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White light induced covalent modification of graphene using phenazine dye

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Herein, we report a novel strategy for a covalent modification of graphene nanoplatelets with photoactive dyes. Functionalization of the graphene surface was carried out using white light to photochemically generate phenazine radicals and the reaction progress was followed up spectrophotometrically. Characterization of the modified material was carried out by FTIR, XRD, UV-vis absorption, fluorescence, Raman spectroscopy and SEM imaging. This hybrid material has improved solubility, shows an optical band gap of 1.95 eV and is highly emissive in the visible wavelength region.

An interest in sunlight as a renewable source to develop green and sustainable chemical processes has dramatically intensified in recent years. Photochemical methods attract their simplicity as highly reactive intermediates can be generated through absorption of light by the substrate, and can be carried out under mild conditions without the requirement of catalysts.[1] Graphene is a zero band-gap material with a wide range of unique physical, mechanical and electronic properties.[2] Being optically transparent (97.7%), it only weakly absorbs light (2.3%),[3] which limits its use as the active element in conventional photonics[3c]. However, to realize its full potential, covalent functionalization of graphene with light-harvesting moieties may allow its band gap structure to be tuned and to modulate its electronic characteristics.[4,5] The chemical reactivity of graphene is lower than that of other carbon based materials such as fullerenes and nanotubes, dropping further with an increase in the number of layers. Essentially, covalent derivatization of graphene with organic moieties provides anchor functionalities, allowing successive modifications with biomolecules, light harvesting groups, catalysts and macromolecules.[6] Although, a range of chemical transformations via cycloaddition, amidation, metal mediated couplings and "click" chemistry have been explored, the reactive intermediates may offer a powerful functionalization strategy of the graphene inert surface.[7] Diazonium chemistry introduced by Haddon et al.[8a] to graphene, proves to be very practical and allows a high degree of graphene functionalization (<20%).[8] Generation of free-radicals via thermal or electrochemical decomposition of the diazonium salt is the rate-limiting step in the reaction. It requires an efficient overlap between the electronic density of states of the graphene and the diazonium salt to avail covalent bonding between the components.[9] Subsequently, applicability of the method has been only demonstrated for the small aryls, which have a bandgap greater than 4 eV and carry limited additional functionality for the resulting hybrid system. Although, diazonium born free-radicals can also be generated photochemically via a homolytic pathway,[10] photochemistry involving diazonium and graphene has not yet been explored. To the best of our knowledge, only one rare example of the graphene's photochemical reactivity using visible light laser activation is reported; there, phenyl free-radicals have been produced from benzoyl peroxide under laser illumination to chemically modify a monolayer of graphene (SiO$_2$/G).[11]

Herein, we report a first successful and technically simple method for the covalent modification of graphene with phenazine radicals generated from phenazine diazonium salt via white light photochemical activation. Our choice of chemistry is governed by two main objectives: (i) modification of the graphene surface by planar, electron-rich molecules sensitive to photochemical electron/ energy transfer with high extinction coefficient in the visible region; (ii) the reaction conditions allowing quick, efficient and solution-processable functionalization of graphene.

We have anticipated that, naturally occurring phenazine dyes may have several advantages; these π-conjugated dyes with

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electron rich substituents, have planar rigid structure. They are known sensitizers with rich redox chemistries and capable of
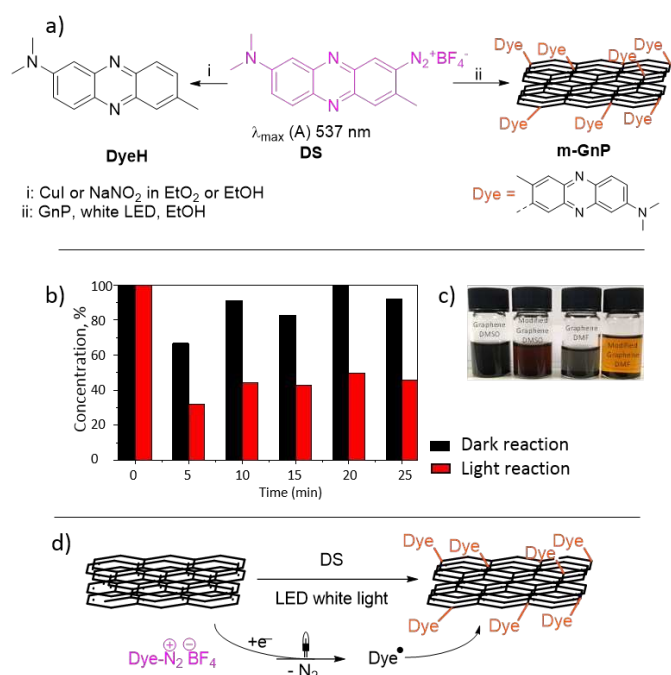

Fig. 1. (a) Hydrodediazoniation of the phenazine diazonium salt (DS) to reduced dye (DyeH). Photochemical modification of graphene (GnP) with DS. (b) Reaction progress under dark and light conditions as the function of the DS concentration. (c) Photograph of the samples of GnP and modified m-GnP suspension in DMSO and DMF. (d) Schematic presentation of covalent bonding of Dye• to graphene.

electron transfer.[12] Neutral Red is non-toxic commercially available dye that can be synthetically modified via diazonium chemistry. Phenazine diazonium salt DS was generated from the reaction of Neutral Red with $NaNO_2$ in HBF_4 (30%) and precipitated with ethanol-ether solvent system (Fig. 1a). The purple diazonium dye has the absorption maximum at 537 nm in visible region. As functionalization chemistry of the surface using diazonium salts proceeds via free-radical mechanism, electron transfer is required from a substrate to reach the diazonium ion. We have tested the ability of DS to generate Dye• in the presence of an electron donor such as CuI and $NaNO_2$ in Et_2O or EtOH (Fig. 1a). In all cases (under ambient light conditions), DS was rapidly converted into a sole product DyeH via hydrodediazoniation (H-atom abstraction),[10b] which indicates a free-radical pathway.

Having in hand a dye suitable for generating free radicals, we have investigated its reactivity towards graphene surface. The graphene nanoplatelets (GnPs) are considered as the next generation of materials[13], as they offer a high degree of crystallinity with minimal distortion of the graphitic basal area. In our study, we have chosen commercially available graphene nanoplatelets (surface area 500 m^2/g, average particle size 25 microns, average thickness 6 nm) and used them without any treatment to demonstrate their applicability in inexpensive and simple modification. GnPs were dispersed in ethanol; the resulted GnP suspension was treated with DS under

illumination with white light at room temperature for a maximum of 40 min.

The effect of light was studied by following the reaction under light and dark conditions. (Fig. 1b) On its own, under light illumination and in the absence of electron donors, DS showed a reasonable stability within a suitable concentration range (obeying $A=\varepsilon cl$; see Supporting Information; ESI Fig. 1) allowing UV-vis absorption spectroscopy to be used as a primary analytical tool to monitor the progress of the graphene modification. A change in the concentration of free DS in the solution was recorded at 537 nm for both settings. Photochemical conversion progressed very rapidly, with no change in the DS concentration after 20 min (Fig. 1b, red), leaving only 46% of the free dye in solution. The initial drop in the absorption intensity of free DS in both dark (68%) and light (32%) reactions can be explained via a physisorption of DS by GnP caused by π-π stacking and van der Waals interactions. However, this is a reversible process, which showed stabilization of the concentration of free DS in the solution after 10 min to 91% and 44% for dark and light reactions, respectively. Also, the covalently modified GnP with the dye (m-GnP) showed an improved solubility in DMSO and DMF (Fig. 1c).

The mechanism proposed for thermal decomposition of an aryl is a reduction by graphene, whereby the diazonium salt is required to be in a close proximity to the surface of the graphene allowing initial electron transfer.[9] Moreover, the LUMO of the electron acceptor (aryl diazonium salt) should lie lower than the corresponding LUMO of the donor (graphene). The reaction in the dark does not show any product formation confirming that it is not energetically favorable. Despite the life time of the photoexcited carriers of graphene being very short,[11a,14] it has been shown that a photogenerated hot-electron can be transferred from photoactivated graphene to benzoyl peroxide forming free Ph• radicals.[11a] We suggest that a possible mechanism involving light activation may follow a similar route via a delocalized electron transfer from graphene[9] to DS leading to Dye•, which immediately reacts with GnP (Fig. 1d).

Striking differences between the isolated samples from light and dark reactions have been shown by powder XRD, which proved to be very efficient in analyzing such materials (Fig. 2a). It confirmed that the modified graphene sample obtained from light reaction (further referred as m-GnP) showed a high crystallinity, which comes from covalent modification. The PXRD pattern of the GnP and m-GnP samples exhibited a typical GnP phase (Fig. 2a, denoted as „o"). PXRD peaks of the light sample arise from the GnP and phenazine phases and denoted as „x" in Fig. 2a. Moreover, the m-GnP sample displayed a widening of the graphene peak, which indicates the crystal lattice distortion from the original GnP sample. In contrast, the XRD pattern of the dark sample indicated the likelihood of a co-agglomeration of the polyaromatic phenazine dye and the layers of graphene. In order to distinguish between physisorption and covalent bonding between components, further experiments have been carried out to mimic potential

co-aggregation. DyeH and GnP were dispersed in EtOH in the same stoichiometric ratio as used for modification of GnP with DS following a similar work up. Powder XRD analysis of these nanoplatelets shows a very similar pattern to one collected for the dark reaction sample, confirming no co-aggregation between DyeH and GnP. (see Supporting Information; ESI Fig. 7)
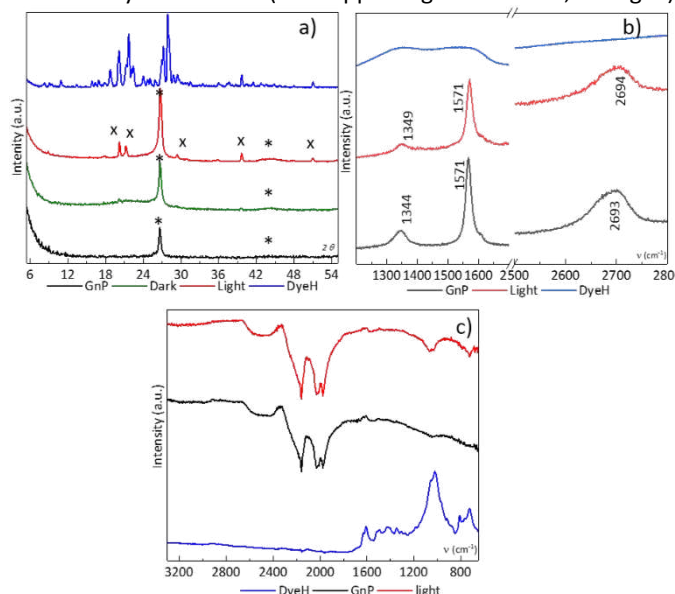

Fig. 2 (a) Normalized powder XRD spectra of GnP and the isolated samples from dark and light reactions. (b) Normalized Raman spectra of GnP and m-GnP. (c) Normalized FTIR (absorbance) spectra of GnP and m-GnP.

Raman spectroscopy has been used in the characterization of various forms of graphitic structures. It allows assessment of the degree of defect sites introduced into the periodic graphene lattice[15] as well as the π-electron distribution[16]. Raman spectra were recorded, using a 514 nm laser source, the modified sample m-GnP showed characteristic D, G and 2D frequencies at 1347 cm^{-1}, 1571 cm^{-1} and 2700 cm^{-1}, respectively (Fig. 2b). The positions of the peaks were determined by acquiring several Raman spectra from multiple positions of the sample (see Supporting Information; ESI Tables 1 and 2), the base line was subtracted and the positions were determined by Lorentzian fit.[15a,17] Also, a considerable broadening of the signals indicated a high degree of graphene functionalization. In turn, Raman spectrum recorded from pure DyeH exhibits featureless fluorescence background. FT-IR spectra of m-GnP revealed the enhanced and new bands at 1055 and 730 cm^{-1}, which fall within the range of C-N stretches, =C-H bending (out-of-plane) and ring torsion within the sample (Fig. 2c).

The surface morphologies of graphene and dye-graphene composites were monitored using scanning electron microscopy (SEM). Figure 3 shows SEM images of pristine GnP (a) and functionalized m-GnP (b, c) samples. All SEM images were taken using an FEI Nova 450 FEG-SEM operating at 3 kV using deceleration mode and CBS detector. The SEM image of pristine GnPs shows nanoplatelets of different sizes that form agglomerations of various densities. Although GnPs and m-GnPs have been prepared in the same manner, the dye-modified m-GnPs exhibit more uniform size of approximately 25 microns.

These results show that dye-modified GnPs have an improved solubility which allows to filter out smaller (and therefore, lighter) GnPs during sample preparation for SEM imaging.
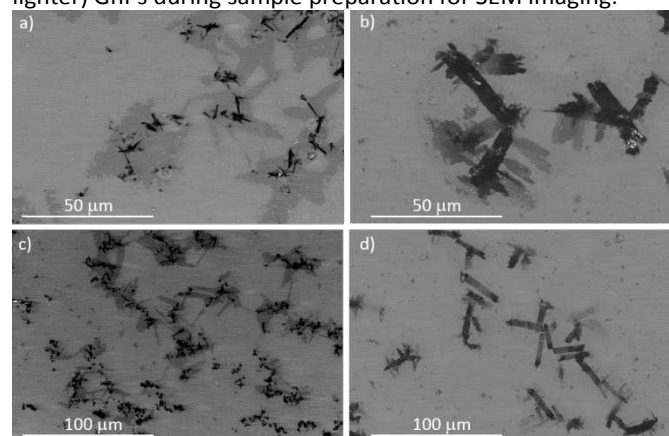
Fig. 3 3kV SEM images recorded with CBS detector of (a), (c) pristine GnPs and (b), (d) the dye-modified m-GnPs.

The effect of the modification on the optical properties of the m-GnP sample has been studied using UV-visible (UV/vis) absorption and fluorescence spectroscopy. (Fig. 4) The modification leads to a drastic change in optical properties of graphene hybrid material. The absorption spectrum of m-GnP in DMF confirms the presence of phenazine dye. A new long-wavelength at 465 nm comes from dye electronic transitions and it is blue shifted in comparison to a pure DyeH (480 nm). The optical band gap of m-GnP, estimated from UV-vis absorption spectra of the modified sample, is 1.95 eV.
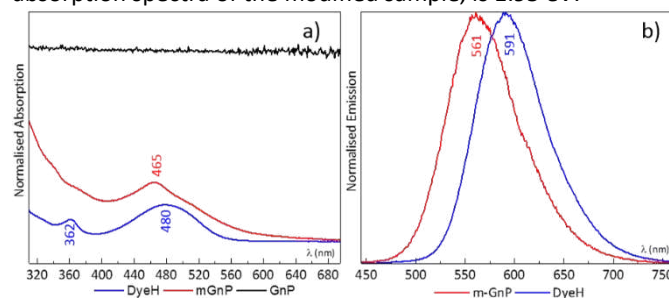

Fig. 4 (a) Normalized UV-vis absorption spectra of GnP, m-GnP and DyeH in DMF. (b) Emission spectra of the modified sample m-GnP and DyeH in DMF excited at 440 nm.

Moreover, the modified sample produced a bright orange emission upon irradiation (excitation at 440 nm), with the fluorescence maxima at 561 nm in DMF. Again, emission maximum of m-GnP is also blue shifted from a pure DyeH band (591 nm).

In conclusion, we have shown a powerful photochemical method, which offers a graphene modification using photoactive dyes to produce a new type of 3D-graphene hybrids. This method has several advantages, allowing: (i) direct covalent modification via light induced radicals under mild conditions and without external linkers; (ii) the reaction is rapid and easy to set up. Moreover, chemical modification with the phenazine moieties improves the solubility, providing solution-

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based processability, and integrates visible light harvesting groups to the graphene surface. In this way, the crystallinity on the GnP basal plane can still be preserved to minimally scarify the outstanding natural properties of graphene, whilst improving the optical properties and modulating the band gap of the new hybrid structure with respect to pristine graphene. Overall, the graphene-dye hybrid structure developed here can assist in the design of a new type of 3D functional graphene nanocomposites for use in photonics and energy applications.

Notes and references

1   N. Hoffmann, *Chem. Rev.* 2008, **108**, 1052.
2   (*a*) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 2004, **306**, 666; (*b*) A. K. Geim, K. S. Novoselov, *Nat. Mater*. 2007, **6**, 183; (*c*) A. K. Geim, *Science* 2009, **324**, 1530.
3   (*a*) S. Pang, Y. Hernandez, X. Feng, K. Müllen, *Adv. Mater*. 2011, **23**, 2779; (*b*) R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, *Science* 2008, **320**, 1308; (*c*) H.-X. Wang, Q. Wang, K.-G. Zhou, H.-L. Zhang, *Small* 2013, **9**, 1266.
4   (*a*) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* 2008, **321**, 385; (*b*) Chen, S.; Wu, Q.; Mishra, C.; Kang, J.; Zhang, H.; Cho, K.; Cai, W.; Balandin, A. A.; Ruoff, R. S. *Nat. Mater*. 2012, **11**, 203.
5   (*a*) Novoselov, K. S.; Falko, V. I.; Colombo, L.; Gellert, P. R.; Schwab, M. G.; Kim, K. *Nature* 2012, **490**, 192; (*b*) Cao, X.; Yin, Z.; Zhang, H. *Energy Environ. Sci*. 2014, **7**, 1850; (*c*) Yin, Z.; Zhu, J.; He, Q.; Cao, X.; Tan, C.; Chen, H.; Yan, Q.; Zhang, H. *Adv. Eng. Mater*. 2014, **4**, 1300574.
6   (*a*) A. Criado, M. Melchionna, S. Marchesan, M. Prato, M. *Angew. Chem*. 2015, **54**, 10734; (*b*) S. Eigler, A. Hirsch, *Angew. Chem*. *Int. Ed*. 2014, **53**, 7720.
7   J. Park, M. Yan, *Acc. Chem. Res*. 2013, **46**, 181.
8   Examples: (*a*) E. Bekyarova, M. E. Itkis, P. Ramesh, C. Berger, M. Sprinkle, W. A. de Heer, R. C. Haddon, *JACS* 2009, **131**, 1336; (*b*) Q. Wu, Y. Wu, Y. Hao, J. Geng, M. Charlton, S. Chen, Y. Ren, H. Ji, H. Li, D. W. Boukhvalov, R. D. Piner, C. W. Bielawski, R. S. Ruoff, *Chem. Commun*. 2013, **49**, 677; (*c*) Q. H. Wang, Z. Jin, K. K. Kim, A. J. Hilmer, G. L. C. Paulus, C.-J. Shih, M.-H. Ham, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, J. Kong, P. Jarillo-Herrero, M. S. Strano, *Nat. Chem.* 2012, **4**, 724; (*d*) X. Fan, R. Nouchi, K. Tanigaki, *J. Phys. Chem. C* 2011, **115**, 12960; (*e*) S. Niyogi, E. Bekyarova, M. E. Itkis, H. Zhang, K. Shepperd, J. Hicks, M. Sprinkle, C. Berger, C. N. Lau, W. A. DeHeer, E. H. Conrad, R. C. Haddon, *Nano Lett*. 2010, **10**, 4061; (*f*) R. Sharma, J. H. Baik, C. J. Perera, M. S. Strano, *Nano Lett*. 2010, **10**, 398; (*g*) H. Lim, J. S. Lee, H. J. Shin, H. S. Shin, H. C. Choi, *Langmuir* 2010, **26**, 12278; (*h*) M. A. Bissett, S. Konabe, S. Okada, M. Tsuji, H. Ago, *ACS Nano* 2013, **7**, 10335; (*i*) J. Greenwood, T. H. Phan, Y. Fujita, Z. Li, O. Ivasenko, W. Vanderlinden, H. Van Gorp, W. Frederickx, G. Lu, K. Tahara, Y. Tobe, H. Uji-i, S. F. L. Mertens, S. De Feyter, *ACS Nano* 2015, **9**, 5520; (*j*) N. Morimoto, K. Morioku, H. Suzuki, Y. Nakai, Y. Nishina, *Chem. Commun*. 2017, **53**, 7226.
9   G. L. Paulus, Q. H. Wang, M. S. Strano, *Acc. Chem. Res*. 2013, **46**, 160.
10 (*a*) H. Zollinger, *Acc. Chem. Res*. 1973, **6**, 335; (*b*) C. Galli, *Chem. Rev*. 1988, **88**, 765.
11 (*a*) H. Liu, S. Ryu, Z. Chen, M. L. Steigerwald, C. Nuckolls, L. E. Brus, *J. Am. Chem. Soc*. 2009, **131**, 17099; (*b*) L. Liao, H. Wang, H. Peng, J. Yin, A. L. Koh, Y. Chen, Q. Xie, H. Peng, Z. Liu, *Nano Lett*. 2015, **15**, 5585.
12 (*a*) A. Price-Whelan, L. E. P. Dietrich and D. K. Newman, *Nat. Chem. Biol*. 2006, **2**, 71; (*b*) J. B. Laursen and J. Nielsen, *Chem. Rev.*, 2004, **104**, 1663; (*c*) M. K. Singh, H. Pal, A. V. Sapre, *Photochem. Photobiol.* 2000, **71,** 300.
13 I.-Y. Jeon, S.-Y. Bae, J.-M. Seo, J.-B. Baek, *Adv. Funct. Mater*. 2015, **25**, 6961.
14 D. F. Eaton, *Pure Appl. Chem*. 1988, **60**, 1107.
15 (*a*) A. C. Ferrari, J. Robertson, *J. Phys. Rev. B* 2000, **61**, 14095; (*b*) M. M. Lucchese, F. Stavale, E. H. M. Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete, A. Jorio, *Carbon* 2010, **48**, 1592.
16 T. Wassmann, A. P. Seitsonen, A. M. Saitta, M. Lazzeri, F. Mauri, *J. Am. Chem. Soc*. 2010, **132**, 3440.
17 (a) A. J. Glover, M. Cai, K. R. Overdeep, D. E. Kranbuehl, H. C. Schniepp, *Macromolecules* 2011, **44**, 9821. (b) F. Tai, S Lee, J. Chen, C. Wei, S. Chang, *J. Raman Spectrosc.* 2009, **40**, 1055. (c) J. Robertson, *Mater. Sci. Eng. R* 2002, **37**, 129.

TOC

Photochemical method to covalently modify graphene with dye was developed. Hybrid-material has band-gap of 1.95eV and emits light at 591nm.