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Photoactive Graphene —
From Functionalization to Applications

Hang-Xing Wang and Hao-Li Zhang

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Abstract

Photoactive graphene fabricated by chemical functionalization of pristine graphene with different light-harvesting molecules has become one of the most exciting topics of graphene research in the last few years, which remarkably sustains and expands the graphene boom due to its great potentials in various applications. This chapter presents some important issues of photoactive graphene, covering material synthesis, electron/energy- transfer interaction, organic photovoltaic and photocatalystic applications. Of particular interest is the utilization of graphene as a two- dimensional platform to anchor organic conjugated aromatic molecules and their applications in photo-energy conversion and photocatalysis. Challenges currently faced by researchers and future perspectives in this field are also discussed.

Keywords: Photoactive graphene, light-harvest, functionalization, photovoltaics, photo-catalysis

1. Introduction

Graphene, a monolayer of graphite, has attracted intense interest in recent years because of its unique two-dimensional structure and excellent physical and chemical properties such as high electronic and thermal conductivity, great mechanical strength, and huge specific surface area. [1-4] However, due to its zero bandgap semiconductor characteristic and a highly transparent property in the visible spectrum, pristine graphene is severely limited in optoelectronic and photo-energy conversion applications.

Photoactive graphene in recent years bring up impressive phenomena that remarkably sustain and expand the graphene research interests. The rise of photoactive graphene in photonics and optoelectronics is evidenced by a spate of latest reports, typically photovoltaics and photoca-

talysts. Although there is some available literature covering various aspects of photoactive graphene,[1, 5, 6] a strategic update that reflects the newest progress, growing trends, and opening opportunities of photoactive graphene is required. This chapter pays particular attention to the development of photoactive graphene, including material preparation, the photophysical progress of excited organic molecules and graphene, as well as its applications in optoelectronics and photocatalysis.

1.1. What is photoactive graphene?

The term "photoactive graphene" generally refers to graphene that undergo a chemical or physical reaction when interacted with sunlight and/or ultraviolet light. Unlike the transparent pristine graphene, photoactive graphene shows optical response characteristics when light passes through it.

To date, two different approaches toward the preparation of photoactive graphene can be found in the literature. As shown in Figure 1 (a), the first is based on the bandgap engineering (opening and tuning) of pristine graphene,[7] and in the second strategy the photoactive graphene is obtained by chemical functionalization with photoactive moieties.[8] The most reported examples of the first route are roughly classified into four categories: (1) heteroatom doping;[9-11] (2) chemical modification;[12] (3) electrostatic field tuning;[13, 14] and (4) cutting graphene into nanoribbons.[15-19] As shown in Figure 1 (b), the second strategy for giving photoactive to graphene is chemical functionalization of graphene with photoactive units, including organic conjugated molecules and polymers, inorganic semiconductors particles and quantum dots, rare-earth metal complexes, and so on. This approach has been demonstrated to be a feasible route to achieve the photo-electron response of graphene to light.[8, 20] Herein, we will only discuss the progress and challenges related to the chemical functionalization approach to preparing photoactive graphene.
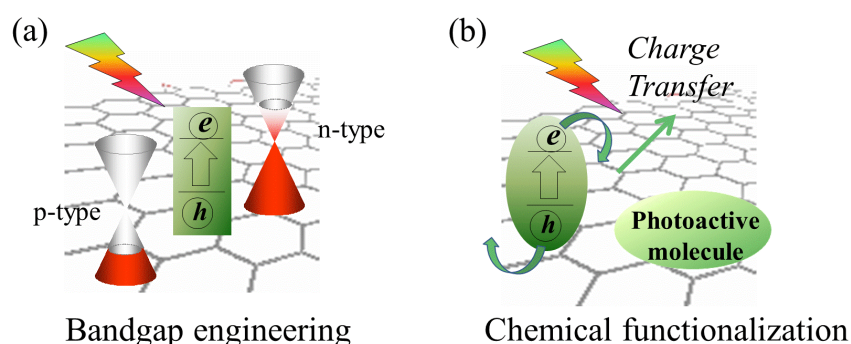

Figure 1. Two different approaches toward the photoactive graphene. One is based on the bandgap opening and tuning of pristine graphene (a), another strategy is chemical functionalization of graphene with photoactive moieties (b).

1.2. Why photoactive graphene?

Pristine graphene is made of sp^2 hybrid carbon atoms with the s, p_x, and p_y orbitals on each carbon atom forming three strong σ bonds with other three surrounding atoms.[21] The

formed valence and conduction bands touch at the Brillouin zone corners (so-called Dirac or neutrality points) making graphene a zero bandgap semiconductor with poor photoactive characteristic.[22, 23] Experimentally, the transmittance of the mechanically exfoliated graphene is overwhelming (97.7%), and thus it absorbs only 2.3% of light that passes through it (Figure 2).[2, 24] So it is impossible for graphene to absorb light when used as a photoactive material (Geim *et al.*, 2008).
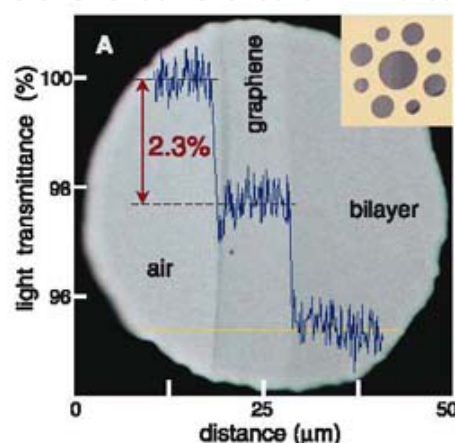
Figure 2. Optical adsorption property of graphene and its layer (Geim *et al.*, *Science* 2008, 320, 1308).

The poor photoactive characteristic of graphene leads to some major drawbacks in photo-energy conversion applications. For photovoltaic devices, using pristine graphene as active layer may significantly reduce the open circuit voltage, compared to conversional semicon-ductors.[25] Moreover, graphene is unfavorable for efficient photocurrent generation in photovoltaic devices. From a dynamics point of view, to output a photocurrent in an external circuit, the photo-generated carrier needs to separate from the photo-generation region before recombination.[26, 27] However, for graphene based transistor, the lifetime of photo-generated hot carriers was cooled down within several hundred femtoseconds, followed by electron–hole recombination on a picosecond timescale.[28, 29] Therefore, in order to improve the photo-energy conversion efficiency of graphene, it is necessary to extend the lifetime of photo-generated carriers of graphene.

Recently, endowing graphene photoactive property has been viewed as an effective approach to exploit the advantages of graphene in photovoltaics and photocatalytics.[30] The photoac-tive graphene can play a significant role in photovoltaics and photocatalysts resulting from the synergy effect of the charge transfer based in the photoactive graphene. For photoactive graphene, the propensity of graphene to interact with excited state photoactive moiety is often involve energy- and/or charge-transfer processes, where the excited fluorescent moieties is served as excellent probes by monitoring their emission evolution.[31] Meanwhile, the high charge mobility of graphene promotes it can be used as efficient acceptors to enhance photo-induced charge transfer for improving photocurrent conversion performance. The effective nonradiative deactivation of the excited photoactive moieties on graphene surface by interfa-

cial charge transfer is necessary for the improvement of the conversion efficiency from optoelectronic and photo-energy to electricity.

In recent years, there has been a growing interest in graphene functionalized with photoactive units owing to their significance in both fundamental research and practical applications. Recent research results have demonstrated that chemical functionalization of graphene with photoactive moieties is a necessity to harvest its full potential.[8]

2. Rational design of photoactive graphene

Graphene can be functionalized at the basal plane and the edges.[32] On the basal plane, sp^2 hybridization of carbon leads to a strong covalent bonding, as well as delocalization of the π electrons. The sheet edges are considered the most reactive sites,[33] and the dangling bonds at edge sites of graphene are highly reactive to guest atoms or molecules. In addition, the functional molecules attached onto the basal plane of graphene lead to modification of the π–π conjugation and thus the physical and chemical properties and the electron density distribution. There are generally three major purposes for chemically functionalizing graphene: enabling its solution processing, tuning its energy level and gap, as well as providing photoactive functionalities.[8]

2.1. Processability

A major obstacle in the synthesis and processing of bulk-quantity graphene sheets is the preparation of monolayer graphene and its insolubility, with the latter being responsible for poor handling and manipulation during graphene processing.[34, 35] Graphene has a strong tendency to cluster together into aggregation, caused by the electrostatic forces and the strong π–π interaction between individual graphene flakes, which make further manipulation and device fabrication using graphene difficult.[36] For this reason, covalent and noncovalent manners for modification of graphene have been developed for exfoliation and dispersion of graphene.[37] Besides, by derivatizing graphene with different moieties, the solubility of graphene can be tuned to suit varied solvents needed for different applications. For example, chemically grafted CH_2OH-terminated regioregular poly(3-hexylthiophene) (P3HT) onto carboxylic groups of graphene oxide (GO) *via* amidation reaction; the resultant P3HT-grafted GO sheets are soluble in common organic solvents, which facilitates the structure/property characterization and the device fabrication by solution processing.[38]

2.2. Energy level tuning

Experiment and theory studies demonstrated that semiconductor graphene (p-type and n-type) can be obtained by modifying graphene with organic semiconductor molecules (electron-acceptor and electron-donor), which provides a simple and nondestructive way of tuning the Femi level and controlling the charge carriers concentration of graphene.[39] As shown in Figure 3, for the p-type graphene, the Fermi level shifts upward relative to the Dirac point when the electron-acceptor coverage increases. In contrast, for the n-type

graphene, the Fermi level shifts downward relative to the Dirac point when the electron-donor coverage increases.[40]
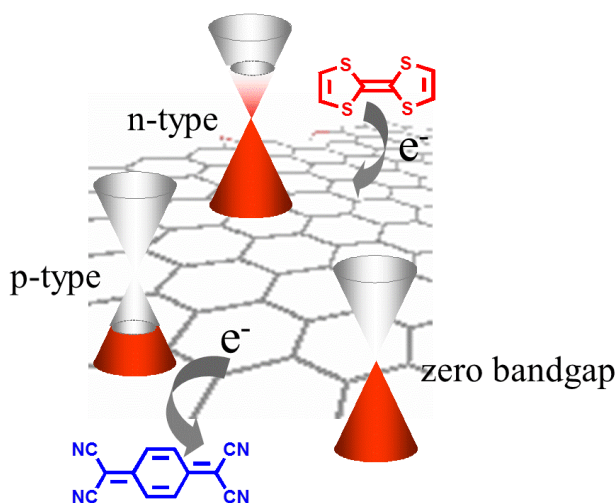
Figure 3. Doping graphene with semiconductor donor and acceptor molecules move the Fermi level up or down with respect to the Dirac point.

Wang *et al.* presented an effective route for preparation of both n-type and p-type graphene through adsorbing organic semiconductor molecules: one is the tetracyanoquinodimethane derivative (F4-TCNQ) and the other, the vanadyl-phthalocyanine (VOPc). The Kelvin probe force microscopy characterization results demonstrated that the F4-TCNQ molecules obtained electrons from graphene, but VOPc donated electrons to graphene. This phenomena indicated that chemical functionalization of graphene is a feasible approach for bandgap opening and tuning of graphene, which may have great implications for future large-scale applications of graphene-based nanoelectronics.[41] Pati *et al.* studied the modification in the electronic structure, as well as optical and transport properties of graphene induced by molecular charge transfer using ab initio density functional theory and Raman spectroscopic studies of modified graphene systems. They found that donor and acceptor molecules adsorbed onto the graphene surface exhibited effective molecular charge transfer, giving rise to mid-gap molecular levels with tuning of the band gap region near the Dirac point.[42]
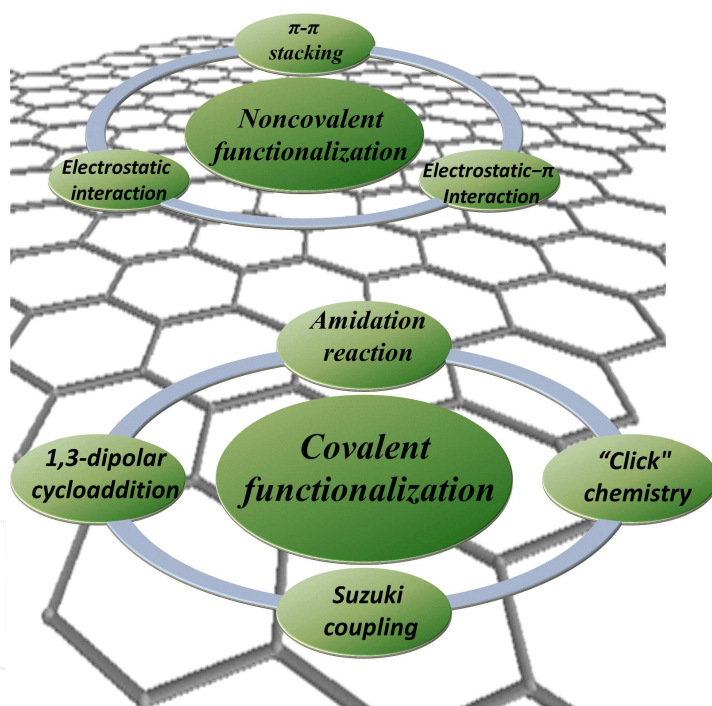
2.3. Chemical functionalization

The chemistry of graphene is a powerful route to tailor its properties through introduction of various chemical functional groups to graphene.[32] For most applications, graphene need to be integrated with other functional materials, and the modification of graphene *via* chemical approach holds promise for tuning the electronic and optical properties of graphene, controlling interfaces with other materials, and tailoring surface chemical reactivity.[43] Therefore, functionalization of graphene with various functional components is considered to be crucial for graphene processing.[44, 45]

Similar to fullerenes and carbon nanotubes (CNTs), functionalization of graphene with different functional groups can open up new routes to hybrid materials that exhibit even more exciting features than graphene itself.[46] The design and feature tuning/altering of transparent pristine graphene by integrating a versatile electron-donor system has attracted more attention. However, modification of the flat and rigid structure of graphene is a more challenging work than that of the curvature structured fullerenes and carbon tubes because of the necessity to overcome a high-energy barrier.[47, 48]

Recently, rational design and efficient strategy for preparation of photoactive graphene have achieved considerable progresses, which are motivated by many potential applications of photoactive graphene. For example, a large number of photoactive graphene with different properties and structures have been designed and synthesized. As shown in Figure 4, photoactive moieties and graphene were linked through either covalent functionalization approach, such as amidation reaction, cycloaddition, Suzuki coupling, "click" chemistry, or noncovalent functionalization manner, including π–π interaction, electrostatic interaction, and electrostatic–π interaction.

Figure 4. Chemical functionalization approach for preparation of photoactive graphene.

Photoactive organic moieties, including small molecules and conjugated polymers have been used to prepare photoactive graphene. The above-mentioned organic photoactive molecules are generally planar, electron-rich, and liable to photochemical electron-transfer process and show remarkably high extinction coefficients in the visible region. It is expected that by combining graphene with photoactive molecules, multifunctional graphene composites for optical and/or optoelectronic applications may be generated.[49]

2.3.1. Covalent functionalization of graphene

Recently, combining graphene with photoactive organic functional components, including small molecules and polymers, has attracted widespread attention, and a number of important photoactive moieties have been attached either to edge or the basal plane of graphene surface through covalent functionalization or noncovalent functionalization approaches.

Covalent functionalization of graphene with photoactive small molecules offers key advantages such as greater stability of the composite materials, and control over the degree of functionalization, and good reproducibility.[50] Meanwhile, conjugated polymers are one of the most successfully exploited classes of materials due to the incredible variety of chemical structures and their relatively low cost, facile processing, and their possible recyclability and applicability as sustainable materials.[51] Employing these organic photoactive molecules to functionalize graphene has grown to become a crucial branch in nanoscience and nanotechnology, which offers significant potential in the development of advanced photoactive graphene materials in numerous and diverse application areas.[52]

Amidation reaction: Chen *et al.* reported the first example of covalently attaching porphyrin units onto graphene, and explored the photophysical properties of the graphene composites. [53] The synthesized porphyrin–graphene composites consist of amino-containing porphyrin ($TPP-NH_2$) molecule and GO covalently bonded together *via* amidation reaction. Fourier transform infrared (FTIR) spectroscopic characterization confirmed that the $TPP-NH_2$ molecules had been covalently bonded to the edge of GO by the amide linkage. The linear relationship between the absorption and the concentrations of graphene moiety in the composites indicates good dispersibility of composite. Moreover, the fluorescence quenching of $TPP-NH_2$ was observed, indicating that there is a strong interaction between the excited state of $TPP-NH_2$ and graphene moieties in the composite. Kang *et al.* used arylamine-containing conjugated polymer TPAPAM to covalently modify GO.[54] The covalent attachment of TPAPAM onto the GO *via* amide linkage was confirmed by XPS and FTIR spectroscopy. In contrast to fluorescence quenching often observed in luminescence molecule–graphene systems, the steady-state fluorescence spectra showed that electronic interaction between TPAPAM and GO entities resulted in enhancement of the fluorescence intensity of the parent TPAPAM. In addition to the examples provided above, amidation reaction was also applied to link fullerene,[55] phthalocyanine zinc (PcZn),[56] and oligothiophene moieties to the surface of graphene.[57]

Cycloaddition reaction: Feringa *et al.* applied one-pot cycloaddition approach to prepare porphyrin derivative functionalized graphene composites.[37] The excited state energy/electron-transfer processes between graphene and the covalently attached porphyrin molecules was demonstrated from fluorescence quenching and reduced fluorescence lifetime phenomenon.[58] Guldi *et al.* presented their work on linking photoactive phthalocyanines (Pcs) to graphene surfaces.[50] Covalent functionalization of the fewer-layered graphene with Pcs was achieved through 1,3-dipolar cycloaddition and the esterification reaction yielded Pcs-graphene nanoconjugate.

Suzuki coupling reaction: The 2010 Nobel Prize for Chemistry rewarded a family of palladium-catalyzed coupling reactions for forging carbon–carbon bonds, which have already helped to create new graphene hybrid materials. Ma *et al.* reported covalent functionalization of graphene with polythiophene through Suzuki coupling reaction.[59] A donor–spacer–acceptor triad conjugated polymer containing fluorene, thiophene, and benzothiadazole moieties, which was covalently attached to r-GO *via* Suzuki polymerization procedure.[60] These polymer–graphene composites show excellent solubility in different type of solvents and exhibit superior optical-limiting performance. Moreover, Loh *et al.* applied Heck reaction to synthesize dye molecule functionalized graphene composite.[61] In their work, r-GO was covalently modified by diazonium, followed by the Heck reaction to give a 4-(2-(pyridin-4-yl)vinlyl)phenyl group modified graphene. Considering the high efficiency of the palladium catalyzed C-C coupling reaction, we believe that more and more attention will be paid to the synthesis of photoactive-moieties–graphene hybrid materials.

"Click" chemistry: "Click" chemistry has emerged as a useful strategy for rapid and efficient attachment of functional groups to various materials since its reinvention in 2001.[62] In previous works, "click" chemistry has succeeded in linkage of various functional groups onto CNTs and fullerenes.[63, 64] Zhang *et al.* reported a facile approach for covalently attaching various photoactive organic molecules onto graphene surfaces *via* "click" chemistry.[65] Kaminska *et al.* presented a one-step protocol for simultaneous reduction and functionalization of GO with a dopamine derivative bearing an azide function. The chemical reactivity of the azide moieties was demonstrated by a post-functionalization with ethynylferrocene using "click" chemistry.[66] Salvio *et al.* treated GO suspension with sodium azide, and the obtained azido derivative can be used to functionalize the graphene oxide with long alkyl chains through a "click" chemistry approach. This functionalization results in the exfoliation of this material in organic solvent.[67] Salavagione *et al.* reported the preparation of polyfluorene-modified graphene by azide–alkyne "click" coupling.[68]

2.3.2. Noncovalent functionalization of graphene

Noncovalent functionalization strategy is advantageous in the preservation of the properties of the graphene, while weak forces between absorbed molecules and graphene may lower the load transfer in the composite, and as a result of free molecules and molecules adsorbed on graphene exist in equilibrium in the solution. Moreover, photoactive small molecules are commonly planar in structure and electron-rich; these advantages promote the interaction between the small molecules and graphene *via* π–π stacking, electrostatics interactions, and electrostatic–π interactions, as illustrated in Figure 4. Meanwhile, conjugated polyelectrolyte with highly electron-delocalized backbones and ionic side chains are water-soluble, fluorescent, rigid-rod polymers, which thereby combine the electronic properties of conjugated polymers with the electrostatic behavior of electrolytes. The conjugated polyelectrolytes and graphene hybrid materials generally have good solubility in polar solvents.

Via π–π stacking: Highly aromatic molecules may assemble themselves onto graphene surface *via* π–π stacking interaction. The π–π stacking interaction between aromatic skeleton of graphene and conjugated planar molecules afford synergistic binding interactions. Loh *et al.*

observed that the perylene wire could be coated on graphene surface to form a hybrid system. Such type of synergistic interaction between organic nanostructures and graphene affords a novel route to synthesis of hybrid materials with new properties and novel functions.[69] Mai *et al.* synthesized methyl blue functionalized graphene which exhibited excellent solubility and stability in water due to the photoactive molecules that were noncovalently stacked onto the basal plane of graphene.[70]

Via electrostatic interaction: GO and r-GO in aqueous dispersion is expected could act like a two-dimensional conjugated polyelectrolyte because of they are negatively charged, on which the cationic aromatic derivatives can be assembled through electrostatic and π–π stacking interactions. Shi *et al.* reported the supramolecular assembly and complexation of r-GO sheets with cationic porphyrin derivative in aqueous media.[71] In the UV-visible spectra, the Soret band of prophyrin showed a large bathochromic shift (37 nm) after linking on r-GO sheets. This phenomenon was attributed to the structure isomerization of porphyrin, which was caused by twist of their cationic methylpyridinium groups. For the structure of the unstrained porphyrin derivative, four cationic methylpyridinium moieties are nearly perpendicular to the plane of porphyrin because of the strong steric hindrance.[72] When the pyridinium groups rotate toward the coplanar conformation with respect to the flattened porphyrin ring, the π conjugation and electron-withdrawing effect of porphyrin will be enhanced.[73] Zhang and coworkers employed a specially designed anionic CPE to stabilize r-GO during the hydrazine-mediated reduction in aqueous solution.[74] The conjugated-polyelectrolyte (CPE) function-alized r-GO sheets show good solubility in a variety of polar solvents, because of the presence of double bonds along the backbone-endowed $PFVSO_3$ with a preferred coplanar backbone geometry, which matched the flat shape of r-GO and thus further enhanced the π–π interactions.

Via electrostatic–π interaction: The chemistry community now recognizes the electrostatic–π interaction as a major force for molecular recognition.[75] Jia *et al.* presented a novel molecular strategy based on cationic dye Rhodamine B (RhB) to functionalize graphene *via* in situ reduction.[76] RhB was designed to prevent the aggregation of graphene when it was modified to graphene surface through cation–π and π–π interaction. Zhang *et al.* reported the design and synthesis of a novel amphiphilic graphene composite by using amphiphilic coil–rod–coil conjugated triblock copolymer (PEG-OPE) as stabilizer to improve the dispersibility of r-GO. The rational designed PEG-OPE is composed of one lipophilic π-conjugated oligomer and two hydrophilic PEG coils. The conjugated rigid-rod backbone of PEG-OPE prefers to adsorb onto the basal plane of r-GO *via* strong π–π interaction; whilst the lipophilic side chains and two hydrophilic coils of the backbone would fly away from the surface of r-GO to form an amphiphilic outer layer, consequently facilitating the dispersion of modified r-GO common solvents.[77]

3. Energy transfer and charge transfer

It is believed that electron-transfer and energy-transfer processes between photoactive chromophores and graphene are the two fundamentally important processes responsible for the photophysical processes of photoactive graphene.

Generally, each decay step of an excited photoactive molecule is characterized by its own rate constant and each excited state is characterized by its lifetime. In solution, when the intramolecular deactivation processes are not too fast, that is, when the lifetime of the excited state is sufficiently long, an excited photoactive molecule may have a chance to encounter graphene. In such a case, some specific interaction can occur, leading to the deactivation of the excited state by second-order kinetic processes.[78]

Disentangling the detailed charge-transfer and energy-transfer dynamics in photoactive graphene composite is essential for a full understanding of their photophysical properties, and is expected to open new avenues for their unique and specific applications.[79] For this purpose, characterization of charge- and energy-transfer rates is essential. Although the investigations on the properties of the excited states and excitons are very challenging, this generally involves delicate fluorescence lifetime and transient absorption spectroscopic measurements.

3.1. Charge transfer

Excited-state photophysical processes between graphene and photoactive moieties have been of much importance because of their relevance to optoelectronic and photo-energy conversion applications.[80] In a considerable number of cases, the phenomena of graphene to quench fluorescence of aromatic molecules is shown to be associated with photo-induced electron-transfer process, and can be conveniently verified by the fluorescence decay and time-resolved transient absorption spectroscopic characterizations. These measurement results provide quantitative insights, both kinetically and spectroscopically, into the nature of the interactions of graphene and photoactive molecules.

Kamat *et al.* reported the excited electron-transfer interaction between the photo-excited porphyrin and graphene (Figure 5).[81] In their work, cationic 5,10,15,20-tetrakis (1-methyl-4-pyridinio)porphyrin tetra (p-toluenesulfonate), noted as TMPyP, was employed to noncovalent functionalization of graphene (Kamat *et al.*, 2010). Upon complexation with graphene, the fluorescence lifetime of porphyrin was significantly reduced from 5 ns to 1 ns. Moreover, the femtosecond transient absorption measurements confirmed the formation of a short-lived singlet excited state of ^{1}(TMPyP)* and a subsequent longer-living porphyrin radical cation of (TMPyP)$^{·+}$ with an absorption maximum around 515 nm, which clearly indicated the occurrence of electron-transfer process between TMPyP and graphene. Furthermore, it inferred that electron injection from the ^{1}(TMPyP)* to the graphene film is feasible because the oxidation potential of the ^{1}(TMPyP)* is -0.29 V *vs* normal hydrogen electrode (NHE), which is lower than the Fermi level of the graphene material (0 V *vs* NHE); the resulting energy gap hence provides sufficient driving force for the charge-transfer process.[7, 82]

Malig and coworkers reported the transient absorption characterization studies on the interactions of zinc phthalocyanines (ZnPc) oligomer–graphene composite both in the ground state and excited state. The experiment results confirmed that the nature of these interactions is electron transfer from ZnPc to graphene, both in the ground and in the excited state, affords an electron-transfer product that survives for several hundred picoseconds.[83] More interestingly, by combining with characterization results of the steady-state and femtosecond time-
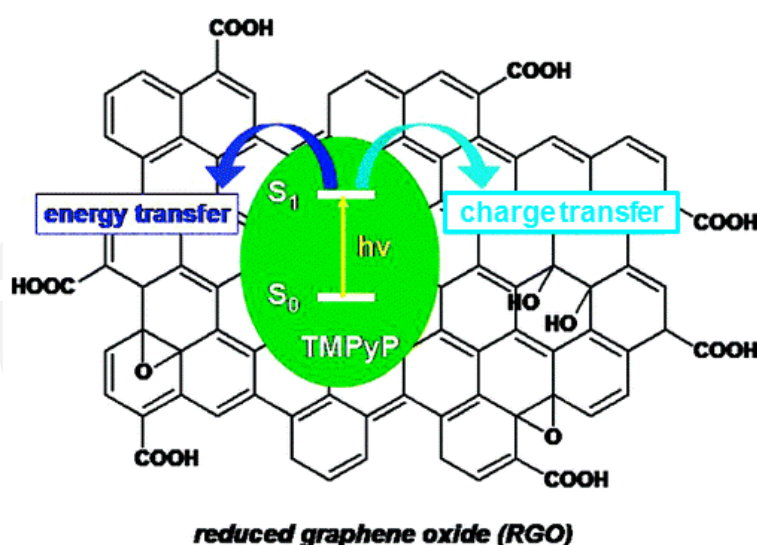
Figure 5. Photo-excited TMPyP molecules undergo charge-transfer interaction with r-GO (Kamat *et al., ACS Nano* 2010, 4, 6697-6706).

resolved spectroscopy, Mohammed *et al.* found that the charge-transfer process at the porphyrin–graphene carboxylate interfaces could be tuned from zero to very sufficient and ultrafast by changing the electronic structure of the meso unit and the redox properties of the porphyrin cavity.[84]

3.2. Energy transfer

Graphene exhibits metallic behavior in many respects, in particular, graphene is shown to be a good exciton sink due to the highly efficient nonradiative energy transfer from the nearby fluorescent units through dipole–dipole coupling, which is also known as Forster-type resonant energy transfer (FRET).[85-89] Recently, FRET has been employed for interpreting the energy interaction of graphene combined with photoactive materials such as semiconductor nanoparticles and dyes (Figure 6).

Theoretical and experimental studies have disclosed efficient energy transfer to graphene and the process was found to be useful in identifying graphene sheets both on substrates and in solution.[90] Sebastian *et al.* studied the distance dependence of the rate of resonance energy transfer from the excited state of a dye (pyrene and nile blue) to the π skeleton of graphene.[91] Using the tight-binding model for the system and the Dirac cone approximation, the analytic expression for the rate of energy transfer from an electronically excited dye to graphene was obtained. It was found that graphene is a very efficient quencher of the electronically excited states and that the rate is proportional to d^{-4} (d is distance). Koppens *et al.* measured Rhodamine emitter lifetimes as a function of Rhodamine–graphene distance d, and found agreement with a universal scaling law, governed by the fine-structure constant. The observed emitter decay rate is enhanced 90 times (energy-transfer efficiency of ~99%) with respect to the decay in vacuum at distances d ≈ 5 nm.[88] Zhao *et al.* reported

their study on employing ethidium bromide (EB) as a model for constructing an inexpensive and label-free biosensor to improve the sensitivity performance of GO–DNA-based sensors. Experiment results indicated that the fluorescence of EB was quenched by GO in the process of long-range resonance energy transfer.[92]
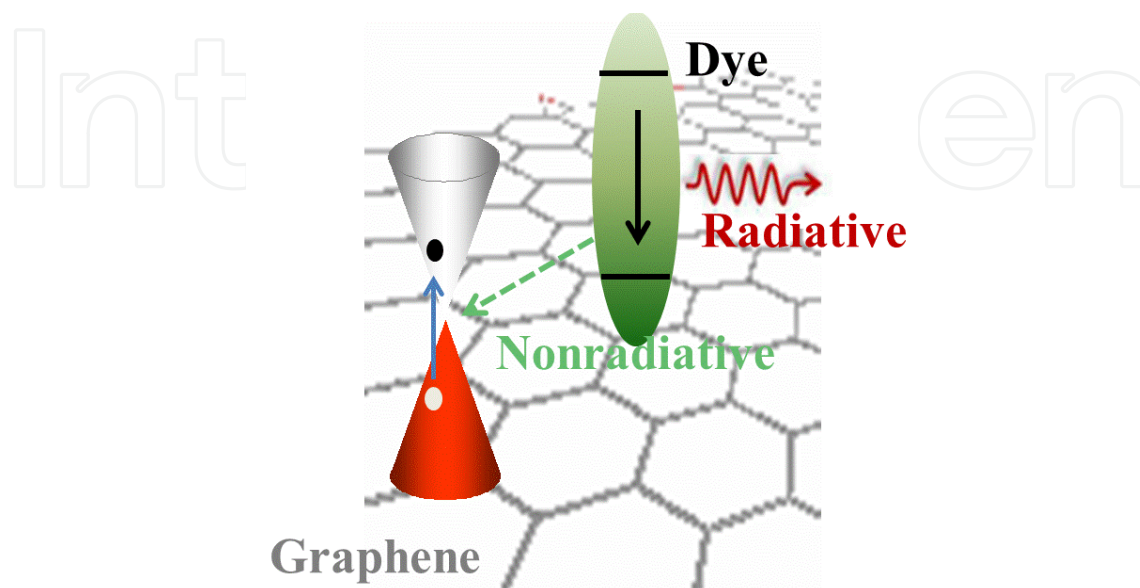
Figure 6. Nonradiative decay by dipolar coupling to electron–hole pair transition in the graphene surface and to a lower extent through the emission of radiation.

4. Applications of photoactive graphene

Covalent or noncovalent functionalization of graphene with various photoactive components has been considered to be crucial for graphene processing.[44, 45] The photoactive graphene *via* chemical approach holds promise for optimizing dispersibility in common solvents, tailoring surface chemical reactivity, and tuning the electronic properties of graphene.[43] Therefore, chemical functionalization strategy produced photoactive graphene has many advantages over pristine graphene and bare photoactive molecules, especially in the field of photo-energy conversion devices and as synergistic catalyst for organic synthesis reactions.[93, 94]

4.1. Organic Photovoltaic (OPV)

A typical OPV cell consists of a transparent conductor, a photoactive layer, and an electrode. OPV cells rely on organic small molecules or polymers for light absorption and charge transport. Different from the traditional inorganic semiconductors where free electrons and holes are easily generated under solar illumination, in OPV device, neither bilayer and planar heterojunction structure or an intermixed bulk heterojunction (BHJ) structure, a strongly
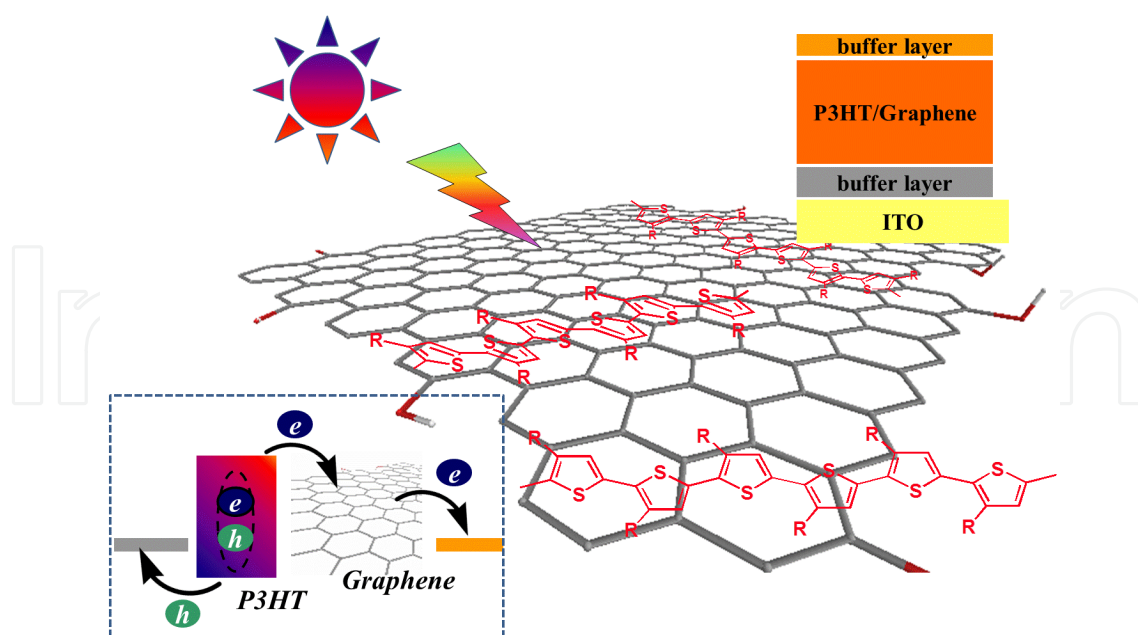
Figure 7. Organic solar cells prepared by using P3HT/graphene composite as photoactive layer.

bound electron–hole pair is generated, and the electron–hole pair needs to be separated by a acceptor material.[95, 96]

As shown in Figure 7, for P3HT-modified graphene-based solar cells, graphene is expected to be a good electron-acceptor candidate, because large donor/acceptor interfaces for charge generation and a continuous pathway for electron transfer will be formed owing to the large two-dimensional plane structure and the one-atom thickness property of graphene.

Dai *et al.* created a bilayer photovoltaic device with solution-cast P3HT-GO heterostructure as donor and electron acceptor of thermally evaporated C60 layer C_{60}.[38] The power conversion efficiency (PCE) of P3HT-GO solar cells is two times larger than that of the P3HT/C_{60} device. Liu *et al.* prepared a novel type OPV device with BHJ active layer of a solution-processable functionalized graphene (SPFGraphene) as the acceptor material and electron donor compound of P3HT.[97] In the ITO/PEDOT:PSS/P3HT:graphene/LiF/Al photovoltaic device, a PCE of 1.1% was achieved. The SPFGraphene acts as charge dissociation and provide percolation paths for electron transfer, which promote the active layer yields better carrier mobility, easy excitons splitting, and suppression of charge recombination, thereby improving photovoltaic action. Liu and coworkers introduced SPFGraphene in P3HT/PCBM photovoltaic devices. By taking advantage of the electron-accepting feature of fullerenes and the high electron transport capability of graphene, a PCE as high as 1.4% was obtained.[98]

4.2. Photocatalysts

Graphene-involved semiconductor photocatalysts have attracted extensive attention because of their usefulness in environmental and green chemical catalyst applications.[99] Recently, photoactive-graphene-based photocatalysis has been widely used to catalyze various organic
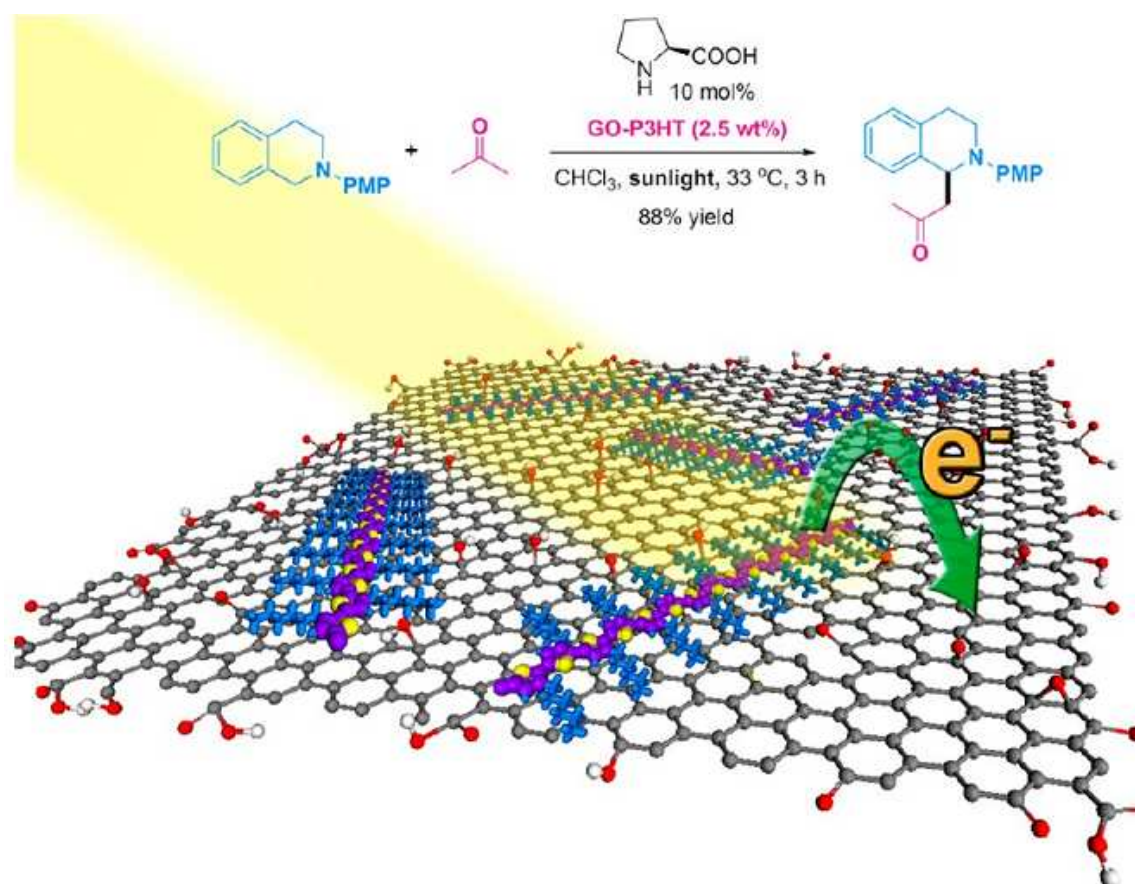
Figure 8. GO/P3HT composite as a synergistic photocatalyst (Loh *et al.*, *J. Phys. Chem. Lett.* 2012, 3, 2332-2336).

reactions. For example, in Figure 8, photoactive graphene of noncovalently bonded graphene–polymer (P3HT) composite shows significant advancement of photocatalystic performance in Mannich reaction over commercial photocatalyst P25 (Loh *et al.*, 2012).[100] Transient optical absorption studies have inferred that the tertiary amine is oxidized by the positive hole on the highest occupied molecular orbital (HOMO) of P3HT *via* single electron transfer to form the radical cation. At the same time, the excited electron is injected from the lowest unoccupied molecular orbital (LUMO) of P3HT into GO, which is then used to activate molecular oxygen to form the dioxygen radical anion; the latter can be stabilized by the aromatic scaffold in GO. [93] Pan *et al.* found that incorporation of Rose Bengal (RB) with GO sheet can provide higher catalyst actively of the visible light induced oxidative C-H functionalization of tertiary amines, even there was no direct physical interactions between RB and GO.[101]

5. Conclusions and outlooks

This chapter presented some important features of photoactive graphene, from material synthesis, electron/energy-transfer interaction to organic photovoltaic and photocatalystic applications. Of particular interest is the utilization of graphene as a two-dimensional platform

to anchor organic conjugated aromatic molecules and their applications in photo-energy conversion and photocatalysis.

However, despite many successful examples showing that photoactive graphene holds excellent properties and great potentials in various applications, there are still some problems that need to be overcome. One major drawback for the use of photoactive graphene in photo-energy conversion and photocatalystic application is light absorption without directly generating long-lived charge carriers.[21] Hence, one needs to take caution in optimizing the modification degree of photoactive moieties functionalized to graphene surface. Moreover, optimization of the charge carriers transfer channel of photoactive graphene, as well as precisely controlling any combination of direction, position, and distance of graphene and photoactive molecules are also necessary for high-efficiency photo-energy conversion application. More careful design of the chemical functionalization is necessary to exploit the electronic properties of graphene and photoactive groups, for example, multifunctional graphene materials with different moieties can provide new ways to design charge-transfer systems for light energy conversion.

From another point of view, chemists will be needed to develop strategies for rational design and facial synthesis of photoactive moiety; not only morphology and electronic structure, but also redox properties are also important for tuning the charge-transfer process of photoactive graphene, because the more precisely manipulated the charge-transfer efficiency of photoactive moiety–graphene interfaces, the more favorable it is to improve the photo-electron conversion efficiency and photocatalytic performance. With more progresses in the material optimization and novel device design, we believe that photoactive graphene will lead to a wide range of applications.

Finally, the photoactive graphene researches are still at their initial stages. With the multidisciplinary efforts from chemistry, physics, and materials science, we believe that much more progresses in the applications of photoactive graphene will become a reality in the near future.

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