

# Graphene oxide: Exploiting its unique properties toward visible-light-driven photocatalysis

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## ABSTRACT

The oxygen-containing functionalities on the aromatic scaffold of graphene oxide (GO) enable these materials to facilitate both ionic and non-ionic interactions with a huge range of molecules. Endowed with a plethora of extraordinary properties, GO demonstrates remarkable potential in the field of photocatalysis. Furthermore, the tunability of its physicochemical properties by the facile exploitation of surface modifications and edge defects renders GO an even more intriguing nanomaterial. In this paper, the fundamental aspects on the manipulation of GO for the enhancement in photocatalytic performance will be thoroughly discussed. To mediate further research and development in this area, the current technical challenges faced as well as future research directions will also be included in this paper.

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## 1. Introduction

At present, frontier scientific and technological research into the fields of energy and environmental protection are becoming increasingly challenging due to the need for key materials with high efficiency and functionality. Ignited by immense technological potential, the research on advanced carbon nanomaterials, particularly graphene has experienced an extensive growth over the past decade [1–4]. Fig. 1 depicts the exponential increase in the number of publications based on graphene and its derivatives from 2004 to 2014. As a simple hexagonal lattice of carbon atoms, graphene provides a highly electronic and thermally conductive surface, which is also the thinnest known material and the strongest ever reported [5].

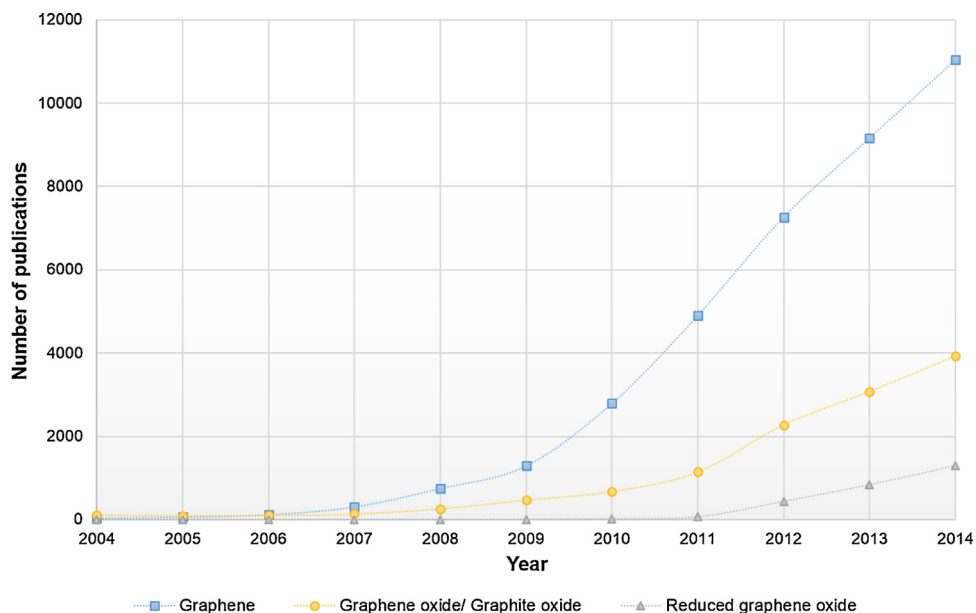
One specific branch of graphene research is focused on chemically derived graphene oxide (GO) [6,7]. As a newly emerging two dimensional (2D) material, GO possesses many intriguing properties, including mechanical, electronic, optical, electrochemical and chemical reactivity [8]. GO sheets are composed of two primary regions: (1) the hydrophobic  $\pi$ -conjugated  $sp^2$  domains and (2) the  $sp^3$  domains with hydrophilic oxygen-containing functional

groups. The widely accepted structure of GO depicts carboxylic acid at the edges, and hydroxyl and epoxide groups residing at the basal plane [6]. Despite the distortion of the intrinsic conjugated  $\pi$  system, these complex cocktails of functionalities can provide potential advantages for employing GO in numerous applications. The polar oxygen-containing groups on GO render it strongly hydrophilic, allowing it to be dispersed in a number of solvents, particularly in water [9]. Furthermore, the physicochemical properties of GO can be tuned by engineering its atomic and chemical structures [10]. From a broader perspective, the fascinating properties and tunability inherent to GO sheets are very promising for facilitating a wide range of applications, including but not limited to electronics (conductive films and sensors) [11], composite materials [12], clean energy devices [13] and biology [14]. Several reviews on these topics have been reported in literature [15–20]. However, to the extent of our knowledge, no review articles on the application of GO in the field of photocatalysis have been published.

Photocatalysis has become one of the most studied fields due to the increasingly cogent call for environmental remediation [21]. The direct conversion of solar energy into chemical energy through this system provides an opportunity to simultaneously address both the environmental and energy issues faced today. While many different photocatalytic materials such as semiconductors, transition-metal complexes *etc.* have been developed [22], the possibility of employing pure GO nanosheets for efficient

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**Fig. 1.** Plot detailing the number of publications on graphene and its derivatives between 2004 and 2014; data were obtained using Scopus: keywords “graphene”; “graphene oxide OR graphite oxide” and “reduced graphene oxide”; respectively.

photocatalysis is extremely thought-provoking. Hence, in the paper, we will present a concise account on some fundamental aspects of GO and discuss how its properties can be controlled and tuned to benefit the process of photocatalysis. Advancements on the use of GO as a photocatalytic material will also be thoroughly reviewed. Finally, a brief summary and an outlook on the major challenges and opportunities for future research will be presented. It should be noted that historically, GO sheets have functioned mainly as heterogeneous supports for semiconductor nanoparticles [23–25], and its use as a standalone photocatalytic material is very rare. Hence, the main objective of this paper is to provide some insights into the possibility of employing bare GO sheets as efficient “carbocatalysts” in photocatalytic applications as varied as dye degradation, water splitting and so forth.

## 2. Unique properties of GO—key criteria affecting photocatalytic performance

### 2.1. Structural features

In essence, the structure GO can be viewed as graphene but covalently decorated with oxygen-containing groups on its planes and edges. In that account, GO still physically retains its original 2D nature and the benefits entailed with this structure. First and foremost, 2D materials associate to large specific surface area, yielding a theoretical value of as high as  $\sim 2630 \text{ m}^2/\text{g}$  as seen in the case of pristine graphene [26]. In fact, through atomic force microscopy (AFM), the apparent thickness of single-layer GO was found to be around  $\sim 1 \text{ nm}$  (Fig. 2(a)), which is a small deviation to the thickness of pristine graphene that varies in the range 0.3–0.6 nm [27–29]. This difference is accounted to the presence of bounded oxygen functionalities and the out-of-plane protrusion of  $\text{sp}^3$ -hybridized carbon atoms. From a photocatalysis viewpoint, this massive area is helpful as GO can host a great number of active sites that can be directly accessible to the reactive species. In addition to that, the 2D structure of GO can also eliminate the occurrences of volume recombination from which ordinary bulk semiconductor suffers, that will be detrimental to the efficiency of the photocatalytic process [30]. This is understandable since the atom-thin structure of GO guarantees the rapid transfer of carriers to the surface, thus

leaving more carriers at disposal which can be successively consumed by acceptor molecules to drive the desired redox reaction.

Unlike having a definite physical structure, the chemical structure of GO is somewhat ‘fluid’, as its stoichiometry varies depending on sample-to-sample variability and their synthesis protocol [8]. This is further made complex by the inhomogeneities in the GO structure in which the precise identity and distribution of oxygen functional groups remain an ambiguous subject. A widely adopted model of GO structure [31,32] depict that epoxide and hydroxyl are the dominant oxygen functionalities on the basal plane, while carboxylic acid, ketones, phenols and lactols groups accommodate at edge terminations (Fig. 2(b)). Together, these cocktails of oxygen functionalities act in concert to endow properties, which although relevant to GO are not typical of pristine graphene. The interaction of the basal plane with oxygen-functionalized groups leads to the modification of the  $\pi$ - $\pi$  conjugation and thus the electron density distribution, yielding the differences in its electrical and chemical properties, which benefit photocatalysis.

### 2.2. Electrical and optical properties

Even today, the precise electronic band structure of GO has not been clearly elucidated owing to the nano-scale inhomogeneities of the structure. The functionalization of graphene with oxygen groups involves a complex interplay of phenomena which influences graphene’s collective electrical, optical and chemical attributes. Essentially, the covalent addition of oxygen functionalities on the basal plane of graphene converts the original, unsaturated planar  $\text{sp}^2$ - of carbon atoms into a tetrahedral  $\text{sp}^3$ -electronic hybridization [34]. These in turn impose a structural disorder on the lattice, as shown in Fig. 3, which acts as transport barriers, since they interrupt the continuity of  $\pi$ -network which ordinarily allows classical carrier transport to occur. This removal of  $\pi$  electrons plays a mechanistic role in the change of electric properties by introducing a band gap *via* the symphonious removal of electronic states and emergence of new energy states from functionalizing oxygen groups. In that context, GO is viewed as an electronically hybrid material containing both conducting  $\pi$ -states from graphitic  $\text{sp}^2$ -hybridized carbons and a large energy gap between the  $\sigma$ -states from its  $\text{sp}^3$ -hybridized carbon

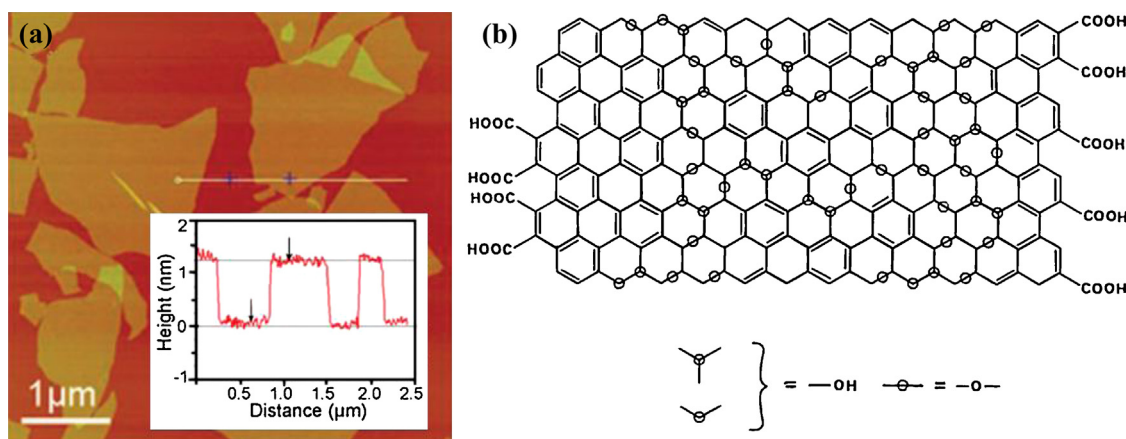


Fig. 2. (a) AFM image of GO sheet and an inset of its corresponding height profile [33] and (b) Structural model of GO as proposed by Lerf and Klinowski [32].

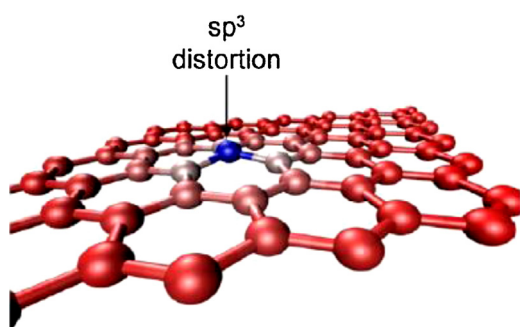


Fig. 3. Structural distortion resulting from  $sp^3$  electronic hybridization of carbon atoms in the graphene plane [34].

[35]. As a result, the variation of these  $sp^2$  and  $sp^3$  carbon fractions in GO by controlling oxidation or reduction parameters can be useful for manipulating bandgap energy in GO, and thereby allowing the tunability of its electrical properties to especially cater for photocatalytic application.

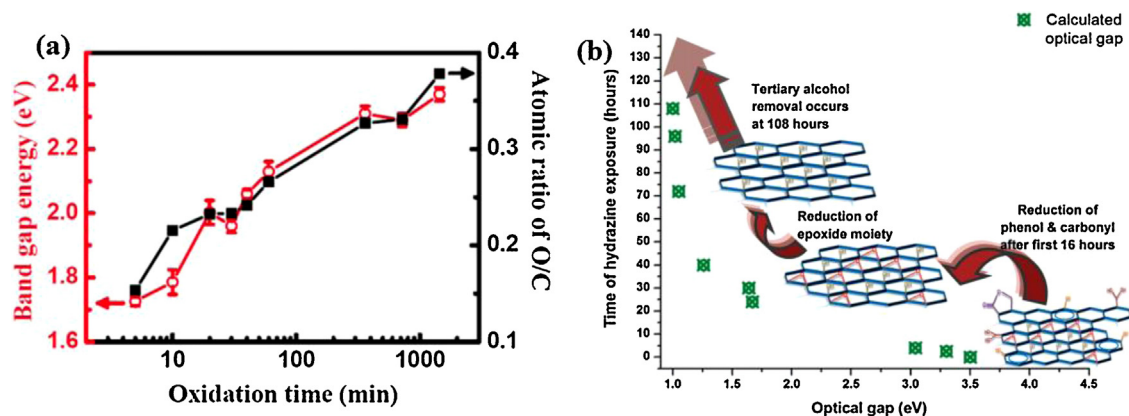
In agreement with this, a number of computational and experimental studies pertaining to GO reported an increase of bandgap energy in conjunction to oxygen coverage density (or O/C ratio) [36–41]. In particular, Jeong [36] have achieved this modulation in bandgap energy through varying the oxidation time during the Hummers process, while Mathkar [41] showed a different approach by reducing a highly oxidized starter GO which is shown in Fig. 4. The latter also showed the influence and accountability that specific functional groups have on the bandgap by probing the instance of removal for each functional group during the reduction process. It has been well established that for an ideal graphene, its empty  $\pi^*$  (anti-bonding) band and a filled ( $\pi$ -bonding) band, which makes up its conduction band (CB) and valence band (VB) respectively, degenerate and meet at the Dirac point in the Brillouin Zone, indicating that graphene has zero bandgap. The oxidation of graphene will however lead to the disruption of the graphene  $\pi$ -network which in turn causes the opening of a direct electronic bandgap. This is because the adsorption of oxygen groups breaks the sublattice symmetry and the oxidized sites creating strongly repulsive barriers for the  $\pi$ -electron wave functions, resulting in the gap opening at the Brillouin Zone boundary and the change in the electronic states from a semimetal to a finite gap semiconductor [42].

In a paper by Ito et al. [38], the authors studied the electronic properties of GO using first-principle calculations, though was modelled by only the adsorption of epoxy groups on one side of the graphene sheet. Fig. 5 shows the transition in the band dispersion with the increasing of O/C ratio. It was revealed that there occurs

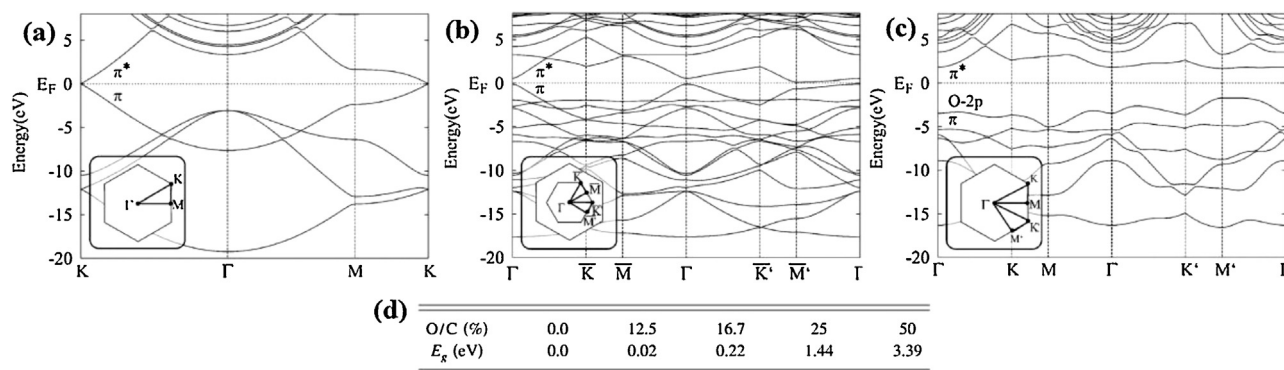
a hybridization between bonding  $\pi$  orbital of graphene and O  $2p_z$  orbital of epoxy group which weakens bonding between carbon atoms C–C. From Fig. 5(a–c), it can be witnessed that the width of the  $\pi$  band progressively narrowed with the O/C ratio, which indicated the localization of electronic states, and thus a decrease in transfer integral between C–C atoms in the graphene. As a result, at a high enough O/C ratio of 50%, the highest occupied molecular orbital (HOMO) which makes up the valence band state counter-changed from C–C  $\pi$ -orbital to a more positive O $2p$  orbital and the bandgap nature of GO changes from a direct to an indirect gap. Meanwhile the conduction band edge is mainly formed by the antibonding  $\pi^*$  orbital. This reconstruction and appearance of new energy state allows the opening of an energy gap in the range 2.8 eV–4.6 eV [38,43].

Additionally, Eda et al. claimed that isolated  $sp^2$  regions also exhibit quantum confinement-induced semiconducting behavior [44,45]. As previously stated, GO carries coexisting two domains consisting of  $sp^2$  and  $sp^3$  regions. The presence of these finite-sized molecular  $sp^2$  domains shrouded in  $sp^3$  matrix results in the confinement of  $\pi$  electrons in GO which are strongly localized [46]. In this case, the optical properties are governed by the  $\pi$  and  $\pi^*$  electronic levels of the  $sp^2$  clusters that lie within the band gap of  $\sigma$  and  $\sigma^*$  states of the  $sp^3$  matrix [47]. The outcome of the bandgap depends on the size, shape and fraction of these  $sp^2$  domains. From calculations based on density functional theory (DFT), local energy gaps of  $\pi$ - $\pi^*$  transition vary depending on the size of  $sp^2$  domains as surmised from Fig. 6(a). The calculated energy gap between HOMO and LUMO of a single benzene ring is  $\sim 7$  eV which reduces to  $\sim 2$  eV for an increased cluster of 37 rings. This implied that the higher the oxidation degree of GO, the more the  $sp^3$  fraction and proportionally the smaller the  $sp^2$  fraction, which formulate to higher energy gaps. In this sense, due to the random distribution and size of the coverage of oxygen groups on the GO sheet, GO will not show a well-defined bandgap as that seen from that in typical semiconductor materials. The schematic band structure of GO is shown in Fig. 6(b) where pink and blue represent conduction band and valence band respectively. The smaller  $sp^2$  cluster fragment has large energy gap due to quantum effects thus allowing photo-generation of electron-hole pairs. As a proof of concept, GO has also been subjected to photoconductivity studies [48], and a strong photoconductivity response of  $10 \mu\text{s}$  was observed that rose in intensity with increasing photon energy, which validated the presence of band gap and the generation of photo-induced charge carriers

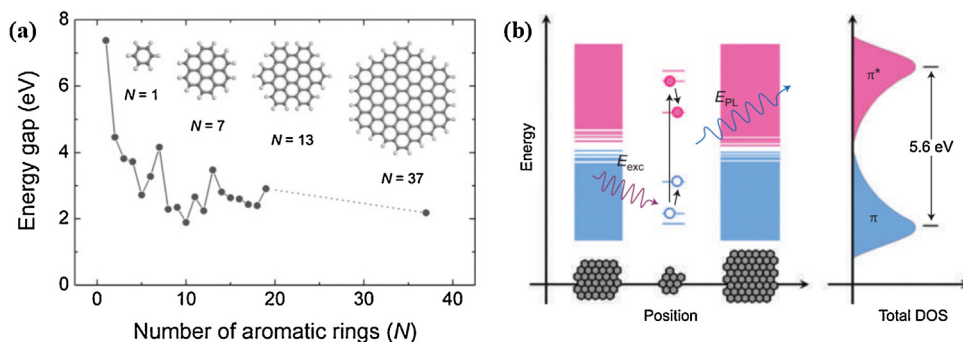
Essentially, GO with a bandgap energy of as wide as 2–4 eV can be obtained, which is theoretically more than sufficient to drive a number photocatalytic reactions; for example, 1.23 eV in the case of



**Fig. 4.** (a) Resultant bandgap of GO as a function of oxidation time in the Hummer's method [36], and (b) gradual decrease in bandgap upon a stepwise reduction of highly oxidized GO. Inset Figure shows a schematic of the approximate reduced graphene oxide (rGO) structure at that specific point of time [41].



**Fig. 5.** Band structure of (a) ideal graphene sheet (b) graphene sheet with 16.7% O/C ratio (c) graphene sheet with 50% O/C ratio, and (d) corresponding bandgap values for different O/C ratios [38].



**Fig. 6.** (a) Local  $\pi$ - $\pi^*$  energy gap and its correlation to number of aromatic benzene rings ( $N$ ) or analogously size of  $sp^2$  cluster retrieved from DFT calculations [44].

water splitting and 1.06–1.43 eV for  $\text{CO}_2$  photo-reduction reactions. Because of this, GO may become a popular next-generation photocatalyst because of its tunable electronic properties, which can be made optimal depending on its application. In addition to that, another unique feature of graphene is that it exhibits a strong optical absorption cross-section despite being a single-layer material, which is a beneficial trait for photocatalytic application [49].

### 2.3. Chemical reactivity

Although GO and its related materials such as rGO have been employed extensively as supports for various semiconductors and metal nanoparticles in photocatalysis [50–53], the graphene moiety in these hybrid or composite is not considered as the catalytically active component in the presence of other catalytically

active nano-crystals which are tethered on the graphene surfaces. It is thus worth noting that individually active graphene materials should be established in order for it to be functional as a standalone photocatalyst. In the case of an ideal graphene, they are in fact highly inert due to the absence of catalytically active sites. This can be traced to its homogeneity and unpaired electrons in the  $p_z$  atomic orbitals which are strongly stabilized in a highly delocalized, self-passivating  $\pi$ -network [54]. Although this  $\pi$ -bonding system can act as a kind of  $\pi$  ligand, where it can render complexation reactions for graphene, e.g. with organic compounds or transition metals through  $\pi$ - $\pi$ , H- $\pi$  and metal- $\pi$  interactions, the interaction formed is however weak and minimal [55–58]. Conversely, GO has been demonstrated to possess a plethora of oxygen functionalities and structural defects in the form of nano-voids which are engendered in the material from its harsh oxidation preparation



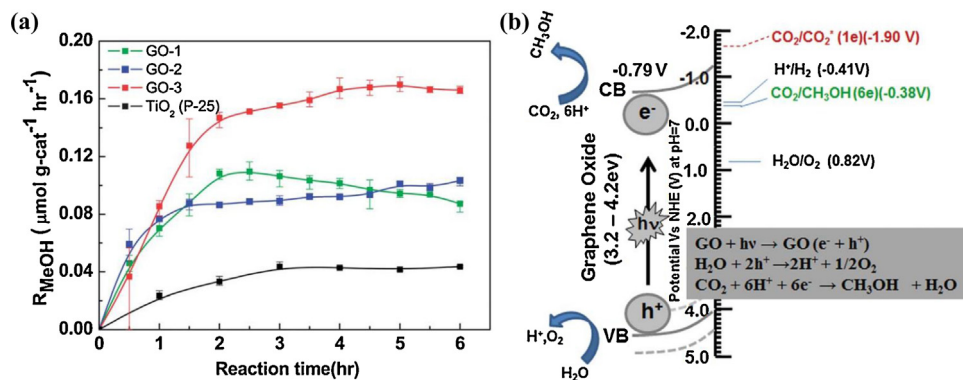


Fig. 7. (a) Photocatalytic CH<sub>3</sub>OH production rate over GO and TiO<sub>2</sub>; (b) Schematic illustrating the photocatalytic CO<sub>2</sub> reduction mechanism on GO [76].

process [29,59]. These components in turn endowed graphene with liable bonds, highly localized orbitals, dangling bonds, and asymmetric spin density throughout its aromatic backbone that can act as catalytically active sites [60–63]. Vacancy defects and edges in the graphene sheet is also equipped with unpaired spins, which can also aid in the activation of molecules by a spin flip process [34].

The papers by Nguyen-Phan et al. [64] and Thangavel et al. [65] have both demonstrated that the higher the oxygen groups in question, the better the adsorption capacity of methylene blue (MB). This is since the ionic interactions between cationic dyes like MB and the negatively charged oxygen groups can also be formed in the company of  $\pi$ - $\pi$  interaction between methylene molecules and the aromatic fractions from graphene oxide. Moreover, it is widely acknowledged that GO is strongly hydrophilic due to the presence of polar oxygen functional groups. This gives GO its excellent dispersibility in water, which will be useful in the event of an aqueous photocatalytic system. Moreover, the strong hydrophilicity of GO also furnishes strong hydrogen bonding interactions to water molecules, which will in particular benefit photocatalytic water splitting applications [66,67]. CO<sub>2</sub> photoreduction into energy fuels is another important photocatalytic reaction that has received serious attention nowadays. It is known that for CO<sub>2</sub> reduction following the Langmuir-Hinshelwood mechanism, the adsorption of CO<sub>2</sub> on the active catalytic site is an important step. The chemisorption of CO<sub>2</sub> on the graphene sheet could occur on its armchair edge, and therefore GO with high density of structural defects and edge exposures is likely to be more effective for CO<sub>2</sub> adsorption and their successive reactivity [68–70]. Wood et al. have further shown through density functional theory that the presence of functional groups such as -COOH is a promising candidate for enhancing CO<sub>2</sub> adsorption capacity by strengthening its adsorption and activating exposed edges and terraces to introduce additional binding sites [71].

Despite the general understanding that structural defects and oxygen functionalities on GO help in facilitating active sites, much work remains to clarify the specific active sites which are in play for a particular photocatalytic reaction. In some instances, due to the wide range of chemical compositions present in GO, multiple reactions with undesired functionalities are possible. Therefore a deep mechanistic understanding of the subject should be grasped so that future work can focus on controllable and effective isolation of the active sites and the selective removal of the undesired active sites from the surfaces of graphene in a controlled manner, in order to yield a highly selective GO photocatalyst. In all, since the oxidation of graphene into GO can simultaneously introduce a bandgap and made graphene catalytically capable, GO is then capable to be utilized as an intrinsic photocatalyst on its own.

### 3. Photocatalytic applications and mechanisms using graphene oxide

As described in the previous sections, the theoretical underpinning for the significance of GO in photocatalysis is the very specific properties that govern them. Enhanced efficiency in photocatalytic applications can be achieved by the rational design and property control of GO. Herein, we will discuss the advancements made in the application of bare GO toward several photocatalytic applications such as waste removal, water splitting for H<sub>2</sub> evolution, reduction of carbon dioxide (CO<sub>2</sub>) for hydrocarbon fuel production and so forth [43,72–74].

The application of GO as a photocatalytic material relies heavily on the modulation of oxygenated functional groups, as discussed in Section 2. The isolated sp<sup>2</sup> clusters on GO with such functionalities (C–OH or C–O–C) could lead to the localization of electron-hole pairs on its basal plane [75]. Upon light irradiation, the photoinduced electrons (e<sup>-</sup>) and holes (h<sup>+</sup>) would migrate to the surface of GO, and serve as oxidizing and reducing sites, respectively to react with the adsorbed reactants [76]. Isotope analysis confirmed that the methanol was formed through CO<sub>2</sub> reduction instead of photodissociation of GO. In comparison to the conventionally used TiO<sub>2</sub> photocatalyst, standalone GO showed a 6-fold increase in CH<sub>3</sub>OH production rate from the photoreduction of CO<sub>2</sub> under visible light and ambient conditions (Fig. 7(a)) the [76]. The reduction potential of e<sup>-</sup> in the GO CB was estimated to be -0.79 V (vs. NHE), which was more negative than the reduction potential of CO<sub>2</sub>/CH<sub>3</sub>OH (-0.38 V vs. NHE) and hence served as a donor. On the other hand, the oxidation potential of the h<sup>+</sup> in the GO VB (4 V vs. NHE) was higher than the potential of H<sub>2</sub>O/O<sub>2</sub> and acted as an acceptor. Therefore, the photocatalytic conversion of CO<sub>2</sub> with H<sub>2</sub>O into the CH<sub>3</sub>OH product could proceed via a six-electron reaction, as described by Equations in the inset of Fig. 7(b).

The energy band levels of graphite oxide, with an appropriately oxidized level also allows for an efficient production of hydrogen (H<sub>2</sub>) gas from the photocatalytic water splitting process [43]. The CB edge of graphite oxide, which is primarily formed by the antibonding  $\pi^*$  orbital exhibits a higher energy level than that needed for H<sub>2</sub> production, hence leading to rapid electron injection into the solution phase for H<sub>2</sub> generation. Using electrochemical analysis along with the Mott-Schottky equation, it was found that with appropriate oxidation, the electronic structure of graphite oxide could be suitable for both reduction and oxidation of water [77]. The CB edge was found to have little variation with the oxidation level, while the VB edge governed the bandgap width of GO. The results were further justified by employing graphite oxide as photocatalyst to produce H<sub>2</sub> and oxygen (O<sub>2</sub>) gases in CH<sub>3</sub>OH and AgNO<sub>3</sub> solutions, respectively. The evolution of H<sub>2</sub> was observed to reach approximately 11000 μmol after 6 h of reaction time, while

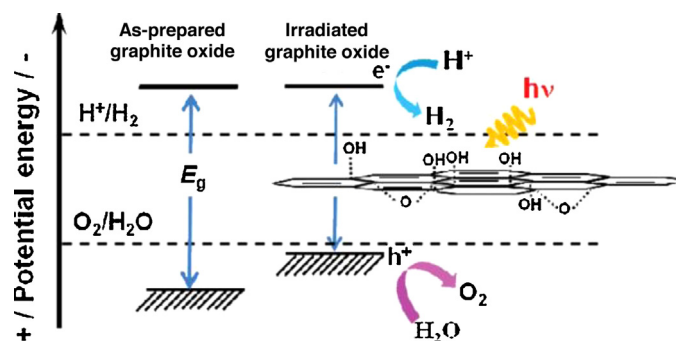


Fig. 8. Schematic energy-level diagram of GO relative to the levels for  $H_2$  and  $O_2$  evolution from water [77].



Fig. 9. Structural models of GO (a) before and (b) after the photoreaction. Various oxygen functional groups, especially epoxy C—O—C and hydroxyl COH were reduced to produce defects; (c) Energy diagram of the bands of GO nanosheets during photoreaction [74].

the amount of  $O_2$  produced was negligibly small (*ca.* 20  $\mu\text{mol}$ ) due to mutual photocatalytic reduction of GO with the upward shifting of the VB edge (see Fig. 8). When  $\text{NaIO}_3$  was replaced as the sacrificial reagent, the mutual reduction mechanism was suppressed, leading to strong  $O_2$  generation [77]. The findings from this work highlight that chemical modification can be used to tailor the electronic properties of graphite oxide for specific photosynthetic applications. It is necessary to point out that GO being explored as an independent photocatalyst should be validated for the true nature of its activity. Close attention needs to be paid if activity stems from adhering catalytic properties from the oxygen functionalities or whether they originate from the resultant band gap and ensuing charge carriers photo-generation. This is critical as GO has a history of being a functional carbocatalyst facilitating several synthetic transformations including but not limited to hydration, oxidation, polymerization and condensation reactions [78]. The role of band gap in this case is assured since in the aforementioned works, all photocatalytic conversion characteristically exhibited absence of yield at 0 h prior to irradiation, meaning that activity was triggered by a light stimulus. This validates that light is an essential ingredient and that catalytic activity was propelled by photo-generated carriers due to renewed formation of band gap and not self-mediated by oxygen groups or for that matter any unintentional dopants such as metal or other impurities that may have been incorporated during the synthesis process. Furthermore, since these impurities are also normally present in trace amounts provided that proper washing was conducted, they also play a negligible part even in the possibility of band gap opening. Therefore in this case, the plethora of labile oxygen groups and defects on GO only act as high energy active sites to foster chemical reactions from the photo-induced charge carriers. However, dedicated studies on the influence of impurities on the photocatalytic activity are absent from literature and additional investigations need to be conducted for clarification of their role in photocatalysis.

While majority of the work focused on the application of GO, Matsumoto [74] investigated the mechanisms behind the photoreaction of GO nanosheets in water. The absorption of photon energy led to a  $\pi$ - $\pi^*$  excitation in the  $\pi$ -conjugated  $sp^2$  domains of GO [79], resulting in the generation of electron-hole pairs. Consequently, the oxygen-functional groups on GO were reduced by electrons to form defect carbon sites (see Fig. 8(b)), which acted as important active sites for the reduction of water to  $H_2$ . Meanwhile, the holes may oxidize the defect carbons to produce  $CO_2$  gas, leading to the photocorrosion of GO. The band structure of the main  $sp^2$  domains responsible for the photoreaction is illustrated in Fig. 8(c). It has long been demonstrated photo-generated electron-hole pairs are viable mechanism for the removal of oxygen groups on GO, which thus question its chemical stability for its direct use in a prolonged temporal setting such as photocatalysis. As a matter of fact, supporting works on GO functioning as a photocatalyst discovered that photoreduction only occurred only in early irradiation hours and reached an eventual completion during which no further reduction or narrowing in gap energy will occur. This enables GO photocatalyst to steadily evolve photoreaction products under an extended irradiation period. In detail, XPS measurements have revealed that  $-\text{COOH}$  edge groups were removed while C—O and C=O components remained chemically intact to stabilize the band gap width which conceivably sustain the photocatalytic reaction. In this case, photo-generated electron-hole pairs in GO competitively participate either in photoreduction or in catalyzing photocatalytic reactions. As the reaction progresses, photo-generated electron-hole pairs may rapidly be consumed for photocatalytic conversion, which cooperatively help in suppressing the further photoreduction process of GO.

One of the advantage of GO is the tunable gap energy in correlation to its oxidation degree, since in this regard, GO bandgap can be manipulated to emerge as visible light responsive [80]. In addition to the theoretical results, the successful modulation of bandgap for visible light activity ( $<3.0$  eV) has been confirmed experimentally

by either varying oxidation time or through the controlled reduction of highly oxidized GO respectively. Coincidentally, all three works on GO as a photocatalyst [43,72,74], asserted a display in visible-light activity, validating its latent potential as a visible-light active photocatalyst. This positive response to visible-light irradiation is encouraging and reflects the potential of GO in solar-energy conversion (Fig. 9).

#### 4. Conclusions and outlook

In recent years, tremendous effort has been invested in the synthesis and application of 2D GO sheets [81,82]. With respect to photocatalytic properties, the primary advantages of GO include its substantial solubility and processibility, high surface area and abundance of inexpensive source material. Furthermore, the fact that physicochemical properties of GO can be tailored to facilitate specific photocatalytic applications by simple chemical modifications, makes this material even more intriguing. Despite the promising results obtained so far, the study of 2D GO sheets in the field of photocatalysis is still in its infancy and further developments are needed. Much work remains to be done in facilitating the practical applications of GO materials and broadening the scope of their photocatalytic applications in the near future.

Firstly, a clearer understanding on the nature of GO catalytic active sites and the accountability of specific functional groups in the opening of bandgap is necessary. Rigorous theoretical simulations and modeling techniques are imperative to pave the way for the development of highly efficient and durable GO photocatalysts. In addition, studies on the optimization of structure and morphology of GO with respect to its photocatalytic activity and stability remain scarce. To address this, the development of standard tools and testing protocols is essential to validate both of these aspects in the photocatalysis scene. Furthermore, the underlying mechanisms of the photocatalytic enhancement of GO must also be fully understood. This will rely on extensive research into the mechanistic details of photocatalytic reactions as well as a complete determination of electron transport characteristics on the GO sheets. Another major challenge is to develop a synthetic route that precisely tunes the characteristics of GO materials. As discussed in this paper, the properties of GO are dependent on numerous parameters such as size, number of layers and embedded functionalities of the graphene sheets. Hence, the rationale design of GO will not only favor the adjustment of redox potential and the enhancement of light harvesting, but also the interaction between the GO photocatalyst and target reactant molecules.

To summarize, future research directions should go toward realizing the following goals: (1) To achieve effective isolation and exposure of active sites on GO; (2) controllable removal of undesired active species on GO and (3) stabilization of GO during photocatalytic reaction processes. Although a number of challenges remains, it is without a doubt that opportunities abound for GO-based materials due to their facile functionalization and tunability, which render them useful in a wide range of synthetic transformations and catalysis. Therefore, instead of always being assumed as a supporting platform in heterogeneous catalysis, the concept of “carbocatalysis” will certainly be an exciting new direction in the field of chemistry and materials science. It is envisaged that the number of new carbocatalyzed conversions will continue to grow and new forms of carbonaceous nanomaterials with engineered morphology or functionalities, will emerge as powerful catalysts in the near future.

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#### References

- [1] X. Jia, J. Campos-Delgado, M. Terrones, V. Meunier, M.S. Dresselhaus, Graphene edges: a review of their fabrication and characterization, *Nanoscale* 3 (2011) 86–95.
- [2] C. Han, M.-Q. Yang, B. Weng, Y.-J. Xu, Improving the photocatalytic activity and anti-photocorrosion of semiconductor ZnO by coupling with versatile carbon, *Phys. Chem. Chem. Phys.* 16 (2014) 16891–16903.
- [3] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, TiO<sub>2</sub>-graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: is TiO<sub>2</sub>-graphene truly different from other TiO<sub>2</sub>-carbon composite materials? *ACS Nano* 4 (2010) 7303–7314.
- [4] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, Engineering the unique 2D mat of graphene to achieve graphene-TiO<sub>2</sub> nanocomposite for photocatalytic selective transformation: what advantage does graphene have over its forebear carbon nanotube? *ACS Nano* 5 (2011) 7426–7435.
- [5] K.T. Nguyen, Y. Zhao, Integrated graphene/nanoparticle hybrids for biological and electronic applications, *Nanoscale* 6 (2014) 6245–6266.
- [6] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, *Chem. Soc. Rev.* 39 (2010) 228–240.
- [7] Z. Yin, J. Zhu, Q. He, X. Cao, C. Tan, H. Chen, Q. Yan, H. Zhang, Graphene-based materials for solar cell applications, *Adv. Energy Mater.* 4 (2014) 1300574.
- [8] D. Chen, H. Feng, J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications, *Chem. Rev.* 112 (2012) 6027–6053.
- [9] S. Eigler, A. Hirsch, Chemistry with graphene and graphene oxide—challenges for synthetic chemists, *Angew. Chem. Int. Ed.* 53 (2014) 7720–7738.
- [10] K. Hatakeyama, H. Tateishi, T. Taniguchi, M. Koinuma, T. Kida, S. Hayami, H. Yokoi, Y. Matsumoto, Tunable graphene oxide proton/electron mixed conductor that functions at room temperature, *Chem. Mater.* 26 (2014) 5598–5604.
- [11] N.O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, X. Duan, Graphene: An emerging electronic material, *Adv. Mater.* 24 (2012) 5776.
- [12] X. Huang, X. Qi, F. Boey, H. Zhang, Graphene-based composites, *Chem. Soc. Rev.* 41 (2012) 666–686.
- [13] A. Kafy, K.K. Sadasivuni, H.C. Kim, A. Akther, J. Kim, Designing flexible energy and memory storage materials using cellulose modified graphene oxide nanocomposites, *Phys. Chem. Chem. Phys.* (2015).
- [14] C. Chung, Y.-K. Kim, D. Shin, S.-R. Ryoo, B.H. Hong, D.-H. Min, Biomedical applications of graphene and graphene oxide, *Acc. Chem. Res.* 46 (2013) 2211–2224.
- [15] Y. Sun, Q. Wu, G. Shi, Graphene based new energy materials, *Energy Environ. Sci.* 4 (2011) 1113–1132.
- [16] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, H. Zhang, Graphene-based materials: synthesis, characterization, properties, and applications, *Small* 7 (2011) 1876–1902.
- [17] N. Zhang, M.-Q. Yang, S. Liu, Y. Sun, Y.-J. Xu, Waltzing with the versatile platform of graphene to synthesize composite photocatalysts, *Chem. Rev.* 115 (2015) 10307–10377.
- [18] M.-Q. Yang, N. Zhang, M. Pagliaro, Y.-J. Xu, Artificial photosynthesis over graphene-semiconductor composites. Are we getting better? *Chem. Soc. Rev.* 43 (2014) 8240–8254.
- [19] N. Zhang, Y. Zhang, Y.-J. Xu, Recent progress on graphene-based photocatalysts: current status and future perspectives, *Nanoscale* 4 (2012) 5792–5813.
- [20] M.-Q. Yang, Y.-J. Xu, Selective photoredox using graphene-based composite photocatalysts, *Phys. Chem. Chem. Phys.* 15 (2013) 19102–19118.
- [21] L.-L. Tan, S.-P. Chai, A.R. Mohamed, Synthesis and applications of graphene-based TiO<sub>2</sub> photocatalysts, *ChemSusChem* 5 (2012) 1868–1882.
- [22] Y. Qu, X. Duan, Progress, challenge and perspective of heterogeneous photocatalysts, *Chem. Soc. Rev.* 42 (2013) 2568–2580.
- [23] Y. Zhang, N. Zhang, Z.-R. Tang, Y.-J. Xu, Graphene transforms wide band gap ZnS to a visible light photocatalyst. The new role of graphene as a macromolecular photosensitizer, *ACS Nano* 6 (2012) 9777–9789.
- [24] N. Zhang, M.-Q. Yang, Z.-R. Tang, Y.-J. Xu, Toward improving the graphene-semiconductor composite photoactivity via the addition of metal ions as generic interfacial mediator, *ACS Nano* 8 (2013) 623–633.
- [25] C. Han, Z. Chen, N. Zhang, J.C. Colmenares, Y.J. Xu, Hierarchically CdS decorated 1D ZnO nanorods-2D graphene hybrids: low temperature synthesis and enhanced photocatalytic performance, *Adv. Funct. Mater.* 25 (2015) 221–229.
- [26] A. Peigney, C. Laurent, E. Flahaut, R.R. Bacsá, A. Rousset, Specific surface area of carbon nanotubes and bundles of carbon nanotubes, *Carbon* 39 (2001) 507–514.
- [27] L.J. Cote, F. Kim, J. Huang, Langmuir-Blodgett assembly of graphite oxide single layers, *J. Am. Chem. Soc.* 131 (2009) 1043–1049.
- [28] S. Gilje, S. Han, M. Wang, K.L. Wang, R.B. Kaner, A Chemical route to graphene for device applications, *Nano Lett.* 7 (2007) 3394–3398.
- [29] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon* 45 (2007) 1558–1565.



- [30] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO<sub>2</sub> surfaces: principles, mechanisms, and selected results, *Chem. Rev.* 95 (1995) 735–758.
- [31] A. Lurf, H. He, M. Forster, J. Klinowski, Structure of graphite oxide revisited, *J. Phys. Chem. B* 102 (1998) 4477–4482.
- [32] H. He, J. Klinowski, M. Forster, A. Lurf, A new structural model for graphite oxide, *Chem. Phys. Lett.* 287 (1998) 53–56.
- [33] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, S. Guo, Reduction of graphene oxide vial-ascorbic acid, *Chem. Commun.* 46 (2010) 1112–1114.
- [34] J.E. Johns, M.C. Hersam, Atomic covalent functionalization of graphene, *Acc. Chem. Res.* 46 (2013) 77–86.
- [35] G. Lu, K. Yu, Z. Wen, J. Chen, Semiconducting graphene: converting graphene from semimetal to semiconductor, *Nanoscale* 5 (2013) 1353–1368.
- [36] H. Jeong, M. Jin, K. So, S. Lim, Y. Lee, Tailoring the characteristics of graphite oxides by different oxidation times, *J. Phys. D: Appl. Phys.* 42 (2009) 065418.
- [37] D.W. Boukhvalov, M.I. Katsnelson, Modeling of graphite oxide, *J. Am. Chem. Soc.* 130 (2008) 10697–10701.
- [38] J. Ito, J. Nakamura, A. Natori, Semiconducting nature of the oxygen-adsorbed graphene sheet, *J. Appl. Phys.* 103 (2008) 113712.
- [39] A. Nourbakhsh, M. Cantoro, T. Vosch, F. Clemente, M.H. van der Veen, J. Hofkens, M.M. Heyns, S. De Gendt, B.F. Sels, Bandgap opening in oxygen plasma-treated graphene, *Nanotechnology* 21 (2010) 435203.
- [40] H. Huang, Z. Li, J. She, W. Wang, Oxygen density dependent band gap of reduced graphene oxide, *J. Appl. Phys.* 111 (2012) 054317.
- [41] A. Mathkar, D. Tozier, P. Cox, P. Ong, C. Galande, K. Balakrishnan, A. Leela Mohana Reddy, P.M. Ajayan, Controlled, stepwise reduction and band gap manipulation of graphene oxide, *J. Phys. Chem. Lett.* 3 (2012) 986–991.
- [42] Z. Luo, P.M. Vora, E.J. Mele, A.T.C. Johnson, J.M. Kikkawa, Photoluminescence and band gap modulation in graphene oxide, *Appl. Phys. Lett.* 94 (2009) 111909.
- [43] T.-F. Yeh, J.-M. Syu, C. Cheng, T.-H. Chang, H. Teng, Graphite oxide as a photocatalyst for hydrogen production from water, *Adv. Funct. Mater.* 20 (2010) 2255–2262.
- [44] G. Eda, Y.-Y. Lin, C. Mattevi, H. Yamaguchi, H.-A. Chen, I.S. Chen, C.-W. Chen, M. Chhowalla, Blue photoluminescence from chemically derived graphene oxide, *Adv. Mater.* 22 (2010) 505–509.
- [45] G. Eda, G. Fanchini, M. Chhowalla, Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, *Nat. Nanotechnol.* 3 (2008) 270–274.
- [46] C.W. Chen, J. Robertson, Nature of disorder and localization in amorphous carbon, *J. Non Cryst. Solids* 227–230 (1998) 602–606 (Part 1).
- [47] J. Robertson, E.P. O'Reilly, Electronic and atomic structure of amorphous carbon, *Phys. Rev. B: Condens. Matter Mater. Phys.* 35 (1987) 2946–2957.
- [48] X. Lv, Y. Huang, Z. Liu, J. Tian, Y. Wang, Y. Ma, J. Liang, S. Fu, X. Wan, Y. Chen, Photoconductivity of bulk-film-based graphene sheets, *Small* 5 (2009) 1682–1687.
- [49] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine structure constant defines visual transparency of graphene, *Science* 320 (2008) 1308.
- [50] H. Zhang, X. Lv, Y. Li, Y. Wang, J. Li, P25-graphene composite as a high performance photocatalyst, *ACS Nano* 4 (2009) 380–386.
- [51] T. Xu, L. Zhang, H. Cheng, Y. Zhu, Significantly enhanced photocatalytic performance of ZnO via graphene hybridization and the mechanism study, *Appl. Catal. B* 101 (2011) 382–387.
- [52] H. Zhang, X. Fan, X. Quan, S. Chen, H. Yu, Graphene sheets grafted Ag@AgCl hybrid with enhanced plasmonic photocatalytic activity under visible light, *Environ. Sci. Technol.* 45 (2011) 5731–5736.
- [53] B. Li, T. Liu, Y. Wang, Z. Wang, ZnO/graphene-oxide nanocomposite with remarkably enhanced visible-light-driven photocatalytic performance, *J. Colloid Interface Sci.* 377 (2012) 114–121.
- [54] L. Yan, Y.B. Zheng, F. Zhao, S. Li, X. Gao, B. Xu, P.S. Weiss, Y. Zhao, Chemistry and physics of a single atomic layer: strategies and challenges for functionalization of graphene and graphene-based materials, *Chem. Soc. Rev.* 41 (2012) 97–114.
- [55] V. Dua, S.P. Surwade, S. Ammu, S.R. Agnihotra, S. Jain, K.E. Roberts, S. Park, R.S. Ruoff, S.K. Manohar, All-organic vapor sensor using inkjet-printed reduced graphene oxide, *Angew. Chem. Int. Ed.* 49 (2010) 2154–2157.
- [56] J.T. Robinson, F.K. Perkins, E.S. Snow, Z. Wei, P.E. Sheehan, Reduced graphene oxide molecular sensors, *Nano Lett.* 8 (2008) 3137–3140.
- [57] F. Yavari, C. Kritzing, C. Gaire, L. Song, H. Gulapalli, T. Borca-Tasciuc, P.M. Ajayan, N. Koratkar, Tunable bandgap in graphene by the controlled adsorption of water molecules, *Small* 6 (2010) 2535–2538.
- [58] G. Wang, B. Wang, J. Park, Y. Wang, B. Sun, J. Yao, Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation, *Carbon* 47 (2009) 3242–3246.
- [59] C. Gómez-Navarro, J.C. Meyer, R.S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern, U. Kaiser, Atomic structure of reduced graphene oxide, *Nano Lett.* 10 (2010) 1144–1148.
- [60] A. Dhakshinamoorthy, M. Alvaro, P. Concepcion, V. Fornes, H. Garcia, Graphene oxide as an acid catalyst for the room temperature ring opening of epoxides, *Chem. Commun.* 48 (2012) 5443–5445.
- [61] C. Su, M. Acik, K. Takai, J. Lu, S.-j. Hao, Y. Zheng, P. Wu, Q. Bao, T. Enoki, Y.J. Chabal, K. Ping Loh, Probing the catalytic activity of porous graphene oxide and the origin of this behaviour, *Nat. Commun.* 3 (2012) 1298.
- [62] X.-k. Kong, Q.-w. Chen, Z.-y. Lun, Probing the influence of different oxygenated groups on graphene oxide's catalytic performance, *J. Mater. Chem. A* 2 (2014) 610–613.
- [63] S. Tang, Z. Cao, Site-dependent catalytic activity of graphene oxides towards oxidative dehydrogenation of propane, *Phys. Chem. Chem. Phys.* 14 (2012) 16558–16565.
- [64] T.-D. Nguyen-Phan, V.H. Pham, E.W. Shin, H.-D. Pham, S. Kim, J.S. Chung, E.J. Kim, S.H. Hur, The role of graphene oxide content on the adsorption-enhanced photocatalysis of titanium dioxide/graphene oxide composites, *Chem. Eng. J.* 170 (2011) 226–232.
- [65] S. Thangavel, G. Venugopal, Understanding the adsorption property of graphene-oxide with different degrees of oxidation levels, *Powder Technol.* 257 (2014) 141–148.
- [66] R. Bissessur, S.F. Scully, Intercalation of solid polymer electrolytes into graphite oxide, *Solid State Ionics* 178 (2007) 877–882.
- [67] O.C. Compton, S.T. Nguyen, Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials, *Small* 6 (2010) 711–723.
- [68] P. Cabrera-Sanfeliu, Adsorption and reactivity of CO<sub>2</sub> on defective graphene sheets, *J. Phys. Chem. A* 113 (2008) 493–498.
- [69] K.-J. Lee, S.-J. Kim, Theoretical investigation of CO<sub>2</sub> adsorption on graphene, *Bull. Korean Chem. Soc.* 34 (2013) 3022–3026.
- [70] A. Montoya, F. Mondragon, T.N. Truong, CO<sub>2</sub> adsorption on carbonaceous surfaces: a combined experimental and theoretical study, *Carbon* 41 (2003) 29–39.
- [71] B.C. Wood, S.Y. Bhide, D. Dutta, V.S. Kandagal, A.D. Pathak, S.N. Punathanam, K. Ayappa, S. Narasimhan, Methane and carbon dioxide adsorption on edge-functionalized graphene: a comparative DFT study, *J. Chem. Phys.* 137 (2012) 054702.
- [72] H.-C. Hsu, I. Shown, H.-Y. Wei, Y.-C. Chang, H.-Y. Du, Y.-G. Lin, C.-A. Tseng, C.-H. Wang, L.-C. Chen, Y.-C. Lin, Graphene oxide as a promising photocatalyst for CO<sub>2</sub> to methanol conversion, *Nanoscale* 5 (2013) 262–268.
- [73] K. Krishnamoorthy, R. Mohan, S.-J. Kim, Graphene oxide as a photocatalytic material, *Appl. Phys. Lett.* 98 (2011) 244101.
- [74] Y. Matsumoto, M. Koinuma, S. Ida, S. Hayami, T. Taniguchi, K. Hatakeyama, H. Tateishi, Y. Watanabe, S. Amano, Photoreaction of graphene oxide nanosheets in water, *J. Phys. Chem. C* 115 (2011) 19280–19286.
- [75] G. Eda, M. Chhowalla, Chemically derived graphene oxide: towards large-area thin-film electronics and optoelectronics, *Adv. Mater.* 22 (2010) 2392–2415.
- [76] H.-C. Hsu, I. Shown, H.-Y. Wei, Y.-C. Chang, H.-Y. Du, Y.-G. Lin, C.-A. Tseng, C.-H. Wang, L.-C. Chen, Y.-C. Lin, K.-H. Chen, Graphene oxide as a promising photocatalyst for CO<sub>2</sub> to methanol conversion, *Nanoscale* 5 (2013) 262–268.
- [77] T.-F. Yeh, F.-F. Chan, C.-T. Hsieh, H. Teng, Graphite oxide with different oxygenated levels for hydrogen and oxygen production from water under illumination: the band positions of graphite oxide, *J. Phys. Chem. C* 115 (2011) 22587–22597.
- [78] C. Su, K.P. Loh, Carbocatalysts: graphene oxide and its derivatives, *Acc. Chem. Res.* 46 (2013) 2275–2285.
- [79] K.N. Kudin, Zigzag graphene nanoribbons with saturated edges, *ACS Nano* 2 (2008) 516–522.
- [80] L.K. Putri, W.-J. Ong, W.S. Chang, S.-P. Chai, Heteroatom doped graphene in photocatalysis: a review, *Appl. Surf. Sci.* 358 (2015) 2–14.
- [81] W.-J. Ong, L.-L. Tan, S.-P. Chai, S.-T. Yong, A.R. Mohamed, Surface charge modification via protonation of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) for electrostatic self-assembly construction of 2D/2D reduced graphene oxide (rGO)/g-C<sub>3</sub>N<sub>4</sub> nanostructures toward enhanced photocatalytic reduction of carbon dioxide to methane, *Nano Energy* 13 (2015) 757–770.
- [82] W.-J. Ong, L.-L. Tan, Y.H. Ng, S.-T. Yong, S.-P. Chai, Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? *Chem. Rev.* (2016), <http://dx.doi.org/10.1021/acs.chemrev.6b00075>.