the visible and near-infrared spectral regions

❖ at pulse fluences well below the onset of microbubble or microplasma formation.

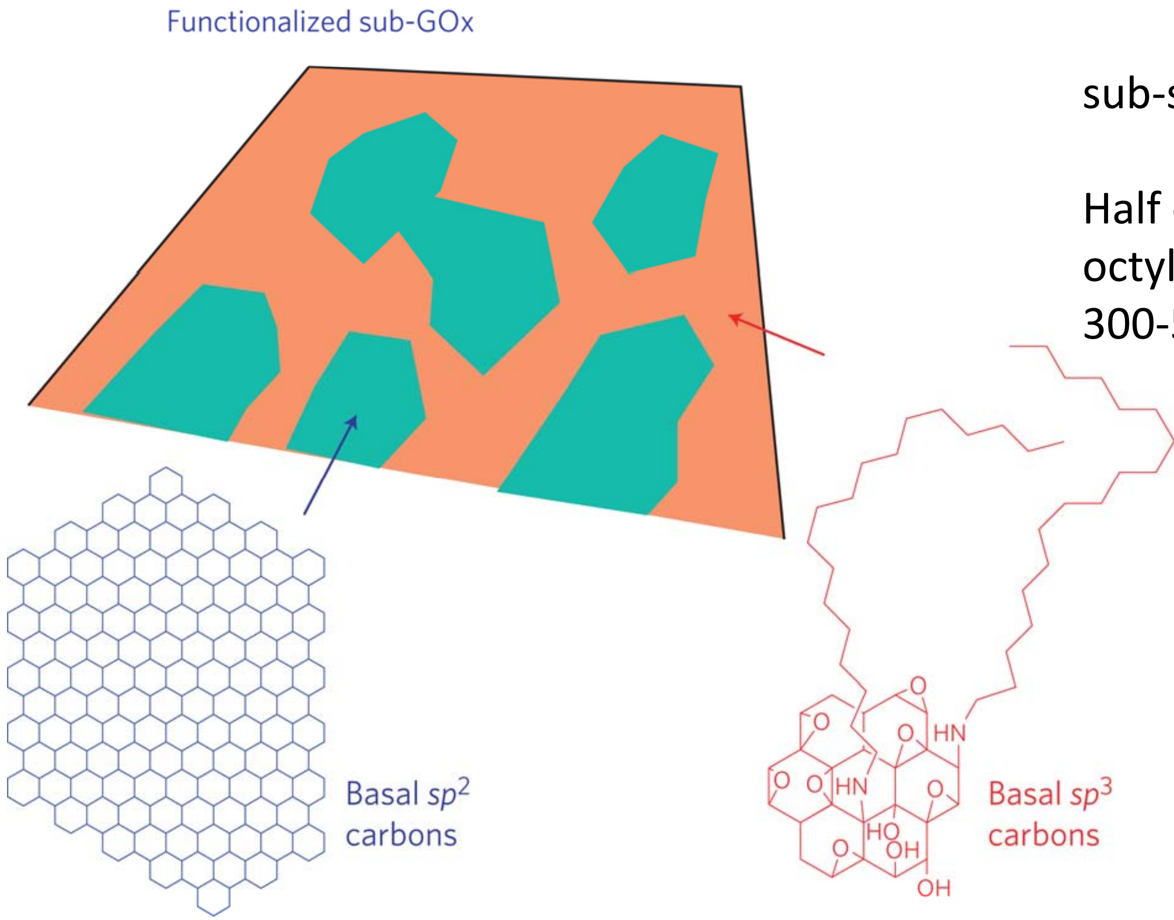
❖ Practical thin films with broadband optical-limiting characteristics can now be fabricated.

❖The optical-limiting threshold achieved here (10 mJ cm^{-2} for a linear transmittance of 70%) for nanosecond pulses in a loose-focus configuration is 5–10 times lower than previously known, which thus sets a new performance benchmark

❖unfunctionalized graphene, which has very limited dispersability, can also exhibit this giant NLO response in an appropriate heavy-atom solvent.

❖This optical-limiting mechanism is therefore a property of the graphene dispersed in the matrix rather than the result of functionalization.

❖Nanosecond pump–probe spectroscopy in chlorobenzene reveals that the nanographene domains switch from the usual broadband photo-induced bleaching to a novel reverse saturable absorption mechanism with increasing excitation densities across this threshold



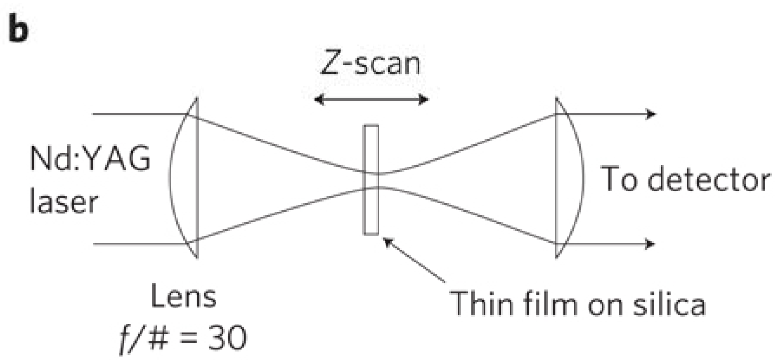
sub-stoichiometric GO

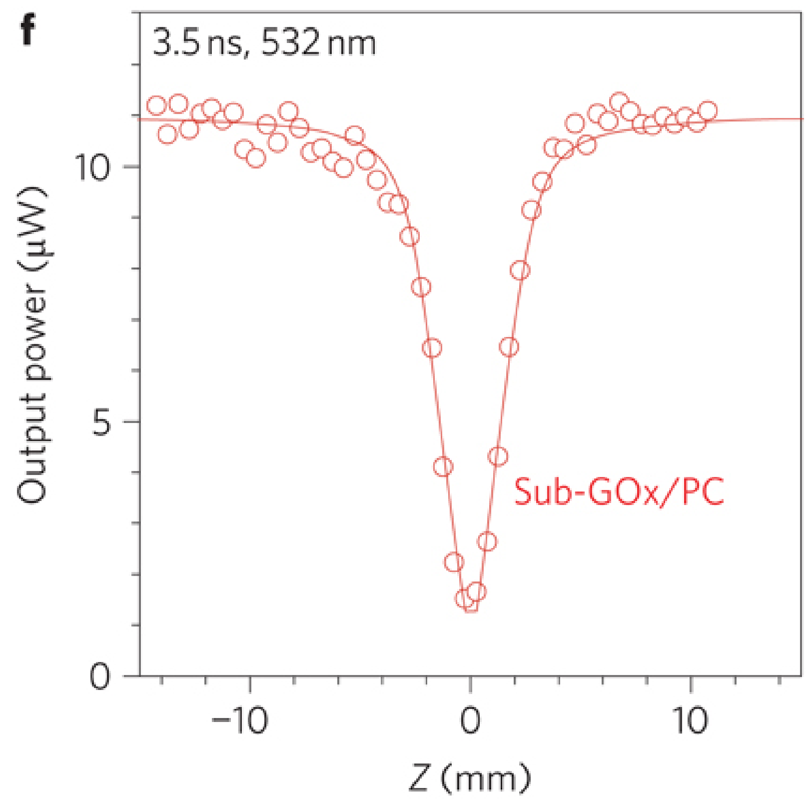
Half oxidising-grafting with octylamine surface chains 300-500 nm

Fully oxidized lack pi electrons

Repeatedly isolated in dry state and re-dispersed in variety of solvents 15 mg/ml

Z-scan profile





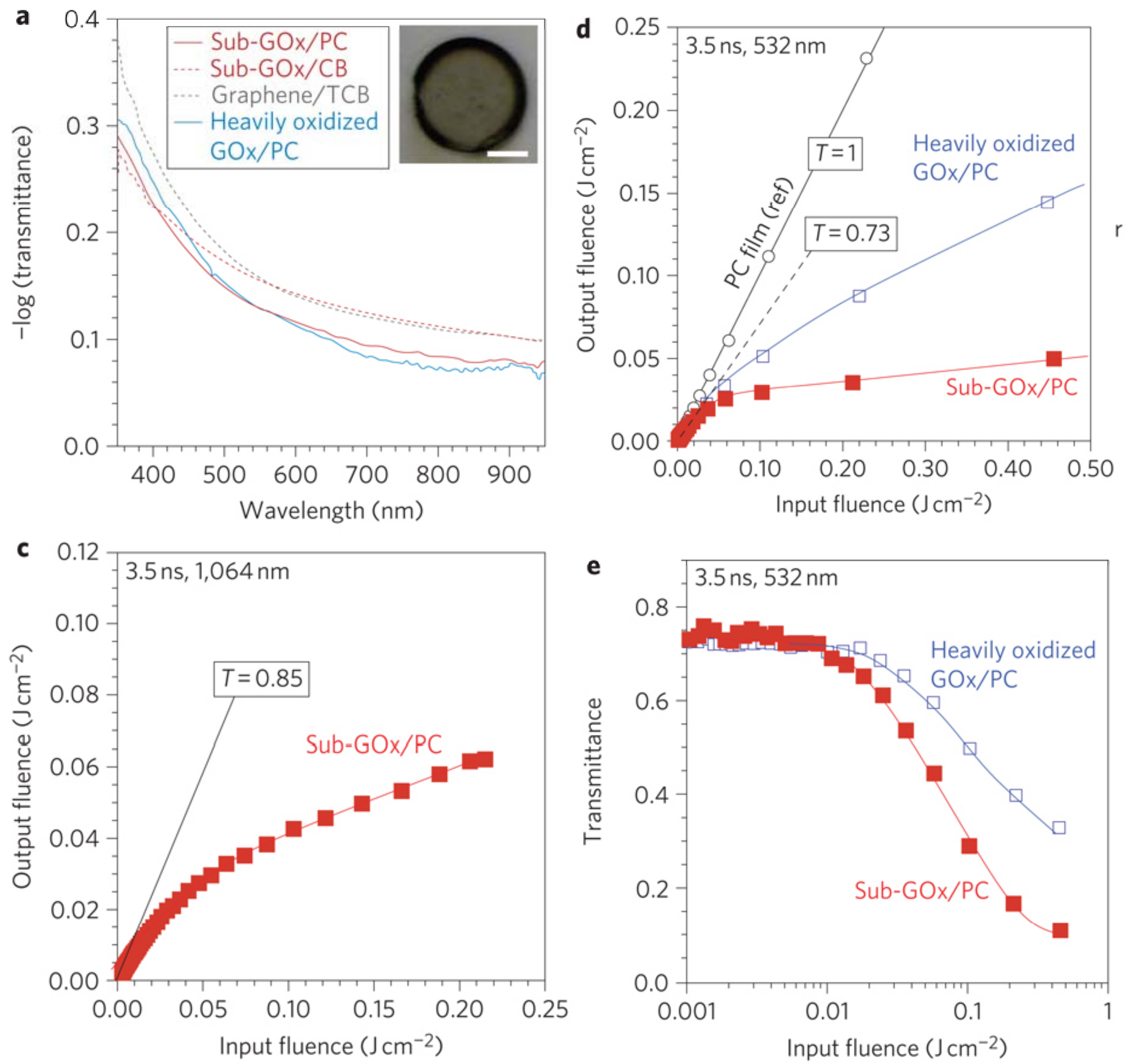
Giant optical limiting

Bisphenol- poly carbonate (PC)

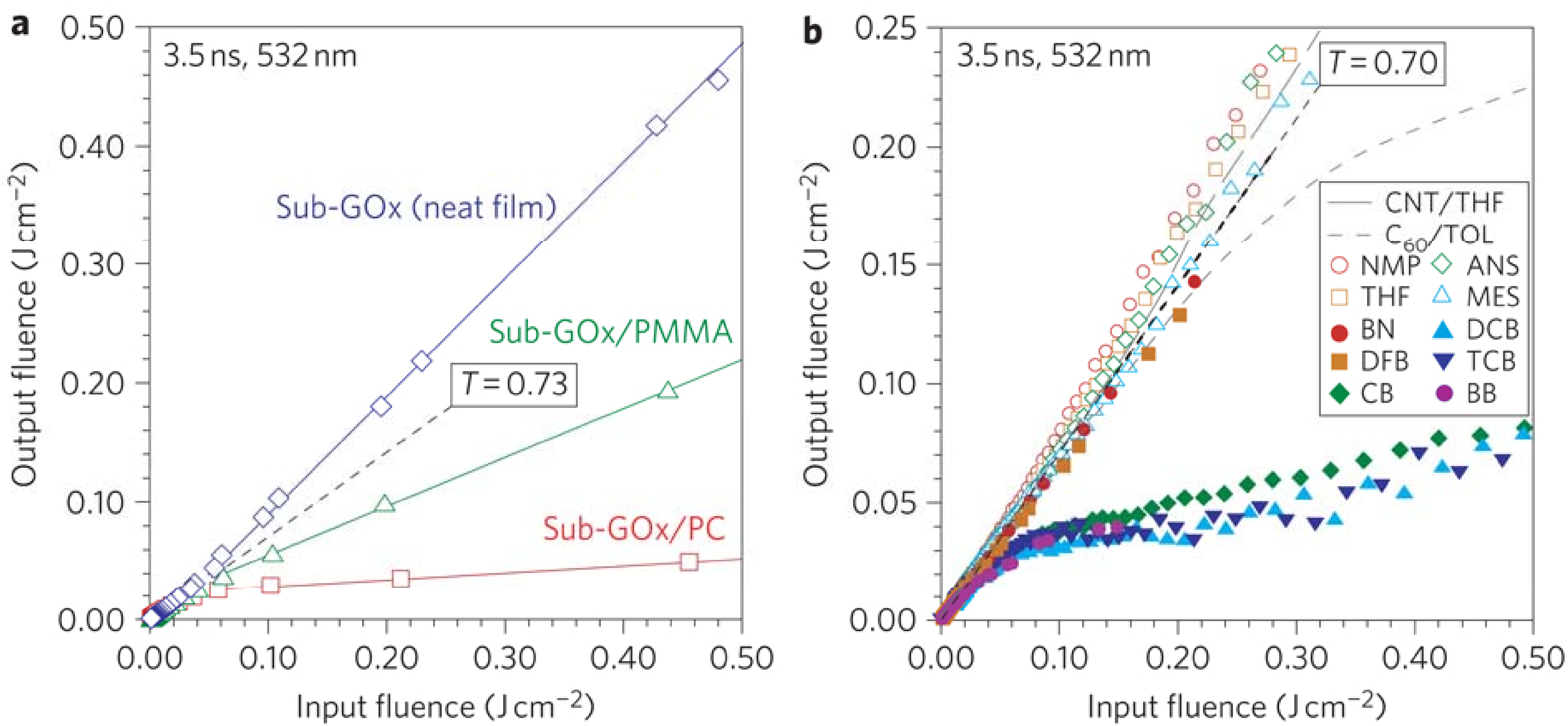
Chlorobenzene (CB)

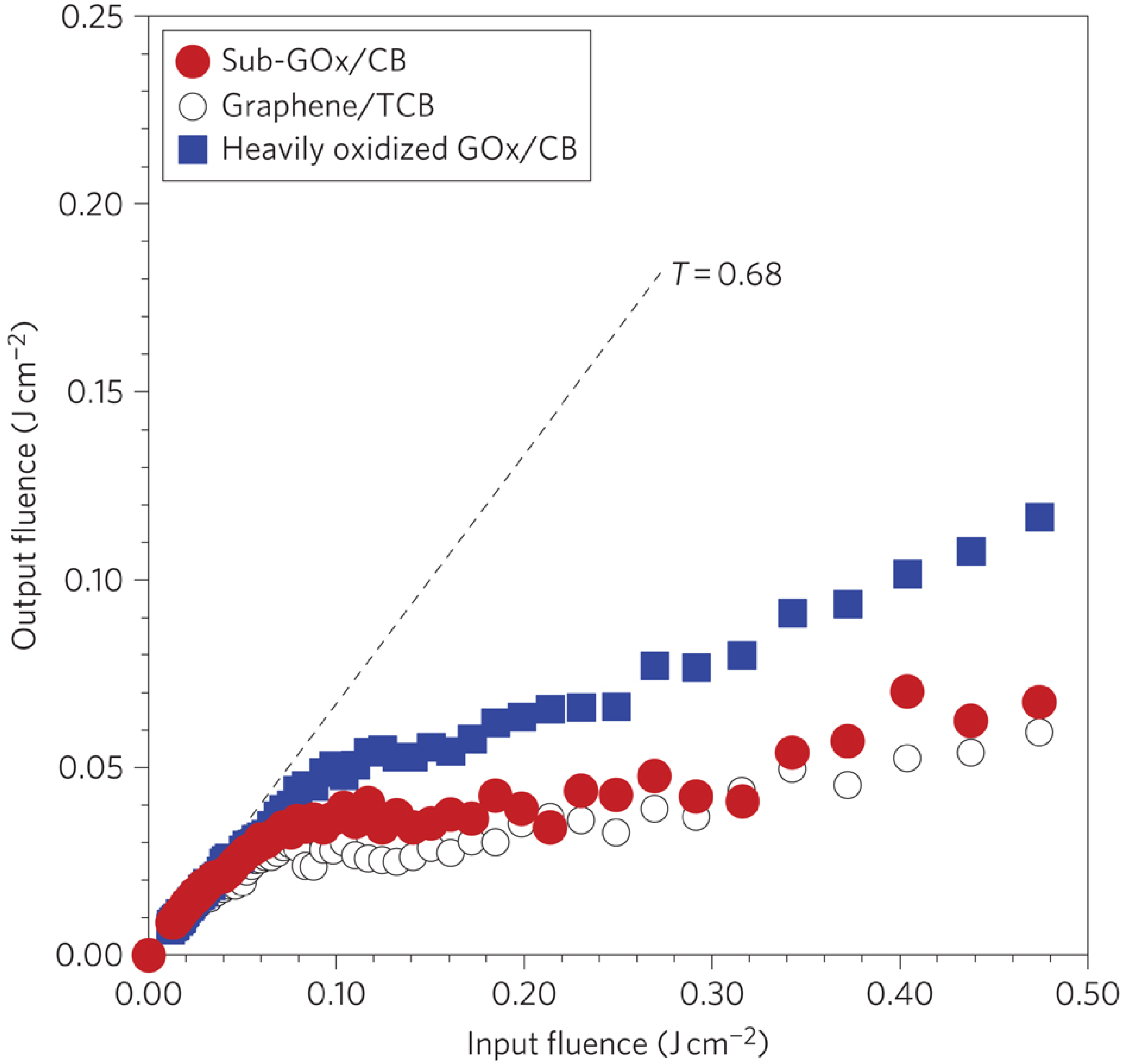
Sonicted graphite in tri CB

20 um spot dia



Strong solvent/matrix effect on the nonlinear optical properties of dispersed sub-GOx

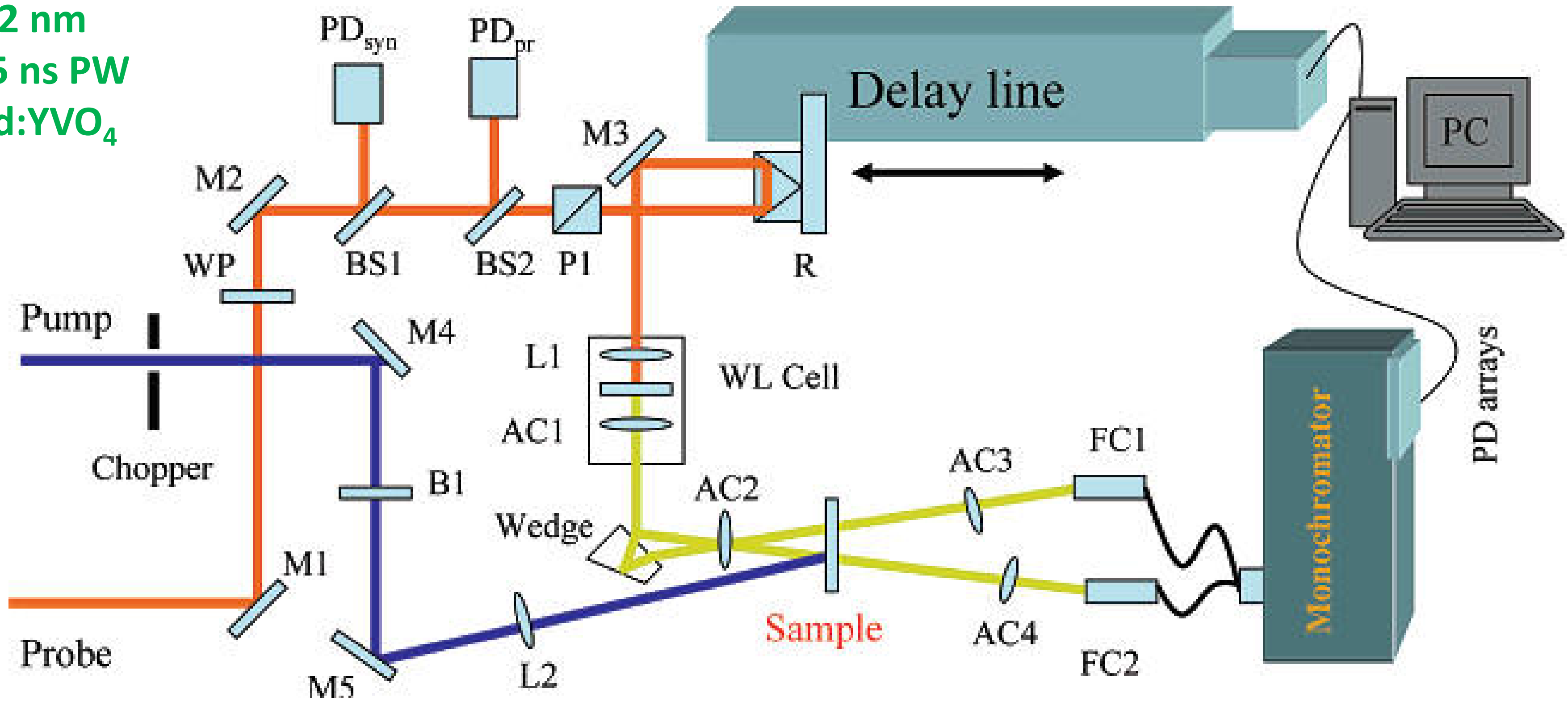




Sub-GOx/CB
Graphene/TCB
Heavily oxidized GOx/CB
T = 0.68
Output fluence (J cm^{-2})
Input fluence (J cm^{-2})
0.00
0.05
0.10
0.15
0.20
0.25
0.00
0.10
0.20
0.30
0.40
0.50

Transient absorption spectroscopy

532 nm
0.5 ns PW
Nd:YVO_4



532 nm
90 fs PW
Ti:sapphire

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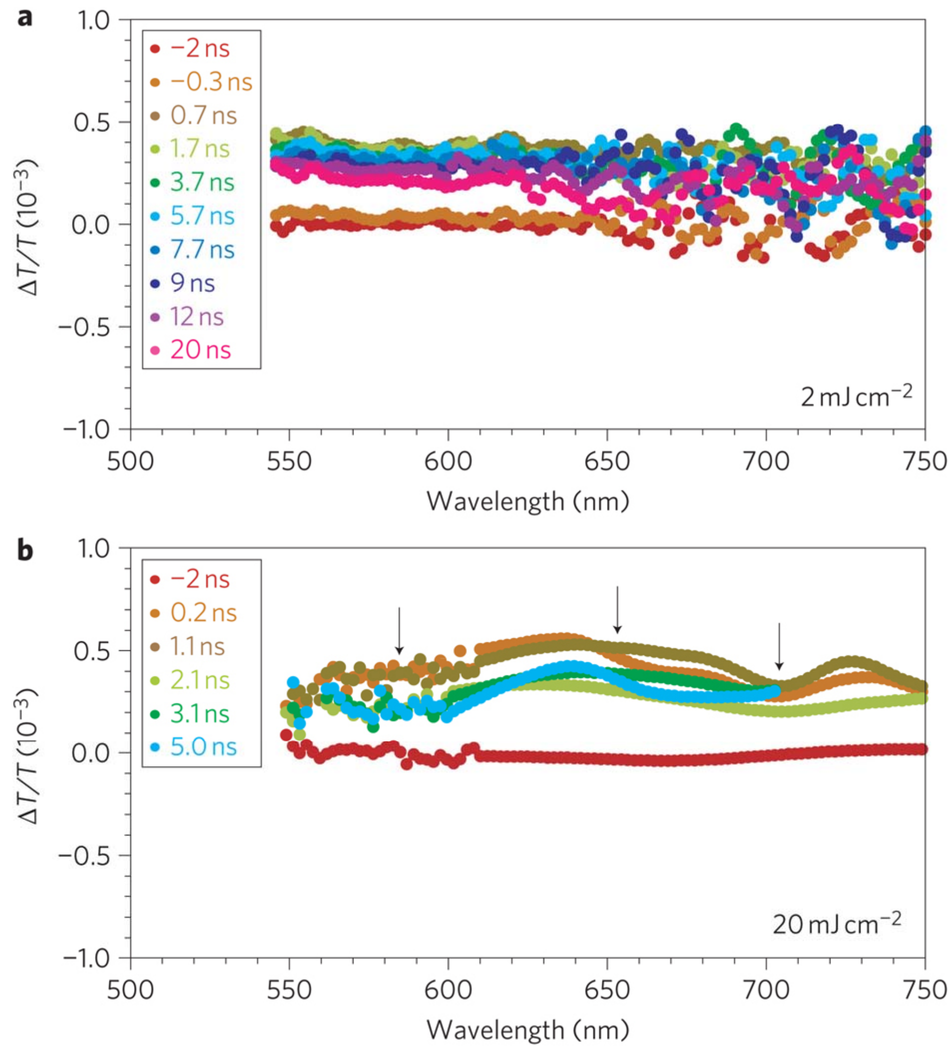
Spectfally flat photo bleaching

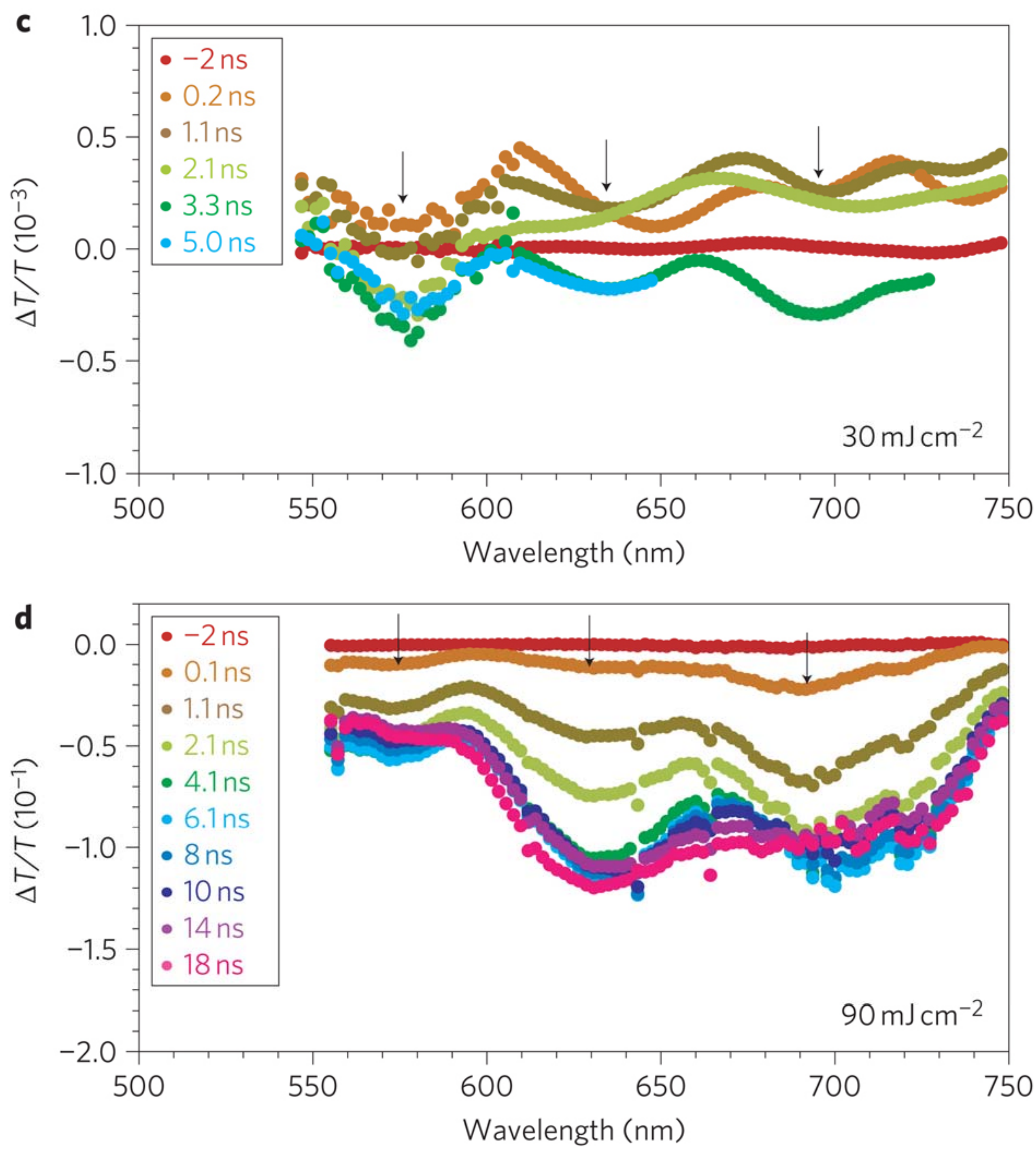


2.1, 1.9, 1.75 eV

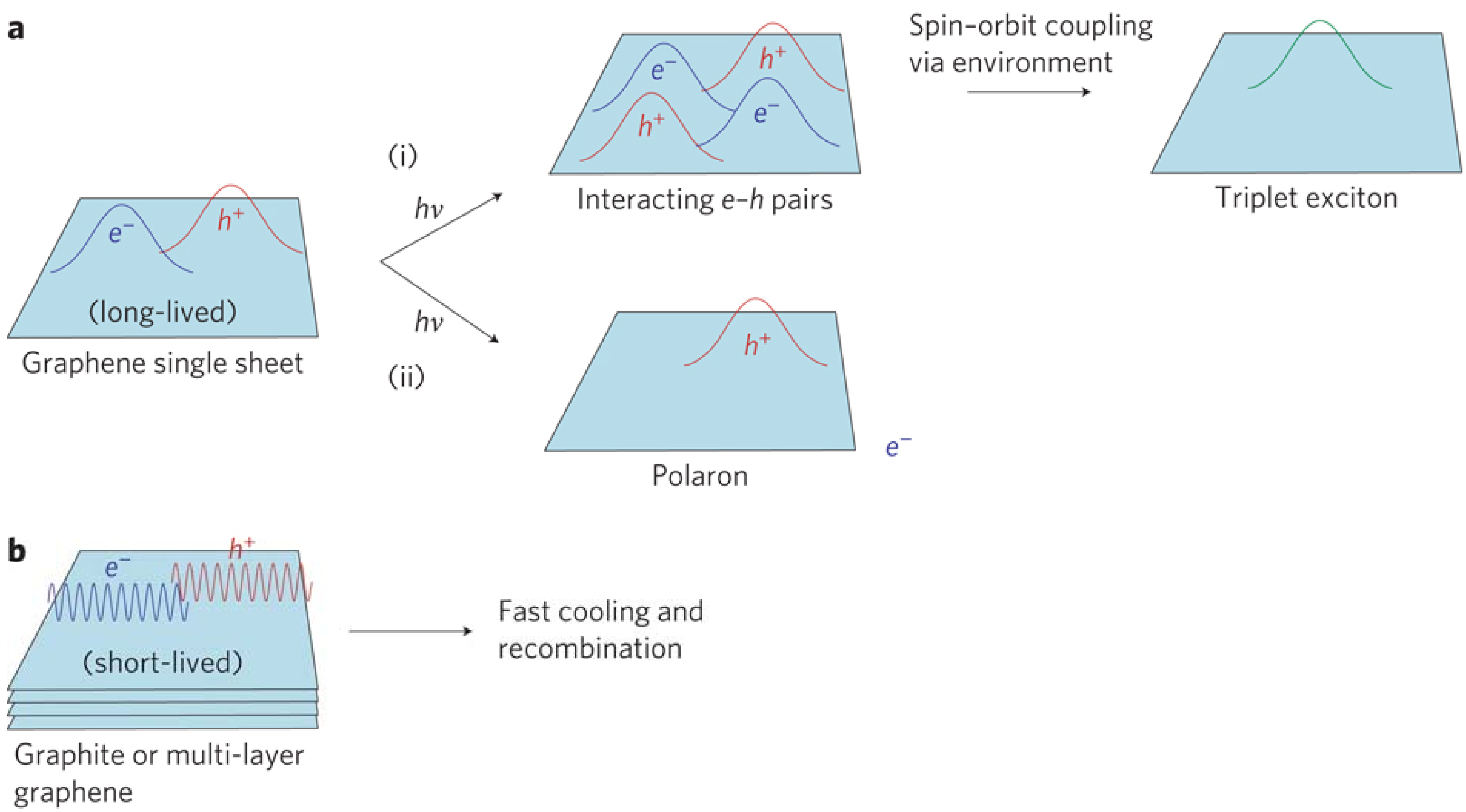
The differential transmittance was obtained by comparing the probe normalized by the split-off reference, with and without the pump in adjacent pulses, and then presented as $\Delta T/T$, defined as $(T_{on} - T_{off})/T_{off}$ in real time, where T_{on} and T_{off} are, respectively, the transmittance with and without the pump pulses.

2.15, 1.95, 1.80

Decrease in absorption beyond 700 nm



Excited state absorption



Summary

- found an unusually efficient nonlinear optical-limiting behaviour that occurs in graphene and alkyl-functionalized sub-GOx when they are dispersed as single sheets in appropriate solvents or film matrices.

- practical broadband optical limiters in both liquid cells and thin films or coatings can now be constructed with performances exceeding those of other carbon nanostructures by a factor of 5–10.

- outlined a new phenomenon in which the initially delocalized electron–hole gas localizes at high excitation densities in the presence of heavy atoms, to give strongly absorbing excitons. The resultant excited-state absorption mechanism can therefore be very effective.

- Eventually the broadband absorption advantage of large π-electron systems has been combined with the intense excited-state absorption advantage of small π-electron systems.

Thank you all