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COMMUNICATION

Photoinduced charge separation in ordered self-assemblies of perylenediimide–graphene oxide hybrid layers

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Remarkably fast photoinduced charge separation in well-ordered self-assemblies of perylenediimide–graphene oxide (TAIPDI–GO) hybrid layers was observed in aqueous environments. Slow charge recombination indicates an effective charge migration between the self-assembled layers of PDI–GO hybrids following the charge separation.

Graphene oxide (GO), a chemically exfoliated graphene derivative, offers new composite materials for photochemical applications.¹ Effective visible light harvesting on GO sheets has been achieved by the decoration with proper organic dye molecules via non-covalent interactions with the π -surface of GO bearing oxygen-containing functional groups. Many hybrids of GO have been formed by employing various organic dyes with hydrophilic substituents (pyrenes, perylenes, porphyrins, coronenes, and semiconducting oligomers and polymers) in aqueous environments.¹ The efforts have been, so far, concentrated on obtaining only single or a few dye-functionalised GO or graphene layers and their photoinduced events.² The studies on the self-assemblies of the well-ordered dye–GO hybrid layers are still limited³ and photoinduced charge generation in these structures has yet to be studied.

In this communication, we report formation of ordered self-assemblies of GO layers functionalised with *N,N'*-di(2-(trimethylammoniumiodide) ethylene)perylenediimide (TAIPDI–GO, Fig. 1 and Fig. S1, ESI) and their photoinduced electron-transfer processes. Perylenediimide (PDI) is an ideal building block for nanohybrids of GO because its strong absorption in the visible region and the low reduction potential make it a powerful light harvester and a good electron acceptor during a possible photoinduced electron-transfer process with the GO sheet.⁴ TAIPDI bears cationic groups enhancing the electrostatic interactions with the functional groups of GO, such as –COOH, and its large aromatic plane establishes strong π – π interactions with the π -surface of the GO sheet. As a result of these interactions, TAIPDI–GO hybrids are expected to form self-assembled organizations in water. Charge migration in the self-assembled layers of TAIPDI–GO following the initial electron-transfer from the GO sheet to closely interacting TAIPDI molecules is proposed upon the excitation of the TAIPDIs (Fig. 1).

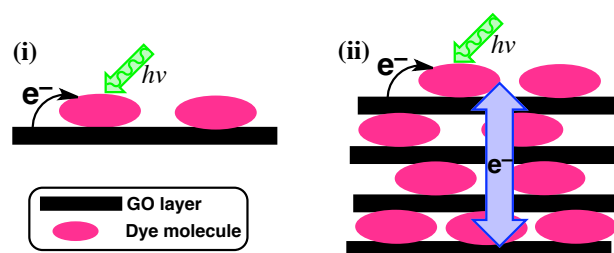


Fig. 1 (i) Photoinduced charge separation in single or a few layers of dye–GO hybrids examined in previous studies. (ii) Proposed photoinduced charge separation and interlayer charge migration in ordered self-assemblies of TAIPDI–GO hybrid layers investigated in this communication.

Self-assembly of TAIPDIs with GO layers was first detected by UV-vis spectroscopy. Absorption maxima of PDI at 501 and 537 nm were shifted to 510 and 548 nm, respectively. Hybrid formation also caused the quenching of TAIPDI fluorescence emission (Fig. 2). Significant spectral changes in the absorption of TAIPDI–GO and the emission quenching indicate π – π interactions between the π -surfaces of PDI and GO, which typically favours the photoinduced electron-transfer processes due to very close distance as observed in the non-covalently functionalized carbon materials with large π -surfaces.^{2f,5}

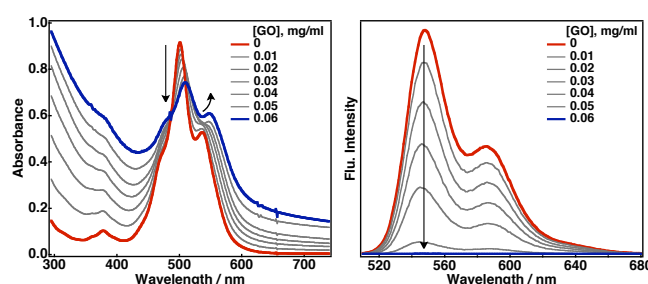


Fig. 2 Absorption (left) and fluorescence emission (right) spectral changes during the addition of GO to the aqueous solution of 0.025 mM TAIPDI, $\lambda_{\text{exc}} = 510$ nm.

Self-assembly of TAIPDI–GO layers leads to supramolecular gel formation in water under mild conditions (see Experimental Section

and Fig. S2-S4, ESI). Apparently, cationic TAIPDI⁶ acts as gelator, enhancing the π - π stacking. Powder X-ray diffraction (PXRD) was utilized to analyze the structural organization in the self-assemblies. GO showed a sharp peak at $2\theta = 10.2^\circ$ correlated with a d -spacing of 8.66 Å between the GO layers, which is very close to previously reported value.³ Incorporation of TAIPDI molecules into the GO layers increases the d -spacing to a value of 10.34 Å as the corresponding peak shifts to $2\theta = 8.6^\circ$ in the PXRD patterns of dried TAIPDI-GO hybrid gel (Fig. 3).

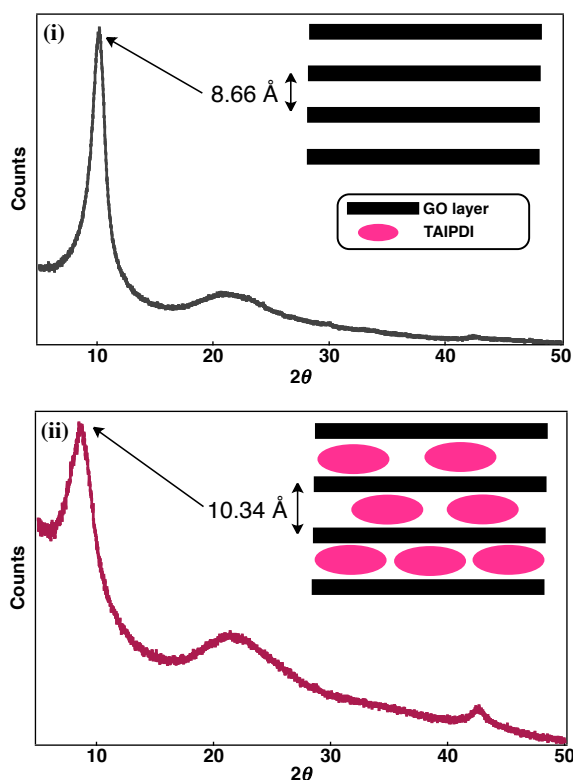


Fig. 3 Powder X-ray diffraction patterns of dried (i) GO and (ii) TAIPDI-GO supramolecular gel. Inset: Representation of GO layers with and without TAIPDIs.

The free energy change of proposed photoinduced charge separation (ΔG_{CS}) in PDI-GO hybrid was calculated according to eqn (1),⁷

$$\Delta G_{CS} = e(E_{ox} - E_{red}) - E_s \quad (1)$$

where E_{ox} is the first oxidation potential of GO, E_{red} is the first one-electron reduction of PDI, and E_s is the lowest ¹PDI*, which was estimated as 2.28 eV from the absorption and emission spectra. First oxidation of GO occurred at 0.88 V vs. SCE in water containing 0.10 M Na₂SO₄ as detected by using cyclic and differential pulse voltammetry (Fig. S7, ESI).⁸ The first one-electron reduction of PDI was found to be -0.25 V vs. SCE in water containing 0.10 M Na₂SO₄.⁹ Hence, the photoinduced electron transfer from GO to ¹PDI* is feasible via the ¹PDI* with a driving force of 1.15 eV.

Photoinduced electron-transfer dynamics of self-assemblies of PDI-GO hybrids were investigated by using femtosecond laser-induced transient absorption spectroscopy. The femtosecond transient spectra of

aggregates of TAIPDI-GO (0.25 mM TAIPDI and 0.6 mg ml⁻¹ GO) in water displayed very fast formation of broad transient absorption around 720 and 960 nm after the selective excitation of PDI at 510 nm (Fig. 4). These transient traits agree very well with those of the radical anion of PDI (PDI^{-•}),^{9,10} providing a valid proof for photoinduced electron transfer from GO to ¹PDI*. By fitting the rise of the transient absorption at 720 nm to a curve of an exponential function, the rate of charge separation (k_{CS}) was estimated to be $3.6 \times 10^{11} \text{ s}^{-1}$ ($\tau = 2.8 \text{ ps}$, Fig S8, ESI). Fast formation rate suggests that the charge separation is very efficient, which rules out the other quenching mechanisms such as energy transfer. The decay at the same wavelength comprises two components, whose lifetime values are extracted by fitting to a sum of two decaying exponentials (Fig. 4, inset). The former component of the fitting curve gives a lifetime for the first charge recombination as 31 ps ($k_{CR1} = 3.2 \times 10^{10} \text{ s}^{-1}$). The lifetime of the eventual charge-separated state is calculated from the latter component as 417 ps ($k_{CR2} = 2.4 \times 10^9 \text{ s}^{-1}$, Fig. 4, inset). Such a two-component decay was also observed in the π -stacks PDI hosting porphyrins via π - π and electrostatic interactions in water. Slow decay was accounted for the presence of electron migration mechanism among the π -stacks of PDI.⁹

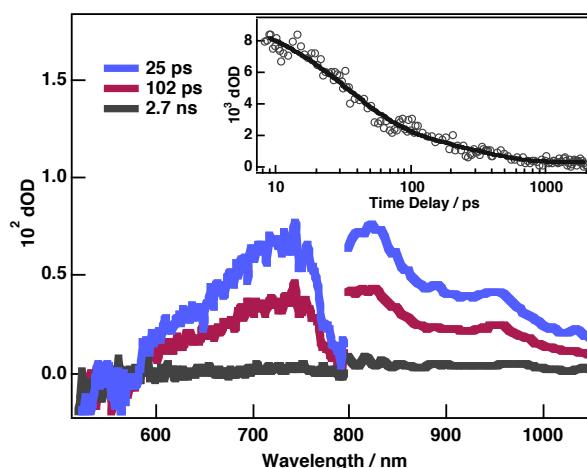


Fig. 4 Femtosecond laser-induced transient absorption spectra of 0.25 mM TAIPDI and 0.6 mg/ml GO in water at indicated time delays, $\lambda_{exc} = 510 \text{ nm}$. Inset: Time profile at 720 nm.

To view the effect of concentration of GO, it increased to 0.9 mg ml⁻¹ by keeping the concentration of TAIPDI at 0.25 mM, which means the lower number of TAIPDI molecules deposited between the GO layers. Consequently, the lifetime values of 21 and 400 ps were respectively obtained from the two-component decay at 720 nm (Fig. S9, ESI). The slight decline indicates that charge migration mainly realizes through the GO sheets whereas the contribution of TAIPDI molecules is limited. In the case of low concentration of GO (0.3 mg ml⁻¹) with 0.15 mM TAIPDI, the first and second component of the decay at 720 nm give lifetimes for charge separation 2.3 and 48 ps, respectively (Fig S10, ESI). This can be explained by the lack of adequate supramolecular organization of TAIPDI and GO. The concentration change of the GO did not have a significant impact on the formation rates of charge separation.

To test the effect of self-assembly on the rates of charge separation, TAIPDI-GO was dispersed in aqueous polyethylene glycol (PEG 200)

solution, in which the gel formation was not observed at the same conditions ($\sim 0.6 \text{ mg ml}^{-1}$ GO and 0.25 mM TAIPDI). The femtosecond laser-induced transient absorption spectra of well-dispersed GO–PDI hybrids in the PEG 200 solution exhibited the excited state absorption peak around 710 nm with bleaching at 550 nm after laser excitation at 510 nm (Fig. S11, ESI). These transient spectra match with those of the $^1\text{PDI}^*$.^{9a} The decay profile of absorbance around 710 nm indicates that the lifetime of the $^1\text{PDI}^*$ (τ_s) is remarkably reduced. There was no transient signal to be attributed to the electron-transfer products (i.e., the radical ion pair) probably because of rapid back electron transfer.¹⁰ The rate of charge separation of PDI–GO hybrids (k_{CS}) in the PEG 200 solution was estimated to be $2.3 \times 10^9 \text{ s}^{-1}$, which is significantly slower than that of self-assembled form of TAIPDI–GO in neat water.¹¹ As a result, the polymer chains of PEG 200 in the solution impede the supramolecular organization of TAIPDI–GO. Although the charge separation is not efficient no other transient trait was obtained to assign for energy transfer mechanism in the femtosecond transient absorption spectra.

Formation of the charge-separated states in the self-assemblies of PDI–GO hybrids in aqueous media was verified by the electron paramagnetic resonance (EPR) measurements, in which the EPR spectrum of PDI^- displays a powder pattern without hyperfine splitting ($g = 2.0041$) in frozen media at 4 K after photoexcitation (Fig. S12, ESI).

The hole (i.e. radical cation) formed after the photoinduced charge separation is expected to easily migrate on the smooth π -surface of a graphene sheet, resulting in slower charge recombination despite the fact that the electron-transfer distance between non-covalently-functionalised, electron-donating graphene and electron-accepting dye molecule is very close due to π - π interactions.^{2f,12} In the case of PDI–GO dispersed in the solution of PEG 200, the fast charge recombination can be rationalized from the close distance between electron donor and acceptor and the lack of the effective hole delocalization on the surface of the GO because of the defects on the honeycomb structure,¹³ resulting from the chemical oxidation.¹⁴ The presence of the functional groups on the GO sheet is practical for the non-covalent functionalisation of the GO by the dye molecules, however, they cause the interruption of the continuous conjugation of the π -surface. Despite the fact that the charge migration on the π -surface is severely inhibited by the defects it can be regenerated between the adjacent π -stacks of PDI–GO hybrid layers in the self-assemblies as indicated by the slow component of the decay time profile (Fig. 4, inset, Fig S9 and S10, ESI). Migration through the π -stacks is likely to promote a “pull effect” for fast charge separation. Dispersion of these hybrid stacks in a polymer environment seems to block such an interlayer charge-hopping mechanism due to the disruption of the supramolecular organization, causing the fast back electron transfer from PDI^- to oxidized GO.

In summary, non-covalent functionalisation of GO with visible light-absorbing PDI was achieved through the π - π and electrostatic interactions in water. TAIPDI–GO hybrids reveal a supramolecular self-assembly as recognized by the gel formation in an aqueous environment PXRD patterns. Our findings have demonstrated that π -stacking is necessary for fast charge separation and slow charge recombination, which is facilitated by a interlayer charge migration mechanism within the ordered self-assemblies of the PDI–GO hybrids during the photoexcitation.

This work was supported by Grant-in-Aid for Scientific Research (Nos. 266201541 and 26288037), an ALCA project from JST. MS thanks JSPS for a postdoctoral fellowship.

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

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