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Review

Environmental transformation of graphene oxide in the aquatic environment

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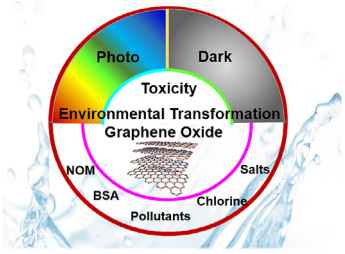
HIGHLIGHTS

- This review gave a through environmental assessment summary of this most popular nanomaterial in the very past decade.
- This review was the first to summarize photo transformation of GO by dividing into different light sources.
- Interactions between DNA and GO was summarized for the assessment of potential risk in the intracellular level.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, research on graphene oxide (GO) has developed rapidly in both academic and industrial applications such as electronic, biosensor, drug delivery, water treatment and so forth. Based on the large amount of applications, it is anticipated that GO will inevitably find its own way to the environment, if used are not restricted to prevent their release. Environmental transformation is an important transformation process in the natural environment. In this review, we will summarize the recent developments on environmental transformation of GO in the aquatic environment. Although papers on environmental transformation of graphene-based nanomaterials can be found, a systematic picture describing photo-transformation of GO (dividing into different irradiation sources), environmental transformation of GO in the dark environmental, the environmental toxicity of GO are still lacking. Thus, it is essential to summarize how different light sources will affect the GO structure and reactive oxygen species generation in the photo-transformation process, how GO will react with various natural constituents in the aquatic environment, whether GO will toxic to different aquatic organisms and what will be the interactions between GO and the intracellular receptors in the intracellular level once GO released into the aquatic environment. This review will arouse the realization of potential risk that GO can bring

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to the aquatic environment and enlighten us to pay attention to behaviors of other two-dimensional GO-like nanomaterials, which have been intensively applied and studied in recent years.

Contents

1. Introduction

Since the discovery of graphene in 2004, a great sensation has been bought by graphene and its derivatives due to their unique structure and excellent properties. Graphene oxide (GO), as the most studied graphene-derivatives, is a precursor material in graphene preparation and has a large number of carboxyl, hydroxyl, carbonyl, and epoxy carboxyl groups on its surface (Dreyer et al., 2010). The presence of the oxygen functional groups on the structure of GO render it extremely hydrophilic (Barroso-Bujans et al., 2010), making it ideal to be used in aqueous solution and expanding the applications. For example, biomedical applications have been developed rapidly to be used for bio-imaging, cancer therapy, photo-thermal therapy and so forth. (Chen et al., 2015; Reina et al., 2017). Especially, environmental applications have also been developed rapidly in recent years. GO could effectively absorb metal ions, dyes and organic micro-pollutants via electrostatic attraction, hydrogen bonding, π interaction and other interaction forces (Khan et al., 2017; Yin et al., 2019). When used as membrane applications, GO membranes have the advantage of anti-fouling, high flux and good selectivity via nano-channels between GO layers due to the unique laminated structure (Liu et al., 2020b; Mi et al., 2018). As photo-catalysts, GO has the greatest advantages of the in situ growth of other nanoparticles on its surface to achieve the best photocatalytic performance, attributed to the abundant functional groups on the surface (Qiu et al., 2018). Recently, Wang et al. summarized the developments of GO on photodegradation of persistent organic pollutants and analyzed roles that GO (i.e. supports, flexible substrates and co-catalysts in composites) acted as photocatalysts (Zhang et al., 2020b). In addition, GO can be excellent antibacterial agents by adjusting its size, orientation or combining with other nanomaterials (Liu et al., 2012a; Lu et al., 2017; Perreault et al., 2015a). GO sensors also show high sensitivity and low detection limit when used for environmental sensing (Anichini et al., 2018). Thus, the wide applications will inevitably release GO into the aquatic environment. When GO appears in water, environmental fate and transport of GO will be changed by both its physicochemical properties and external surrounding aqueous environments. In other ways, GO can interact with a variety of the existing constituents including natural organic matter (NOM), salts, bovine serum albumin (BSA), pollutants and some disinfection agents in the aquatic environment. It is worth noting that photo-transformation of GO is a very important transformation pathway. And GO under various light sources of irradiation will behave differently.

As more applications have been developed, more concerns that GO will bring come along. Thus scientists did series of studies on the toxicity of GO, though it has been controversial for the past decades. At the very beginning, Liao et al. observed that smaller lateral dimensional of GO exhibited higher hemolytic activity to human cells than larger GO nanosheets. And GO showed toxic effects to human skin fibroblasts from viability assay experiments (Liao et al., 2011). GO also exhibited a dose-dependent toxicity to human lung epithelial cells and fibroblasts, while obvious toxicity when doses were above 50 mg/L, suggesting the great potential risk of GO to the health of human beings (Wang et al., 2011). The contact

mode of direct interactions between cell membranes and GO have also been found to destroy cells (Hu et al., 2011). In stark contrast to the above studies, Chang et al. found GO with all lateral dimensional sizes exhibited showed no toxicity to A549 cells (typical human lung cells) (Chang et al., 2011). Different results of toxicity might be due to the various methods through which GO was being prepared. However, there is no doubt that GO could possess potential toxicity to humans and the whole eco-system. Thus thorough environmental assessment of GO transformation should be built up, once GO nanosheets release to the environment.

Until now, there are many review articles in summarizing GO applications in energy storage, hydrogen evolution, biosensors, water purifications and many others (Perreault et al., 2015b; Shao et al., 2015; Zhang et al. 2019c, 2020b). Some reviews on environmental fate and transport of graphene-based materials were reported since scientists have realized their inevitable release to the natural aquatic environment and did a series of potential risk assessment under different circumstances (Ren et al., 2018; Zhao et al., 2014). However, no reviews have been deeply and exclusively reported on environmental transformation of GO. Thus, a systematic picture describing photo-transformation of GO (dividing into different irradiation sources), environmental transformation of GO in the dark environmental, the biocompatibility and environmental toxicity of GO is urgently needed. This review firstly summarized how different light sources affected the GO structure and reactive oxygen species generation in the photo-transformation process, how GO reacted with various natural constituents in the aquatic environment, whether GO was toxic to different aquatic organisms and what were the interactions between GO and the intracellular receptors in the intracellular level once GO releases into the aquatic environment. The objective of this review is to help give a thorough and detailed environmental assessment summary of this most popular nanomaterial, GO, in the very past decade.

2. Photo-transformation of GO

2.1. Environmental photo-transformation of GO

Photo transformation is a very significant transformation process in the natural environment. The light source is extremely important in the photo-transformation process. For example, one recent study compared the efficiency of photocatalytic reduction of CO_2 among simulated sunlight-GO, UV irradiated-GO and pristine could irradiated GO with a CO yield (4 h) ratio of 2.7:2.1:1, respectively (Kuang et al., 2020). The stark contrast arouses us to pay attention to the different photochemical reaction process via various photo irradiation sources. Thus, this part of the review will focus on the photo-transformation of GO by different light sources.

2.1.1. Solar irradiation

The π-bonds in GO can absorb solar spectrum light, thus photochemical transformation might be a significant pathway in the aquatic environment if light absorption is followed with chemical reaction. One study showed that more defects can be generated with GO after simulated sunlight irradiation, evidenced by higher I_D/I_G from Raman Spectra (Zhao and Jafvert, 2015). Adeleye et al. also observed the increased I_D/I_G ratio of GO under solar irradiation, and they found that GO was reduced to rGO and the number of oxygen functional groups decreased. The C/O ratio and abundance of C–C/C=C group increased compared to those on pristine GO (Adeleye et al., 2019). Intermediate photoproducts were observed to be smaller size with fewer oxygen functionalities which obviously had different photo-reactivity compared with the pristine GO (Hou et al., 2015). This whole photochemical transformation process can be summarized as the following equation: GO $\overset{h\vartheta}{\rightarrow}$ CO_2 + rGO species + low MW PAH species (O_2 dependent process) (Here, rGO: reduced graphene oxide; MW: molecular weight; PAH: Polycyclic aromatic hydrocarbons) (Hou et al., 2015). The mechanism of this photo-fragmentation is related with the concurrent oxidation and GO reduction due to the electron-hole pair formation under sunlight irradiation. Most recently, Xing et al. found that GO underwent reduction in a 25-day sunlight irradiation, and completed the transformation process at Day 8. And LMW species produced during the 8-day GO transformation, which was consistent with the previous studies (Zhao et al., 2020a) (Fig. 1A). The aerobic and anoxic conditions were checked to see whether they could influence the physiochemical properties of GO in the solar irradiation process (Chowdhury et al., 2015a). Interestingly, the size of photo-irradiated GO decreased from 200 nm to 120–130 nm in both aerobic and anaerobic conditions. Besides, the reduction trend of GO in sunlight irradiation was also similar under these two conditions, suggesting the aerobic and anoxic conditions don't have much effect on changing the chemical composition of GO. As all research studies showed that GO could undergo degradation, what would be the determined role on the basal plane of GO to have the photochemical reaction? Specifically, the hydroxyl and epoxy functional groups might be the main factors, evidenced by the decreasing number of oxygen-containing functional groups as a function of time (Shams et al., 2019). C–O functional groups decreased mostly in the photochemical reaction, which were normally on the basal plane of GO (Gao et al., 2009), indicating photo-transformed GO might be aggregated by plate-plate interactions (Chowdhury et al., 2015a).

Solar irradiation can also stimulate the generation of ROS. Jafvert et al. firstly found that superoxide and H_2O_2 can be generated, and they proposed that the ROS could be generated by the electron transfer process (Zhao and Jafvert, 2015). GO could act as an electron donor under solar irradiation and pass the electron to molecular oxygen to generate superoxide and H_2O_2 (Zhao and Jafvert, 2015). Some follow-up studies also confirmed with their conclusion (Hou and Wang, 2017; Zhao et al. 2016a, 2016b). Hou et al. found that pH played an important role in H_2O_2 production (Fig. 1B) (Hou and Wang, 2017). The amount of H_2O_2 produced under pH 7 could reach 2-fold increase compared to that under pH 3 (Hou and Wang, 2017). One study demonstrated only singlet oxygen ($^1O_2$) was generated by GO under simulated sunlight with slight oxidation of antioxidant biomolecules due to the electron–hole pairs generated on GO surface (Chong et al., 2017). Another study indicated that GO could form ROS including $^1O_2$, superoxide anion radical and ·OH by using a Xenon lamp with a 295 nm filter to simulate the solar irradiation (Adeleye et al., 2018). The difference in detecting out the different species of ROS might be due to light source, the various light wavelength, light intensity and oxygen-containing conditions, which are all responsible for the photo-transformation process. In addition, different oxygen functional groups can also alter the ability of producing ROS (Yao et al., 2020). Here, we summarized the potentially whole pathway of ROS generation by GO based on the present studies in this area:

$$GO \overset{h\nu}{\rightarrow} [GO]^* \xrightarrow{O_2} {}^1O_2 \text{ (Type II Energy Transfer)} \quad (1)$$

$$[GO]^* \overset{h\nu}{\rightarrow} GO^{\bullet+} + e^-_{aq} \text{ (Type I Electron Transfer)} \quad (2)$$

$$O_{2,eq} + e^-_{aq} \rightarrow O_2^{\bullet-} \quad (3)$$

$$O_2^{\bullet-} + 2H^+ + e^- \rightarrow H_2O_2 \quad (4)$$

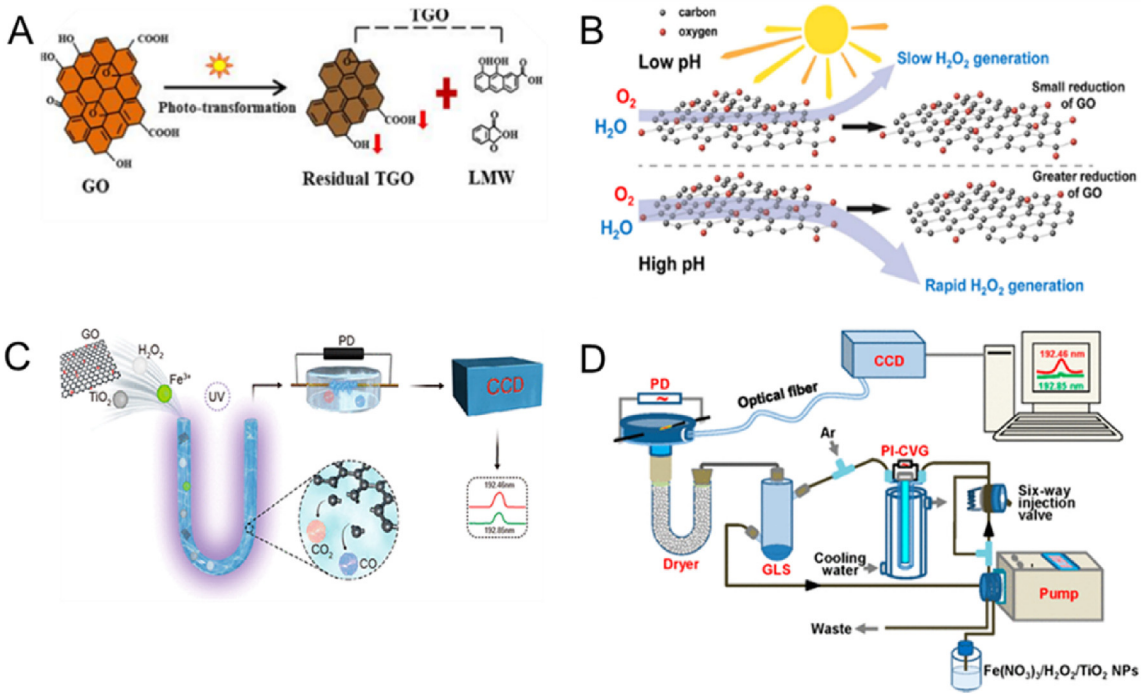

Fig. 1. Phototransformation of GO under sunlight irradiation. (A). Schematic of residual transformed GO (TGO) and LMW production in the photochemical reaction (Zhao et al., 2020). (B) Photocatalytic Production of H_2O_2 by GO (Hou and Wang, 2017) (C) A novel online system tracking of GO photo-degradation (Tan et al., 2020). (D) Schematic of the detection system (Tan et al., 2020).

$$H_2O_2 \xrightarrow{hv} \cdot OH \quad (5)$$

In the natural aquatic environment, the aqueous systems can be more complicated, where it may contain nitrate, natural organic matter (NOM) and so forth. Some studies include these indirect photo-transformation considering the existence of these natural constituents under sunlight in the aquatic environment. Chowhury et al. found that nitrate and NOM in the natural aqueous environment could generate hydroxyl radicals, which could further react with photo-irradiated GO to induce the composition change of GO under sunlight irradiation (Chowdhury et al., 2015a). Most recently, scientists developed a platform to monitor the photodegradation of GO where the concentration limit as low as 87.5 μg/L could be monitored (Fig. 1C and D) (Tan et al., 2020). The developed system was size-dependent, thus make it particularly possible on detecting the aggregation GO at 50 μg/L with 10 mg/L NOM solution. This application enlightened us to make it possible on developing new systems on monitoring the photo-transformation of GO in the aquatic environment.

2.1.2. UV irradiation

Ultraviolet (UV) irradiation, as a commonly adopted method or disinfection and pollutant degradation in environmental engineering, has been shown to play an important role in photo-transformation of GO. Previously, scientists have used the UV irradiation method to prepare reduced GO (rGO) (Guardia et al., 2012; Kim et al., 2009). They found that irradiation of GO aqueous dispersions resulted in production of reduced GO, CO_2 and H_2 (Matsumoto et al., 2011). In addition, more defects were produced (Matsumoto et al., 2011). These defects (i.e., non-aromatic carbon) provided "sites" for H_2 and CO_2 generation (Matsumoto et al., 2011). Yuan et al. found that UV-light 99.1% of GO was photo-transformed after 32 h irradiation in pure water with superoxide anion radical and ·OH generated under UV irradiation (Yuan et al., 2018). GO nanosheets could become more porous in the oxygenated group domains under UV irradiation for several hours, with rGO, CO_2 and O_2 produced in the photochemical reaction (Koinuma et al., 2012). From the XPS analysis, the epoxide and carbonyl groups were observed to be decreased, while hydroxide and carboxyl groups increased. The increasing number of carboxyl groups contributed to the production of O_2. Recently, by ^{18}O (H_2O) isotope labeling experiments combining with mass spectrometry tracking and DFT calculations, researchers proved that O_2 and CO_2 evoluted during GO photoreduction under UV irradiation (Li et al., 2019a). Here, they proposed that the evolution of oxygen evolution in GO photochemical reaction was through water molecules oxidation by two homo-lateral epoxides, while the epoxides or carbonyls on the edge reacted with water molecule to form carboxyls (Li et al., 2019a). Finally, CO_2 was produced by decarboxylation since the participation of water could reduce the energy barrier by changing the reaction pathway. Besides, UV irradiation with short time could exfoliate layered of GO to monolayer, while long time irradiation could restore the new sp2 domain (He et al., 2019). Furthermore, the small monolayer GO sheets could aggregate horizontally to be a large size sheet (He et al., 2019). In addition, photochemical oxidation state of GO highly depended on the irradiation time exposure, evidenced by different I_D/I_G obtained from Raman spectra measurement (I_D/I_G = 1.1, 0.95, 0.90 for pristine GO, GO under UV 15 min, GO under UV 720 min, respectively) (Amadei et al., 2017). Researchers also compared photochemical behaviors of GO under UV irradiation and visible/simulated sunlight irradiation. GO nanosheets broke into small pieces, and lost some of the functional groups containing oxygen on the surface under UV irradiation with ROS generation in the process (Du et al., 2018). Another study indicated that the physico-chemical properties and toxicity of GO were more likely to be changed under UV irradiation than visible light. And once existing in city water and

natural surface water, GO became much more stable and mobile under both UV and visible light irradiation (Gao et al., 2019). A research study also showed that GO activation was more favorable to simulated sunlight than UV irradiation by yielding higher amount of CO (Kuang et al., 2020). From a dynamic light scattering study, we got to know that the size of GO changed at different photo-reduction stages (Andryushina et al., 2014). At the early stage of photochemical reaction, the hydrodynamic size increased since small fragments was produced to allow the sheets to become more flattened (Andryushina et al., 2014). At the deeper stage, a size decrease can be observed due to the reverse crumpling/folding of rGO sheets with the π-π stacking interactions, which was consistent with the previous studies by the numerical modeling (Andryushina et al., 2014; Whitby et al., 2012). Zhao et al. evaluated the oxidation degree effects on the photo-transformation of GO in aqueous environment. They reported that when the oxidation degree of GO was higher, more morphology changes could be observed. More amount of ROS generation ($^1O_2$, $O_2^{\cdot-}$, ·OH) could be detected with an increasing oxidation degree of GO (Zhao et al., 2019).

Indirect photochemical reactions under UV irradiation have also showed the alteration of physico-chemical properties of GO. When the environmental cation was higher, the strong capability in the aggregation of UV-transformed GO could be observed (i.e., $Ca^{2+} > Mg^{2+} > Na^{+}$) (Gao et al., 2020). Another study reported that GO can be oxidized rather than reduced at the circumstance of H_2O_2 in the aqueous system under UV irradiation (Ji et al., 2013). When H_2O_2 was in the system to stimulate the indirect photoreaction, the π-conjugated structures were damaged (Duan et al., 2019). In contrast, the direct photo-transformation of GO alone involved the restoration of π-conjugated structures. The involvement of ·OH in the photochemical process stimulated the reactions between ·OH and oxidized domains, and the electrophilic addition of ·OH to the aromatic domains, resulting in the disintegration of GO structures. And the nitrate concentration played an important role in the photochemical reactions in both direct and indirect photo pathways.

2.1.3. Visible light

Most studies using visible light are often related with the degradation of environmental pollutants of GO composites since GO itself doesn't possess excellent ability to degrade contaminants due to low energy of visible light photons (Zhang et al., 2020b). However, there are still some studies reporting the photo-transformation of GO under visible light. For example, Feliz et al. found that the production of $^1O_2$ by GO was negligible by using a sensitive fluorescent probe (9,10-anthracenediyl-bis(methylene) dimalonic acid, ABDA) (Felip-Leon et al., 2019). Yao et al. demonstrated that reduction of GO was not obvious and a very slight increase in absorbance can be observed, suggesting that light-absorbing products formed under visible irradiation (Du et al., 2018). The structure of GO became wrinkled, but the chemical composition change was negligible (Du et al., 2018). They also detected the ROS generation, including $^1O_2$, $O_2^{\cdot-}$, ·OH under visible light irradiation (Du et al., 2018). Mu et al. found that visible light irradiation could lead to the sp2 structure breakdown in the presence of hypochlorite, generating alkanes, olefins, alcohols and acids with short carbon skeletons. GO under visible light in the presence of hypochlorite also possess strong toxicity, evidenced by the algal reproduction inhibition (Wang et al., 2020). Although some studies reported the chemical composition did not change under visible light, Adeleye et al. observed GO was reduced by degrading the C—OH/C—O—C group at the surface of natural waters (Adeleye et al., 2019).

2.1.4. Ultrafast laser

Laser irradiation was often used for the preparation of reduced GO (Alotaibi et al., 2018; Huang et al., 2011; Liu et al., 2012b). Shall et al. firstly found that converted graphene were produced from GO by using pulsed Nd: YAG laser ($\lambda = 532$ nm, $h\nu = 2.32$ eV, pulse-width $\tau = 7$ ns) (Abdelsayed et al., 2010). Miller et al. used a femtosecond ultraviolet pulse to trigger the GO reduction by photo ionizing the solvent and liberating solvated electrons (Gengler et al., 2013). They proposed that the ultrafast nature of the irreversible GO-rGO transformation was attributed to the solvated electron capture generated by solvent photoionization (Gengler et al., 2013). Razi et al. studied the photochemical reaction of GO under laser irradiation with two laser wavelengths (532 nm and 1064 nm) by using Q-switched Nd: YAG laser irradiation (Ghasemi et al., 2018). They found that laser energy and wavelength played important roles to facilitate the reduction (Ghasemi et al., 2018). By using 0.24 J/cm^2 laser fluence and a 20-min exposure time under 532-nm laser wavelength irradiation, effective GO reduction can be achieved (Ghasemi et al., 2018). By contrast, under 1064 nm wavelength irradiation, GO reduction was not sufficient (Ghasemi et al., 2018). Nishina et al. proposed the GO reduction mechanism from the photon mode versus thermal mode under ultrafast laser irradiation (Hada et al., 2019). The photo mode could selectively remove the epoxy groups on the basal plane of GO, while the thermal mode were more responsible for the reduction of hydroxyl and epoxy groups.

2.2. Photo-transformation with disinfection agents in water treatment systems

2.2.1. Fenton reaction

In water and wastewater treatment process, photo/photo-fenton reactions are often involved with nanomaterials. Zhang et al. demonstrated that the photo Fenton reaction was an effective way to prepare graphene quantum dots (GQDs) (Zhou et al., 2012). They exposed GO with the Fenton reagent under a mercury lamp (500 W), and GO could react with the Fenton reagent at a quite slow rate, while GQDs could be generated after a longer time reaction. They demonstrated that the reaction rate was slow due to small amount of ·OH generated with low power of UV irradiation power. Star et al. proposed the potential mechanism of GO degradation in the photo-Fenton reaction (Bai et al., 2014). Intermediate oxidation products (MW 150−1000 Da) were generated, while these products no longer existed in high abundance after longer reaction time (i.e., days 2 and 3). And graphene quantum dots (GQDs) were dominated in the system. By chemical analysis, they demonstrated that these oxidation products were mostly oxidized polycyclic aromatic hydrocarbons (Bai et al., 2014). In addition, it has also been found that GO could not be reduced at the circumstance of H_2O_2 in acidic system since large amount of ·OH existing in the system. By contrast, GO could slowly being oxidized due to the strong oxidation of hydroxyl radical (Ji et al., 2013).

2.2.2. Chlorine reaction

Fullerenes, as representative carbonaceous nanomaterials, have been reported to be transformed in the presence of free chlorine under UV irradiation (Ou et al., 2019; Wu et al. 2017a, 2017b). GO was also found to be altered with chlorine related radicals. Fragmentation of carbon sheets and further oxidation by Cl· and ClO· free radicals occurred with GO during the process of chlorination (Du et al., 2017). Fortner et al. recently reported that mineralization occurred when GO was exposed to free chlorine and light irradiation (An et al., 2020). Hydroxyl radical, chlorine and other oxygen containing radicals promoted the remaining products resistant to further oxidation. They also demonstrated that the reaction rate

was dependent on GO lateral size and free chlorine concentration. A recent study confirmed with the conclusion, stating that chlorine-containing radicals could help to break down the carbon atomic rings of GO. The existence of hypochlorite in the system of GO under visible light showed strong toxicity, inhibiting the algal reproduction. Therefore, the photo-transformation of GO with the disinfection agents should be noticed and help to understand more about the safety assessment of GO (Wang et al., 2020). Photo-bromination of GO was also studied and researchers reported that the C–OH and COOH groups of GO were lost and rGO was produced in the process. The high oxidation potential of bromine had the ability of oxidizing the remaining carbon nanosheets, thus produce the brominated disinfection by-products. The irradiated free radicals generated in the photochemical process also affected the transformation of GO (Li et al., 2019c). Li et al. proved that GO broke into small fragments and more reactive sites were formed under sunlight irradiation in the presence of chlorine and bromination. Free radicals such as Cl·, Br·, ClO· and BrO·, promoted the formation of DBPs on the GO surface (Liu et al., 2019a).

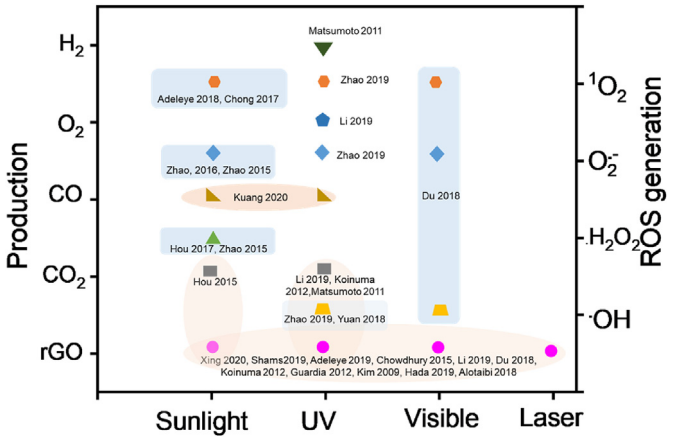

Fig. 2. Photo-transformation of GO under different light sources.

2.3. Summary of photo transformation of GO

Photo transformation is an important transformation pathway with GO in the natural aquatic environment. From the summary of this section, we know that different light sources could induce various photochemical reactions. Under all photo irradiation conditions (i.e., sunlight, UV, visible light, ultrafast laser), rGO was the only product that has always been found, while other products were quite different. Even with the same light source, the results varied due to the complicated light induced conditions and different chemical compositions of GO induced by specific preparation methods. Here, we made a summary on products and ROS generation of GO to give a clear picture on the photochemical process with different light sources (Fig. 2). In water and wastewater treatment process, fenton and chlorine reactions were often used. GO experienced fragmentation into GQDs, followed by further oxidation of produced free radicals (·OH, Cl·, Br·, ClO· and BrO·) in the disinfection reaction process (Fig. 3).

3. Environmental pathway of GO in the dark aquatic environment

In the natural aquatic environment, GO could also come across natural constituents and other contaminants, which could bind with it or affect its stability, mobility and so forth in the dark environment. The transformed GO might possess very different properties with the pristine GO. Therefore, in this part, we will summarize the environmental pathway of GO in the dark aquatic environment by dividing the sections from the perspective of 1)

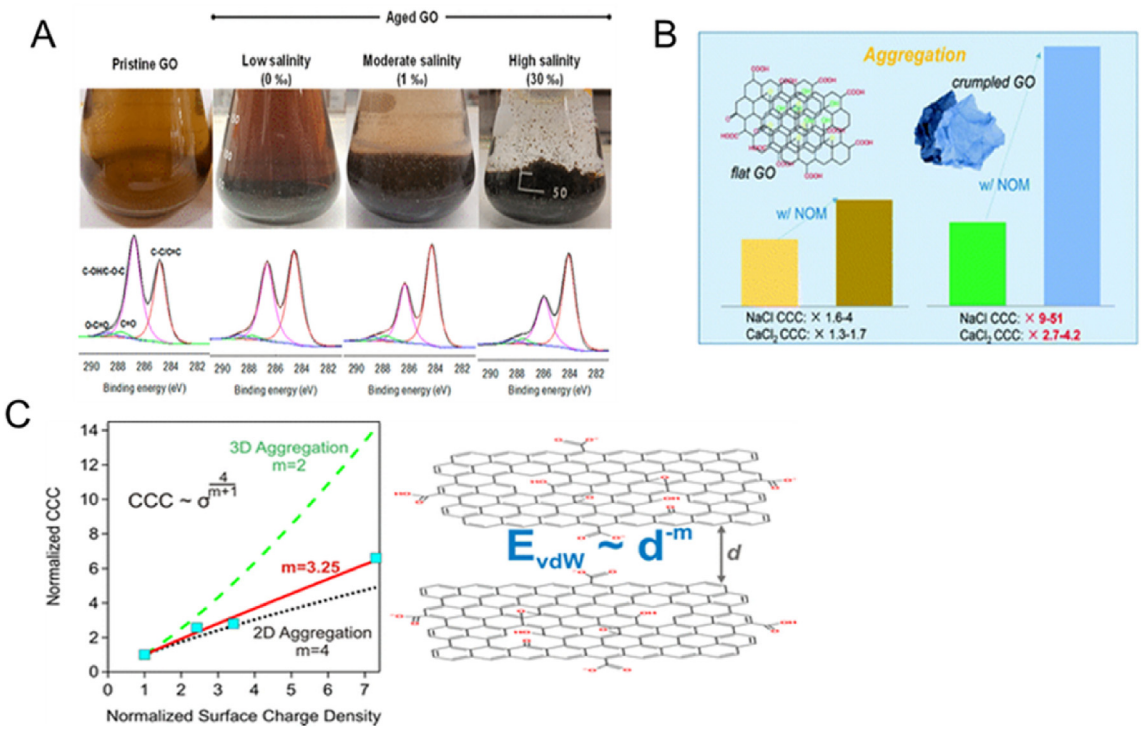

Fig. 3. Environmental Transformation of GO in the Dark Environment. (A). Transformation of GO in marine waters (Adeleye et al., 2019). (B). The stability of GO under NOM and salts. (Jiang et al., 2017). (C). Aggregation of GO in two dimensions (Gudarzi, 2016).

reactions with natural constituents 2) reactions of disinfection agents 3) adsorption of environmental contaminants.

3.1. Environmental reactions with natural constituents in the dark environment

The solution chemistry and natural constituents can greatly affect the colloidal property and stability of GO. Chowdhury et al. showed that pH, ion composition (including counter-ion valence), and NOM concentration played significant roles in the overall stability of reduced graphene oxide (Chowdhury et al., 2015b). Yi et al. confirmed this conclusion by comparing the stability of GO in two salts (NaCl and $CaCl_2$) and three NOMs (Suwannee River humic acid, Suwannee River fulvic acid, and Aldrich humic acid (SRHA, SRFA, and AHA)). The critical coagulation concentrations (CCC) of GO increased with the addition of NOM and the stability followed the order of AHA > SRHA > SRFA > no HA in the presence of NaCl, indicating $\pi-\pi$ interactions might be important in interaction mechanisms (Jiang et al., 2017). GO was found to start aggregating when the ionic strengths were higher than 20, 50, and 100 mM under pH of 2.06, 4.4, and 10.7. They also proved that the CCC of GO was influenced by the level of exfoliation (Gudarzi, 2016). Chen et al. explored the factors that influenced GO stability in natural surface waters by monitoring experiments in natural surface water from Dongpu Lake, Nanfei River and Chaohu Lake in China (Gao et al., 2017). They found that the zeta potential of GO decreased as pH values increased. When pH was above 3.0, zeta potential of GO was less than −30 mV, thus GO was electrostatically stable (Gao et al., 2017). Zhu et al. demonstrated that the stability of GO increased with higher pH and GO became unstable below pH 3 attributed to −COOH protonation at the edge of GO (Sun et al., 2020). Since pH in the natural aquatic environment was between 5.0 and 9.0, GO was quite stable in the natural aqueous system (Chowdhury et al., 2013). Bovine serum albumin (BSA), as a representative NOM in the aqueous system, exhibited concentration-dependent trend towards the GO stability. The electrostatic binding and double layer compression effects between BSA and GO depressed GO stability at low concentration of BSA. The traditional Derjaguin-Landau-Verwey-Overbeek (DLVO) theory fit the aggregation kinetics of GO with electrolyte (NaCl, $MgCl_2$, and $CaCl_2$) and the critical coagulation concentration (CCC) reached 190, 5.41, and 1.61 mM, respectively (Sun et al., 2018). GO nanosheets also had the ability to quench free radicals (30−45% hydroxyl and 12% nitroxide radicals). However, when GO was embedded in epoxy resin (ER), this ability disappeared (Hu et al., 2017). Ubiquitous nanocolloids (Nc) in surface water could also bind onto GO surface with strong affinity (K_d = 5.6 nM) and high adsorption capacity (159.8 mg/g) due to electron transfer, hydrophilic and π-π stacking effects. Interestingly, GO-Nc co-existence reduced the bioavailability of GO using zebrafish embryos as the model (Ouyang et al., 2019). GO was also studied with model proteins (OVA: ovalbumin and BSA). Higher concentration of OVA was required for the similar stability achieved by BSA due to the smaller molecular size and fewer positive charge groups of OVA (Sun et al., 2020).

The aggregation, sedimentation, and transformation of GO are also affected by various inorganic ions (i.e. salts) in water. The rate of sedimentation increased when salinity increased due to GO agglomerates formation. And the residence time of GO agglomerates in the ocean could exceed 500 days (Adeleye et al., 2019). Since $CaCl_2$ could bind with carboxyl and hydroxyl functional groups, the effect induced by $CaCl_2$ was high. And the ability of GO decreased in the presence of $CaCl_2$ as pH increased (Bayati and de Cortalezzi, 2019). A new mechanism of aggregation of GO in the natural aquatic environment was proposed that amorphous $CaMg(CO_3)_2$ nanoparticles could be formed on GO in soft water, and the generated $CaMg(CO_3)_2$ nanoparticles could help with GO aggregation and sedimentation by bridging action. The $CaMg(CO_3)_2$ nanoparticles were more preferred to be formed in neutral and alkaline conditions with GO aggregation (Zeng et al., 2019). The ferrous ion, which was an environmental reductant, could also influence the properties of GO (Wang et al., 2015). GO nanosheets were stacked with the presence of Fe^{2+}, but the stability maintained stable. GO was also reduced, evidenced by the change of oxygen functional groups (loss of epoxy and carbonyl groups, increase of carboxyl group) (Wang et al., 2015). Hassenkam et al. used functionalized AFM tips to study the interaction between GO and nonpolar/polar organic molecules (i.e. with alkyl, $-CH_3$, and carboxyl, −COOH). They found that ion bridging played an important role between −COOH tips and the GO surface, evidenced by the decreased adhesion between GO and tips in the order: Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}. However, for the $-CH_3$ tips, ion dependent adhesion was quite low but the trend was the same as the above order. The pH more greatly affected the adhesion of the −COOH tip rather than the -CH_3 tip. And when it was well-dispersed, GO could better hinder large pores formation and optimize the distribution of pore size than the re-agglomerated GO (Long et al., 2018b).

Besides, in the natural aquatic environment, hydrous oxides and clay minerals exist. GO nanosheets could be aggregated with kaolinite-goethite associations (KGA)-4% and KGA-10% at solution pH below 5 and 6, respectively. And high ratio of GO/KGA might cause toxicity to aquatic organisms (Huang et al., 2016). The interaction between GO and Na-montmorillonite (layered clay mineral) was studied in the presence of U(VI) (Wang et al., 2019b). Kaolin, as a representative clay mineral, could alleviate the toxicity of GO to protozoans, where kaolin served as an antidote to reduce the toxicity of GO (Kryuchkova and Fakhrullin, 2018). Qi et al. studied the interactions between GO and three ubiquitous clay minerals (including montmorillonite, kaolinite and diatomite) under various solution chemistry conditions. The affinity followed the order of montmorillonite > kaolinite > diatomite, indicating surface charge and surface area of clay minerals played important roles on the attachment of GO with clay minerals. In addition, the oxygen functional groups of GO and clay minerals could also affect the attachment between each other (Lu et al., 2019). Chrysikopoulos et al. investigated the interaction between GO and montmorillonite (MMT) colloids (common clay minerals) under different environmental conditions. Results indicated that pH could affect slightly the attachment of MMT onto quartz sand and GO was more preferred to be attached onto MMT than quartz sand (Syngouna et al., 2020). Additionally, Cs^{+} was found to induce GO aggregation by electric double-layer suppression and binding with oxygen functional groups in a weak mode. From DFT calculations, they proposed that the electrostatic distribution and charge transfer determined the radioactive elements destabilizing ability when the valence was higher (Gao et al., 2018). Polycarboxylate-based high range water reducer (P-HRWR) was also found to make GO stable by electrostatic interactions (Long et al., 2018a). When mixed with cement paste, GO could promote hydration products formation in cement paste.

3.2. Environmental reactions with disinfection agents in water treatment systems

Fullerenes have been found to be transformed with chlorine in the dark environment (Wu et al., 2016). Once entered into the water and wastewater treatment systems, GO could also experience changes of physicochemical properties (Li et al., 2016). GO surface O-functionalities changed significantly due to the oxidation of quinone groups under the treatment of chlorination and

chloramination. Large sized GO nanosheets became scrolled, attributed to the benzene ring destruction on the edge (Li et al., 2016). The chlorination process can also alter the surface charge of GO from −45 mV to −50 mV in magnitude due to the oxidation of −OH to −COOH group on the surface (Du et al., 2017). Reduced GO can stimulate anammox activity, which is recognized as the most widely used biological nitrogen removal method in water treatment plants, by bacterial growth stimulation and accelerating the anammox reaction rate, with its own structure oxidized (Tomaszewski et al., 2019). The effect of ozonation and hydroxyl radical attacked has been studied and results revealed that ozonation resulted in GO crumpling, GO edge truncation, holes generation (5–15 nm), and small-sized carbon fragments. When hydroxyl radical was combined in the system, GO could be further oxidized and cleavage some aromatic rings on GO (Du et al., 2019). Studies on interaction between DBP products and GO demonstrated that GO structure was wrinkled and the surface was not obviously crumpled after chlorination. But after bromination, the structure of GO was obviously crumpled and wrinkled, indicating GO was broken into small fragments (Liu et al., 2019a).

3.3. Adsorption of environmental pollutants by GO

Environmental pollutants such as heavy metal ions, dyes and organic contaminants are inevitably released into the natural aquatic environment and then become co-existing matters in the aqueous solution. On the other hand, GO is of importance for adsorbent applications in water treatment technologies due to a large surface area to mass ratio, high negative charge density and abundant oxygen-containing functional groups (Perreault et al., 2015b). Understanding how environmental pollutants interact with GO in water can help us better to understand the probable toxicity effect on human health and ecosystem. The interaction between GO and adsorbed pollutants will have an important influence on the fate and transformation of GO in aquatic environments.

Although the specific interactions for each type of pollutant may be different, several interactions exist between GO and adsorbed pollutants including electrostatic attraction, hydrogen bonding, π bonding interaction and Lewis-base−acid interaction (Wei et al., 2019; Zhao et al., 2014). Due to the presence of ionizable oxygen-containing groups, GO was negatively charged in neutral and basic solutions, and hence electrostatic attraction plays an important role in the adsorption of positively charged pollutants. The adsorption of heavy metal ions (e.g. Pb^{2+}, Cu^{2+}, Hg^{2+}) (Perreault et al., 2015b), cationic dyes (e.g. methylene blue and rhodamine B) (Aniruddha Molla, 2019) and surfactants (e.g. dodecyl trimethylammonium bromide, sodium dodecyl sulfate, Triton X-100) (Zhang et al., 2019a) was mediated through electrostatic interaction between GO and these pollutants (Liu et al., 2019b). Besides, electrostatic interactions was suggested to be one of most important mechanisms contributing to GO interaction with some organic micro-organic pollutants such as tetracycline (He et al., 2020), phenolic compounds (Catherine et al., 2018). Hydrogen bonding interaction was responsible for the adsorption of the adsorbates containing oxygen functional groups by GO (Reynosa-Martinez et al., 2020). For instance, López-Honorato et al. investigated the effect of the degree of oxidation on As(III) adsorption (primarily H_3AsO_3) by GO, and DFT calculation showed the interaction between GO and As(III) through hydrogen bonding (Reynosa-Martinez et al., 2020). The degree of oxidation could affect the adsorption capacity of As(III), but had no effect on cytotoxicity. It is noting that the hydrogen-bonding interaction may be weakened by the formation of hydrogen bonds between GO and water molecules in aqueous solutions. π bonding interaction was used to explain the adsorption of organic micro-pollutants by GO such as pesticides (Wang et al., 2020) and aromatic compounds (Huan Tang et al., 2020). It is also worth mentioning that multiple interactions may operate simultaneously in the adsorption of organic micro-pollutants onto GO in aqueous solution. For instance, Wang group demonstrated that both the π−π interaction and hydrogen bonds played significant roles in the adsorption of tetracycline antibiotics and chlorophenols onto GO, where they were mainly driven by the hydrophobic effect and ultimately stabilized by the hydrogen bonding and π-π interaction. These results were confirmed by using DFT calculation and Molecular Dynamics (MD) simulation (Ai et al., 2019; Wei et al., 2019). Lewis acid−base interactions including ligand exchange, metal ion exchange and complexation have been applied to understand the adsorption of heavy metal ions (Zhao et al., 2014) and some radionuclides (Wang et al., 2016a) in aqueous solution. For example, Wei et al. studied the adsorption performance of GO towards metallic hard (Na^{+}, Mg^{2+}), soft (Cd^{2+}, Pb^{2+}) and borderline ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}), suggesting the adsorption capacities of hard ions were substantially lower than that of soft and borderline ones (Kong et al., 2020). Wang et al. summarized that interactions of fission product elements and actinides with GO, which were mainly dominated by outer-sphere surface complexation at low pH values, and by inner-sphere surface complexation at high pH values. The results were obtained based on the results of batch techniques, surface complexation modeling, spectroscopic analysis and DFT calculations (Wang et al., 2016a).

3.4. Summary of environmental pathway of GO in the dark aquatic environment

The coexistence of GO with natural and discharged components in aquatic environments could alter its stability, transformation, toxicity and so forth. This section focused on summarizing main reactions between GO and natural constituents (NOM, salts and clay minerals)and disinfection agents (chlorine and ozone). The adsorption behaviors of environmental contaminants (heavy metal ions and organic micro-pollutants) by GO in dark aqueous solution was also summarized in this section. DFT calculation has been demonstrated to be very useful for exploring the adsorption mechanisms between environmental contaminants (e.g. organic micro-pollutants, heavy metal ions and radionuclides) onto GO. By combining with DFT calculations, the experimental results can be more accurately analyzed and conclusion can be drew in a solid way (Wei et al., 2019). During the past decades, progress has been made in understanding environmental pathway of GO. However, the aquatic environment is a complex system, thus the combined effects of components such as NOM-heavy metal mixtures, NOM-organic mixtures on GO transformation and related toxicity need to be deeply investigated. Moreover, there is still a great knowledge gap between the laboratory results and the actual transformation behavior of GO in natural aquatic environments. On the other hand, with the rapid development of economic and industry, different types of new chemicals will enter the natural environment, which also render the identification of GO transformation pathways and the associated health and environmental impact assessment as big challenges.

4. Environmental interactions with aquatic organisms and potential toxicity

4.1. Interactions with organism

Once GO released to the aquatic environment, we should

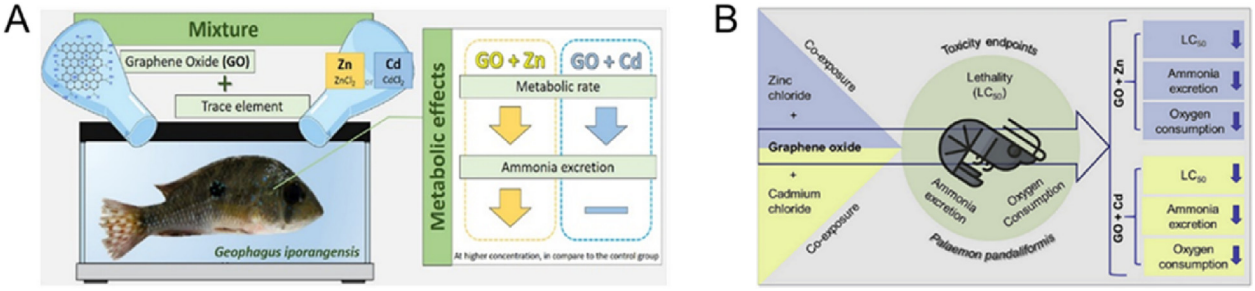

Fig. 4. Toxic effect of GO to freshfish and shrimp. (A) The effect of GO + Cd and GO + Zn on affecting the metabolism rate and ammonia excretion of Geophagus iporangensis. (B) The eco-toxicological effects of GO + Cd and GO + Zn on shrimp (Palaemon pandaliformis as the model) (De Medeiros et al., 2020; De Melo et al., 2019).

concern about its effects on organisms such as fish. Barbieri et al. investigated the toxicity of GO using a freshfish model, *Geophagus iporangensis*, which belonged to the Cichlidae family in the Ribeira de Iguape River basin in Brazil (Fig. 4A). The fish metabolism rate was greatly affected with GO + Cd and GO + Zn system. Ammonia excretion change was negligible with exposure to GO + Cd, in stark contrast to that with exposure to GO + Zn (rate increasing 47%) (De Medeiros et al., 2020). The ecotoxicological effects of co-exposure with GO + Cd and GO + Zn were also monitored by toxicity tests and metabolism evaluation in shrimp (*Palaemon pandaliformis* as the model) (Fig. 4B). For GO alone samples, GO did not exhibit obvious eco-toxicity up to 5.0 mg/L after 96 h exposure. However, the co-exposure of GO + Cd and GO + Zn inhibited the original metabolism of *P. pandaliformis* (De Melo et al., 2019). In addition, GO at expected environmental concentrations (1–100 μg/L) can hinder the development of zebrafish embryos due to excessive ROS generation (especially superoxide anion radical), protein carbonylation and DNA modification (Zhang et al., 2017). GO also possessed potential environmental risk to zebrafish, evidenced by inhibiting the cell growth and delaying the zebrafish embryos when the concentration reached 50 mg/L (Chen et al., 2012). *Acheta domesticus* (Gryllidae, Orthoptera, Insecta), which was native to Southwestern Asia, was often used for initial toxicological tests before mammals. After GO was injected into *Acheta domesticus*, the oxidative stress and enzyme activity enhanced. *Acheta domesticus*, was also trying to cope with the stress, in the very first 24 h. They also found that HSP 70 levels increased, suggesting that new proteins were generated (Dziewiecka et al., 2016). Lee et al. evaluated the toxicity of GO using zebrafish as *in vivo* model system (Jeong et al., 2015). They demonstrated that GO could disturb and mispattern the trunk blood vessel development and exhibit the dose-dependent gross morphological defects (Jeong et al., 2015). The fresh water fish *Anabas testudineus* has also been used as the model fish to evaluate the toxic effects induced by GO. Results revealed that GO could induce oxidative stress within cell and mitochondria in the freshwater fish, evidenced by augmented accumulation of lipid peroxides, enzyme activity, alleviated total red blood corpuscle count and the protein level changes (Paital et al., 2019). When using zebrafish as the model species, GO was also found to change the primary gut microbiota composition in zebrafish, evidenced by increasing the abundance of *Fusobacteria* and the genus *Cetobacterium* and *Lactobacillus* and decreasing that of *Firmicutes* and the genus *Pseudomonas*. The microbial community structure was also shift compared to that without GO treatment (Zheng et al., 2019). Wang et al. used *Caenorhabditis elegans* as the animal model, and they found that GO could greatly disrupt the protein-protein interaction, evidenced by the inhibition of the interaction (Zhao et al., 2020b). In addition, GO could alter the intestinal Wnt signaling pathway, suggesting its toxicity induction in *Caenorhabditis elegans* (Liu et al., 2020a). When GO was at high concentration (500 mg/L), *A. salina* showed lethal effects induced by GO. However, even at low concentration of GO (i.e., 1 mg/L), growth inhibition could be observed. When GO was with Phe or Cd^{2+}, the toxicity enhanced, probably due to the promoted toxicants bioaccumulation (Lu et al., 2018). For adult zebrafish, the antioxidant metabolism can be disturbed by GO. Even after 168 h-recovery in clean water, homeostasis could not be restored completely (Souza et al., 2019). GO could cause acute and chronic effects to *Ceriodaphnia dubia* with the mean effective concentration to be 1.25 mg/L of GO (Souza et al., 2018). GO exposure to adult zebrafish (*Danio rerio*) could result in increasing the number of gill cells, but no genotoxicity was observed in blood cells (Souza et al., 2017). To *Daphnia magna (D. magna)*, GO exhibited significant toxicity with 48 h-LC50 of 84.2 mg/L and the 21 d-LC50 for chronic toxicity of 3.3 mg/L. Additionally, HA mitigated toxicity of GO to *D. magna* by 32.3%. The presence of HA could reduce the body accumulation in D. magna (Zhang et al., 2019d). The effect of HA on the ecotoxicity of GO was also confirmed by Castro and colleagues (Castro et al., 2018). They estimated the toxic effect by using 9 organism in the aquatic environment: *Raphidocelis subcapitata* (green algae), *Lemna minor* (aquatic plant), *Lactuca sativa* (lettuce), *Daphnia magna* (planktonic microcrustacean), *Artemia salina* (brine shrimp), *Chironomus sancticaroli* (Chironomidae), *Hydra attenuata* (freshwater polyp), and *Caenorhabditis elegans* and *Panagrolaimus* sp. (nematodes) (Castro et al., 2018). Hu et al. reported that the heart rate of zebrafish larvae was increased and pericardial edema was induced by changing protein expression. The oxidative stress and disorders of mitochondrial was also observed in the process (Zou et al., 2018).

4.2. Interactions with algae

Some studies have been monitored on evaluating the interaction between GO and algae. For example, GO nanosheets released into the aquatic environment could not alter the algal growth, whereas GO-ER composite could promote algal reproduction by 34% and chlorophyll biosynthesis by 65–127% after 4 days due to the upregulated amino acids metabolism and the downregulated fatty acid biosynthesis (Hu et al., 2017). However, Hu et al. estimated the eco-toxicity of GO to protozoa *Euglena gracilis* as the model algae organism and found that the inhibition growth can be observed and antioxidant enzyme activities enhanced at GO concentration above 2.5 mg/L, suggesting the GO toxicity to the representative algae (Hu et al., 2015). The toxicological effects of GO was also evaluated with green algae *Raphidocelis subcapitata*. The algal density and autofluorescence changed with specific concentrations of GO, thus induce the toxicity of GO. ROS generation and membrane damage could also been observed (Nogueira et al., 2015). GO did not shown obvious damaging effects to the *Microcystis aeruginosa* algal cell, evidenced by the negligible effect on the

algal growth. But extracellular algal organic matter was greatly influenced after the interaction between GO with algae (Xin et al., 2018). The extent of oxidation on GO also played an important role on the toxicity towards algae (*Raphidocelis subcapitata).* GO with heavy oxidation exhibited stronger toxic effects to *Raphidocelis subcapitata* than that with light oxidation. The authors proposed that the difference might be because GO with slight oxidation could serve as a "nano-blade" to induce the mechanical damage to algal cells, due to fewer oxygen functional groups on GO surface (Malina et al., 2019). GO could induce obvious toxicity to *Scenedesmus obliquus (S. obtiquus)* with 20.6 mg/L of 72-h LC50. And the humic acid in the aqueous system could mitigate the toxicity of GO to *S. obliquus* by 28.6% due to the alleviated oxidative damage by HA to *S. obliquus* on surface envelopment (Zhang et al., 2019d). Similarly, Rosal et al. proved that GO-wastewater mixtures (with polar pharmaceuticals, metabolites and artificial sweeteners) were found to be less influenced with lower toxicity to the unicellular green alga *Chlamydomonas reinhardtii* compared with GO alone samples (Martin-de-Lucia et al., 2018). Zhou et al. demonstrated that HA could mitigate the toxicity of GO. They proposed three possible mechanisms with the HA alleviation of toxicity: (1) The contact of GO with algae cells were reduced after HA was adsorbed on GO; (2) The physical penetration and damage was less by decreasing GO deposition on algae cells by interacting with HA; (3) Serving as an antioxidant to react with ROS that might be toxic to algae cells (Zhang et al., 2018). GO could also induce algae toxicity with IC10 of 0.66 mg/L and IC50 of 4.96 mg/L. The inhibition rate could be altered once the media was changed (Markovic et al., 2020).

4.3. Interactions with bacteria

Antibacterial applications are prevalent with two-dimensional (2D) nanomaterials in recent years due to their environmental-friendly mode of antibacterial action. GO has been intensively studied on the antibacterial effects against various bacteria (Tashan et al., 2019). Several reviews have included the antibacterial activities of GO (Fadeel et al., 2018; Xin et al., 2019; Zheng et al., 2020). So here in our review, we filled the gap of most recent antibacterial studies rather than repeat the summary in other reviews that have been reported. Based on previous studies, sharp edges of GO nanosheets played important roles in the antibacterial activities by puncturing or penetrating into the cell membranes, leading to the bacterial cell destruction and leakage of intracellular components (Krishnamoorthy et al., 2012; Liu et al., 2011; Tu et al., 2013). Zhang et al. recently found that GO could act as a chemoattractant that the bacteria could be lured to the sheet surface (Fig. 5A). The mechanism exploration revealed that GO could be attached to the cell membrane and disturb the bacterial signaling network by transmembrane chemoreceptors. Bacterial cell would be aggregated and migrated to the GO surface by an activated chemotactic system. This is quite a new and interesting discovery that proposed the new mechanism on antibacterial activities of GO (Zhang et al., 2020a). The degree of oxidation on GO also exhibited different antibacterial activities toward *E. coli*, evidenced by strongest intracellular ROS and loss of glutathione induced by highly oxidized GO (Barrios et al., 2019). Zhang et al. demonstrated that superoxide anion radical played a very important role by disturbing GO reduction, thus induce GO react with the membrane-bound cytochrome *c* of *E. coli* (Zhao et al., 2018). When using benzophenone chemistry to functionalize GO on the membrane surfaces, functionalized GO membrane showed up to 90% inhibition rate compared to that with pristine membranes (Fig. 5B) (Kaneda et al., 2019). The physical properties have always been demonstrated to be key factors on changing the antibacterial activities of GO. For example, GO with small size exhibited excellent antibacterial efficiency when used as membrane surfaces (Perreault et al., 2015a). By changing the orientation of GO (vertically aligned GO), enhanced antibacterial efficiency could be achieved via increased edge density for preferential membrane disruption (Fig. 5C) (Lu et al., 2017). External factors, such as solar irradiation, was also a key factor on affecting antibacterial activities of GO. Under solar irradiation, GO exhibited greater cell membrane disruption and oxidative stress to bacteria (i.e. *E. coli*), resulting in enhanced antibacterial activities (Hou et al., 2017). GO was found to be able to disrupt the bacteria cell membranes with sharp edges based on the contact. In addition, the Gram-negative bacteria (with outer membrane) can be more resistant than the Gram-positive bacteria (no outer membrane)

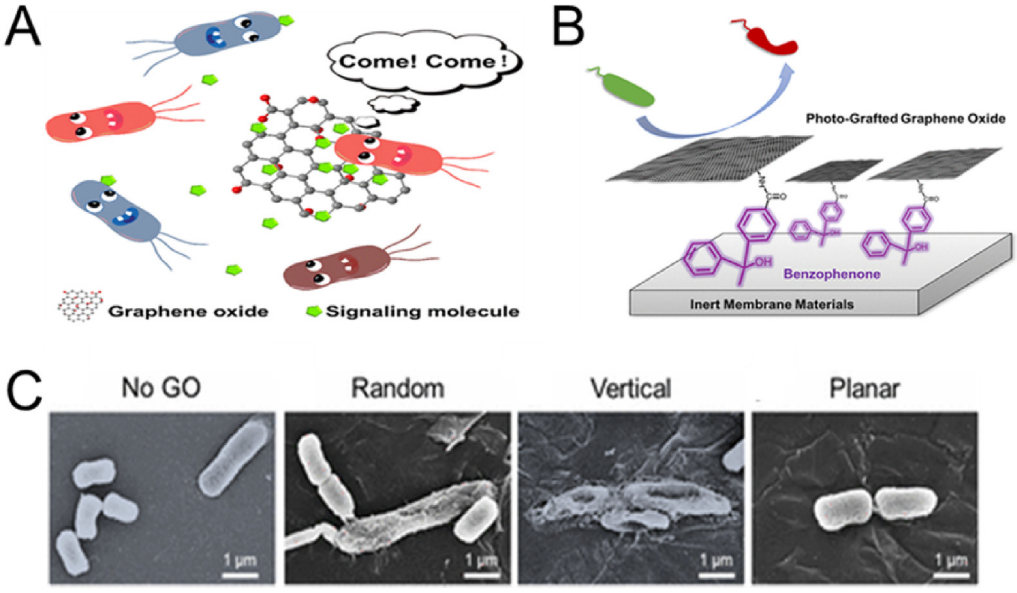

Fig. 5. Antibacterial Activities of GO. (A). GO as a chemoattractant to be lured on the sheet surface (B) Functionalized GO membrane in effectively controlling biofouling (C) Enhanced antibacterial activity exhibited with vertically aligned GO (Kaneda et al., 2019; Lu et al., 2017; Zhang et al., 2020a).

(Akhavan and Ghaderi, 2010). Rodrigues et al. investigated the effects of GO to the wastewater microbial community and they found that GO could significantly impact the bacterial metabolic activity and bacterial viability in the activated sludge due to the generation of ROS (Ahmed and Rodrigues, 2013). Yu et al. conducted the antibacterial activities of GO under light irradiation and found that light-induced electrons could promote the GO reduction, thus enhance the antibacterial activities of GO, due to more carbon-centered free radicals generated (Chong et al., 2017).

4.4. Interactions in the intracellular level

GO, when served as a film, did not show any toxic effects on the mammalian cells, by contrast, promoted mammalian cell attachment and proliferation (Ruiz et al., 2011). Hu et al. demonstrated that GO could induce oxidative stress, alter membrane transport and influence amino acid metabolism when estimating the GO toxicity in the intracellular level (Li et al., 2018b). Chen et al. proposed that cytotoxicity mechanisms were due to the iron deficiency induced by binding with the oxygen functional groups of GO rather than the regular mechanism, such as plasma membrane damage or oxidative stress when using eukaryotes (i.e. *Saccharomyces cerevisiae*, *Candida albicans*, and *Komagataella pastoris*) and prokaryotes (*Pseudomonas fluorescens*) as models (Yu et al., 2017). Size was also a key factor in the interaction between GO and cells. Small nanosheets were proved to be able to enter cells by clathrin-mediated endocytosis, and large size could enhance phagocytotic uptake of GO nanosheets (Mu et al., 2012).

The evaluation of interactions between nanomaterials and DNA is also an important part for the assessment of potential risk of nanomaterials in the intracellular level. For carbonaceous nanomaterials, fullerenes are the most studied (Takenaka et al., 1999; Wang et al., 2009). Here for the first time, we summarized the interactions between GO and DNA (Tang et al., 2012). GO has been proved to possess the DNA cleavage activities (Xu et al., 2019). Recent study showed that a size-dependent trend of DNA intercalation ability into plasmid DNA base pairs was observed, and the ability of smaller size GO was stronger (Xu et al., 2019). GO nanosheets, when combined with Cu^{2+}, can cut DNA in the oxidative and hydrolytic GO/Cu^{2+} system (Ren et al., 2010). Graphene quantum dots (GQDs) together with Ni^{2+} and/or Zn^{2+} conjugate systems could induce DNA cleavage, but GQDS, Ni^{2+}, Zn^{2+} alone didn't have the ability. The ability of the conjugate system was attributed to the ROS generation catalyzed by the metal ions (Liu et al., 2016b). The DNA activity of GQDs/copper ions (Cu^{2+}) can be accelerated by the formation of transient reactive radicals with the GQDs/Cu^{2+} three dimensional metal complexes for high efficient DNA cleavage (Zheng et al., 2014). GQDs can also prove to enhance the DNA cleavage activities of doxorubicin (DOX), when used as anti-cancer drug applications (Wang et al., 2013). GO can induce DNA cleavage obviously, as an electron shuttle to transfer electron to molecular oxygen, producing ROS in the presence of reductant nicotinamide adenine dinucleotide (NADH) (Zhao et al., 2017). Shang et al. found that OH-GQDs could induce DNA damage and cytoskeleton signal pathways in HET-1A cells (Li et al., 2018a). The ability of cleavaging DNA with GO provided insights into the potential environmental risk of GO in the aquatic environment. On the other hand, it might be a way of using GO to dispose and manage the biological contaminants in the environmental fields.

4.5. Summary of environmental interactions with aquatic organisms and potential toxicity

The interactions between GO and the aquatic organism discriminated due to the various synthesis method and composition of GO, as well as the diverse organisms. The excellent antibacterial activities of GO showed great potential in antibacterial applications due to the contact mode of antimicrobial action. The DNA cleavage activities of GO could potentially apply on managing the biological contaminants in the environmental area. However, from the results of evaluating the toxicity of GO, we should pay attention to the safety assessment of GO since some studies showed that GO could be toxic to the aquatic organism. In addition, long-term toxicity assessment and more factors affecting the interactions with aquatic organisms should be considered. Benefits and toxicities induced by GO should be balanced when using it as applications.

5. Outlook and perspective

The potential of GO, the most studied graphene derivative, for environmental and other industrial applications have been well recognized. As the potential for large-scale of production is higher, more concerns come alone due to its inevitable release to the natural aquatic environment. From the current studies, we could know that environmental transformation is very important pathway with GO. This review is the first to summarize photo transformation of GO by dividing into different light sources. The same product of photochemical reaction of GO in all photochemical reaction is reduced GO. And all others products of GO under irradiation are quite different with various sources, thus the light source is extremely important in studying the transformation of GO. When GO is in the dark aquatic environment, GO could interact with a variety of natural constituents including NOM, salts, BSA, pollutants and some disinfection agents in the aquatic environment. The stability and chemical composition can be greatly influenced. And the release of GO could finally possess potential risk to the whole ecosystem. There are still challenges in evaluating the environmental transformation of GO. For example, the difficulty in environmental transformation of GO was limited by the various technical synthesis confusion, short-term evaluation and the complicated constituents in natural waters. Since GO can be synthesized in different methods, the composition of GO on the surface varies, which can make great difference in results in estimating the environmental transformation of GO. Besides, once GO was released into natural aquatic environment, long-term evaluation was needed since the existing studies were mostly in short term. The constituents of natural waters in different areas could also influence the environmental transformation of GO. New emergency of pharmaceuticals and chemicals in natural waters, which could

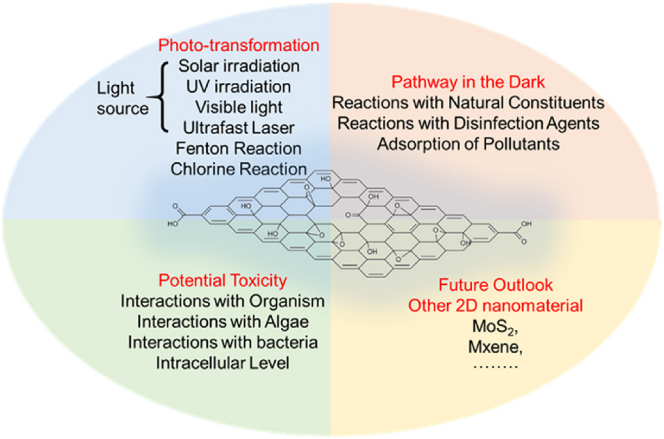

Fig. 6. Overview of this review study and future outlook.

interact with GO, also strengthens the obstacle in estimating the environmental transformation of GO. Therefore, more factors were needed to make thorough assessment of environmental transformation of GO to fulfill the present challenges.

This review enlightens us to pay attention to behaviors of other two-dimensional GO-like nanomaterials, such as MoS_2 (Chen et al., 2017; Karunakaran et al., 2018; Liu et al. 2014, 2016a; Tong et al., 2019; Wang et al., 2016b; Yu et al., 2018; Zhu et al., 2018; Zou et al., 2019), Mxenes (Ding et al., 2020; Kuznetsov et al., 2019; Rasool et al., 2016), black phosphorus (Li et al., 2019b; Wang et al., 2019a; Zhang et al., 2019b; Zhou et al., 2019), which have been intensively applied and studied in recent years (Fig. 6). This review will contribute to give a more thorough and detailed environmental assessment summary of this most popular nanomaterial, GO, in the very past decade.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abdelsayed, V., Moussa, S., Hassan, H.M., Aluri, H.S., Collinson, M.M., El-Shall, M.S., 2010. Photothermal deoxygenation of graphite oxide with laser excitation in solution and graphene-aided increase in water temperature. J. Phys. Chem. Lett. 1 (19), 2804–2809.

Adeleye, A.S., Ho, K.T., Zhang, M., Li, Y., Burgess, R.M., 2019. Fate and transformation of graphene oxide in estuarine and marine waters. Environ. Sci. Technol. 53 (10), 5858–5867.

Adeleye, A.S., Wang, X.Z., Wang, F.L., Hao, R.J., Song, W.H., Li, Y., 2018. Photoreactivity of graphene oxide in aqueous system: reactive oxygen species formation and bisphenol A degradation. Chemosphere 195, 344–350.

Ahmed, F., Rodrigues, D.F., 2013. Investigation of acute effects of graphene oxide on wastewater microbial community: a case study. J. Hazard Mater. 256, 33–39.

Ai, Y.J., Liu, Y., Huo, Y.Z., Zhao, C.F., Sun, L., Han, B., Cao, X.R., Wang, X.K., 2019. Insights into the adsorption mechanism and dynamic behavior of tetracycline antibiotics on reduced graphene oxide (RGO) and graphene oxide (GO) materials. Environmental Science-Nano 6 (11), 3336–3348.

Akhavan, O., Ghaderi, E., 2010. Toxicity of graphene and graphene oxide nanowalls against bacteria. ACS Nano 4 (10), 5731–5736.

Alotaibi, F., Tung, T.T., Nine, M.J., Kabiri, S., Moussa, M., Tran, D.N.H., Losic, D., 2018. Scanning atmospheric plasma for ultrafast reduction of graphene oxide and fabrication of highly conductive graphene films and patterns. Carbon 127, 113–121.

Amadei, C.A., Montessori, A., Kadow, J.P., Succi, S., Vecitis, C.D., 2017. Role of oxygen functionalities in graphene oxide architectural laminate subnanometer spacing and water transport. Environ. Sci. Technol. 51 (8), 4280–4288.

An, S.Y., Wu, J.W., Nie, Y., Li, W.L., Fortner, J.D., 2020. Free chlorine induced phototransformation of graphene oxide in water: reaction kinetics and product characterization. Chem. Eng. J. 381.

Andryushina, N.S., Stroyuk, O.L., Yanchuk, I.B., Yefanov, A.V., 2014. A dynamic light scattering study of photochemically reduced colloidal graphene oxide. Colloid Polym. Sci. 292 (2), 539–546.

Anichini, C., Czepa, W., Pakulski, D., Aliprandi, A., Ciesielski, A., Samori, P., 2018. Chemical sensing with 2D materials. Chem. Soc. Rev. 47 (13), 4860–4908.

Aniruddha Molla, Y.L., Mandal, Bikash, Kang, Sung Gu, Hur, Seung Hyun, Chung, Jin Suk, 2019. Selective adsorption of organic dyes on graphene oxide Theoretical and experimental analysis. Appl. Surf. Sci. 464, 170–177.

Bai, H., Jiang, W.T., Kotchey, G.P., Saidi, W.A., Bythell, B.J., Jarvis, J.M., Marshall, A.G., Robinson, R.A.S., Star, A., 2014. Insight into the mechanism of graphene oxide degradation via the photo-fenton reaction. J. Phys. Chem. C 118 (19), 10519–10529.

Barrios, A.C., Wang, Y., Gilbertson, L.M., Perreault, F., 2019. Structure-property-toxicity relationships of graphene oxide: role of surface chemistry on the mechanisms of interaction with bacteria. Environ. Sci. Technol. 53 (24), 14679–14687.

Barroso-Bujans, F., Cerveny, S., Verdejo, R., del Val, J., Alberdi, J., Alegría, A., Colmenero, J., 2010. Permanent adsorption of organic solvents in graphite oxide and its effect on the thermal exfoliation. Carbon 48 (4), 1079–1087.

Bayati, M., de Cortalezzi, M.F., 2019. Aggregation of graphene oxide in natural waters: role of solution chemistry and specific interactions. J. Environ. Eng. 145 (9), 04019050.

Castro, V.L., Clemente, Z., Jonsson, C., Silva, M., Vallim, J.H., de Medeiros, A.M.Z., Martinez, D.S.T., 2018. Nanoecotoxicity assessment of graphene oxide and its relationship with humic acid. Environ. Toxicol. Chem. 37 (7), 1998–2012.

Catherine, H.N., Ou, M.H., Manu, B., Shih, Y.H., 2018. Adsorption mechanism of emerging and conventional phenolic compounds on graphene oxide nanoflakes in water. Sci. Total Environ. 635, 629–638.

Chang, Y., Yang, S.-T., Liu, J.-H., Dong, E., Wang, Y., Cao, A., Liu, Y., Wang, H., 2011. In vitro toxicity evaluation of graphene oxide on A549 cells. Toxicol. Lett. 200 (3), 201–210.

Chen, L.Q., Hu, P.P., Zhang, L., Huang, S.Z., Luo, L.F., Huang, C.Z., 2012. Toxicity of graphene oxide and multi-walled carbon nanotubes against human cells and zebrafish. Sci. China Chem. 55 (10), 2209–2216.

Chen, S.C., Lin, C.Y., Cheng, T.L., Tseng, W.L., 2017. 6-Mercaptopurine-Induced fluorescence quenching of monolayer MoS2 nanodots: applications to glutathione sensing, cellular imaging, and glutathione-stimulated drug delivery. Adv. Funct. Mater. 27 (41), 1702452.

Chen, Y., Tan, C.L., Zhang, H., Wang, L.Z., 2015. Two-dimensional graphene analogues for biomedical applications. Chem. Soc. Rev. 44 (9), 2681–2701.

Chong, Y., Ge, C.C., Fang, G., Wu, R.F., Zhang, H., Chai, Z.F., Chen, C.Y., Yin, J.J., 2017. Light-enhanced antibacterial activity of graphene oxide, mainly via accelerated electron transfer. Environ. Sci. Technol. 51 (17), 10154–10161.

Chowdhury, I., Duch, M.C., Mansukhani, N.D., Hersam, M.C., Bouchard, D., 2013. Colloidal properties and stability of graphene oxide nanomaterials in the aquatic environment. Environ. Sci. Technol. 47 (12), 6288–6296.

Chowdhury, I., Hou, W.-C., Goodwin, D., Henderson, M., Zepp, R.G., Bouchard, D., 2015a. Sunlight affects aggregation and deposition of graphene oxide in the aquatic environment. Water Res. 78, 37–46.

Chowdhury, I., Mansukhani, N.D., Guiney, L.M., Hersam, M.C., Bouchard, D., 2015b. Aggregation and stability of reduced graphene oxide: complex roles of divalent cations, pH, and natural organic matter. Environ. Sci. Technol. 49 (18), 10886–10893.

De Medeiros, A.M.Z., Coa, F., Alves, O.L., Martinez, D.S.T., Barbieri, E., 2020. Metabolic effects in the freshwater fish Geophagus iporangensis in response to single and combined exposure to graphene oxide and trace elements. Chemosphere 243, 125316.

De Melo, C.B., Coa, F., Alves, O.L., Martinez, D.S.T., Barbieri, E., 2019. Co-exposure of graphene oxide with trace elements: effects on acute ecotoxicity and routine metabolism in Palaemon pandaliformis (shrimp). Chemosphere 223, 157–164.

Ding, L., Li, L.B., Liu, Y.C., Wu, Y., Lu, Z., Deng, J.J., Wei, Y.Y., Caro, J., Wang, H.H., 2020. Effective ion sieving with Ti3C2Tx MXene membranes for production of drinking water from seawater. Nature Sustainability 3 (4), 296–302.

Dreyer, D.R., Park, S., Bielawski, C.W., Ruoff, R.S., 2010. The chemistry of graphene oxide. Chem. Soc. Rev. 39 (1), 228–240.

Du, T.T., Adeleye, A.S., Keller, A.A., Wu, Z.N., Han, W., Wang, Y.Y., Zhang, C.D., Li, Y., 2017. Photochlorination-induced transformation of graphene oxide: mechanism and environmental fate. Water Res. 124, 372–380.

Du, T.T., Adeleye, A.S., Zhang, T., Jiang, C.J., Zhang, M., Wang, H.H., Li, Y., Keller, A.A., Chen, W., 2018. Influence of light wavelength on the photoactivity, physicochemical transformation, and fate of graphene oxide in aqueous media. Environmental Science-Nano 5 (11), 2590–2603.

Du, T.T., Adeleye, A.S., Zhang, T., Yang, N., Hao, R.J., Li, Y., Song, W.H., Chen, W., 2019. Effects of ozone and produced hydroxyl radicals on the transformation of graphene oxide in aqueous media. Environmental Science-Nano 6 (8), 2484–2494.

Duan, L., Zhang, T., Song, W.H., Jiang, C.J., Hou, Y., Zhao, W.L., Chen, W., Alvarez, P.J.J., 2019. Photolysis of graphene oxide in the presence of nitrate: implications for graphene oxide integrity in water and wastewater treatment. Environmental Science-Nano 6 (1), 136–145.

Dziewiecka, M., Karpeta-Kaczmarek, J., Augustyniak, M., Majchrzycki, L., Augustyniak-Jablokow, M.A., 2016. Evaluation of in vivo graphene oxide toxicity for Acheta domesticus in relation to nanomaterial purity and time passed from the exposure. J. Hazard Mater. 305, 30–40.

Fadeel, B., Bussy, C., Merino, S., Vazquez, E., Flahaut, E., Mouchet, F., Evariste, L., Gauthier, L., Koivisto, A.J., Vogel, U., Martin, C., Delogu, L.G., Buerki-Thurnherr, T., Wick, P., Beloin-Saint-Pierre, D., Hischier, R., Pelin, M., Carniel, F.C., Tretiach, M., Cesca, F., Benfenati, F., Scaini, D., Ballerini, L., Kostarelos, K., Prato, M., Bianco, A., 2018. Safety assessment of graphene-based materials: focus on human health and the environment. ACS Nano 12 (11), 10582–10620.

Felip-Leon, C., Puche, M., Miravet, J.F., Galindo, F., Feliz, M., 2019. A spectroscopic study to assess the photogeneration of singlet oxygen by graphene oxide. Mater. Lett. 251, 45–51.

Gao, W., Alemany, L.B., Ci, L.J., Ajayan, P.M., 2009. New insights into the structure and reduction of graphite oxide. Nat. Chem. 1 (5), 403–408.

Gao, Y., Chen, K., Ren, X.M., Alsaedi, A., Hayat, T., Chen, C.L., 2018. Exploring the aggregation mechanism of graphene oxide in the presence of radioactive

elements: experimental and theoretical studies. Environ. Sci. Technol. 52 (21), 12208–12215.
Gao, Y., Ren, X.M., Song, G., Chen, D.Y., Zhang, X.D., Chen, C.L., 2020. Colloidal properties and stability of UV-transformed graphene oxide in aqueous solutions: the role of disorder degree. J. Hazard Mater. 382, 121097.
Gao, Y., Ren, X.M., Tan, X.L., Hayat, T., Alsaedi, A., Chen, C.L., 2017. Insights into key factors controlling GO stability in natural surface waters. J. Hazard Mater. 335, 56–65.
Gao, Y., Ren, X.M., Zhang, X.D., Chen, C.L., 2019. Environmental fate and risk of ultraviolet- and visible-light-transformed graphene oxide: a comparative study. Environ. Pollut. 251, 821–829.
Gengler, R.Y.N., Badali, D.S., Zhang, D.F., Dimos, K., Spyrou, K., Gournis, D., Miller, R.J.D., 2013. Revealing the ultrafast process behind the photoreduction of graphene oxide. Nat. Commun. 4, 2560.
Ghasemi, F., Razi, S., Madanipour, K., 2018. Single-step laser-assisted graphene oxide reduction and nonlinear optical properties exploration via CW laser excitation. J. Electron. Mater. 47 (5), 2871–2879.
Guardia, L., Villar-Rodil, S., Paredes, J., Rozada, R., Martínez-Alonso, A., Tascón, J., 2012. UV light exposure of aqueous graphene oxide suspensions to promote their direct reduction, formation of graphene–metal nanoparticle hybrids and dye degradation. Carbon 50 (3), 1014–1024.
Gudarzi, M.M., 2016. Colloidal stability of graphene oxide: aggregation in two dimensions. Langmuir 32 (20), 5058–5068.
Hada, M., Miyata, K., Ohmura, S., Arashida, Y., Ichiyanagi, K., Katayama, I., Suzuki, T., Chen, W., Mizote, S., Sawa, T., Yokoya, T., Seki, T., Matsuo, J., Tokunaga, T., Itoh, C., Tsuruta, K., Fukaya, R., Nozawa, S., Adachi, S., Takeda, J., Onda, K., Koshihara, S., Hayashi, Y., Nishina, Y., 2019. Selective reduction mechanism of graphene oxide driven by the photon mode versus the thermal mode. ACS Nano 13 (9), 10103–10112.
He, J., Ni, F., Cui, A., Chen, X., Deng, S., Shen, F., Huang, C., Yang, G., Song, C., Zhang, J., Tian, D., Long, L., Zhu, Y., Luo, L., 2020. New insight into adsorption and co-adsorption of arsenic and tetracycline using a Y-immobilized graphene oxide-alginate hydrogel: adsorption behaviours and mechanisms. Sci. Total Environ. 701, 134363.
He, X.X., Zhang, S.J., Pan, H.F., Chen, J.Q., Xu, J.H., 2019. Horizontally aggregation of monolayer reduced graphene oxide under deep UV irradiation in solution. Nanoscale Research Letters 14, 117.
Hou, W.-C., Chowdhury, I., Goodwin Jr., D.G., Henderson, W.M., Fairbrother, D.H., Bouchard, D., Zepp, R.G., 2015. Photochemical transformation of graphene oxide in sunlight. Environ. Sci. Technol. 49 (6), 3435–3443.
Hou, W.C., Lee, P.L., Chou, Y.C., Wang, Y.S., 2017. Antibacterial property of graphene oxide: the role of phototransformation. Environmental Science-Nano 4 (3), 647–657.
Hou, W.C., Wang, Y.S., 2017. Photocatalytic generation of H2O2 by graphene oxide in organic electron donor-free condition under sunlight. ACS Sustain. Chem. Eng. 5 (4), 2994–3001.
Hu, C.W., Wang, Q., Zhao, H.T., Wang, L.Z., Guo, S.F., Li, X.L., 2015. Ecotoxicological effects of graphene oxide on the protozoan Euglena gracilis. Chemosphere 128, 184–190.
Hu, W., Peng, C., Lv, M., Li, X., Zhang, Y., Chen, N., Fan, C., Huang, Q., 2011. Protein corona-mediated mitigation of cytotoxicity of graphene oxide. ACS Nano 5 (5), 3693–3700.
Hu, X.G., Kang, W.L., Mu, L., 2017. Aqueously released graphene oxide embedded in epoxy resin exhibits different characteristics and phytotoxicity of chlorella vulgaris from the pristine form. Environ. Sci. Technol. 51 (10), 5425–5433.
Huan Tang, S.Z., Huang, Tinglin, Cuic, Fuyi, Xing, Baoshan, 2020. pH-dependent adsorption of aromatic compounds on graphene oxide an experimental, molecular dynamics simulation and density functional theory investigation. Journal of Hzardous materials 395, 12680.
Huang, G.X., Guo, H.Y., Zhao, J., Liu, Y.H., Xing, B.S., 2016. Effect of co-existing kaolinite and goethite on the aggregation of graphene oxide in the aquatic environment. Water Res. 102, 313–320.
Huang, L., Liu, Y., Ji, L.C., Xie, Y.Q., Wang, T., Shi, W.Z., 2011. Pulsed laser assisted reduction of graphene oxide. Carbon 49 (7), 2431–2436.
Jeong, J., Cho, H.J., Choi, M., Lee, W.S., Chung, B.H., Lee, J.S., 2015. In vivo toxicity assessment of angiogenesis and the live distribution of nano-graphene oxide and its PEGylated derivatives using the developing zebrafish embryo. Carbon 93, 431–440.
Ji, T.H., Hua, Y.Y., Sun, M., Ma, N., 2013. The mechanism of the reaction of graphite oxide to reduced graphene oxide under ultraviolet irradiation. Carbon 54, 412–418.
Jiang, Y., Raliya, R., Liao, P., Biswas, P., Fortner, J.D., 2017. Graphene oxides in water: assessing stability as a function of material and natural organic matter properties. Environmental Science-Nano 4 (7), 1484–1493.
Kaneda, M., Lu, X.L., Cheng, W., Zhou, X.C., Bernstein, R., Zhang, W., Kimura, K., Elimelech, M., 2019. Photografting graphene oxide to inert membrane materials to impart antibacterial activity. Environ. Sci. Technol. Lett. 6 (3), 141–147.
Karunakaran, S., Pandit, S., Basu, B., De, M., 2018. Simultaneous exfoliation and functionalization of 2H-MoS2 by thiolated surfactants: applications in enhanced antibacterial activity. J. Am. Chem. Soc. 140 (39), 12634–12644.
Khan, A., Wang, J., Li, J., Wang, X.X., Chen, Z.S., Alsaedi, A., Hayat, T., Chen, Y.T., Wang, X.K., 2017. The role of graphene oxide and graphene oxide-based nanomaterials in the removal of pharmaceuticals from aqueous media: a review. Environ. Sci. Pollut. Control Ser. 24 (9), 7938–7958.
Kim, S.R., Parvez, M.K., Chhowalla, M., 2009. UV-reduction of graphene oxide and its application as an interfacial layer to reduce the back-transport reactions in dye-sensitized solar cells. Chem. Phys. Lett. 483 (1), 124–127.
Koinuma, M., Ogata, C., Kamei, Y., Hatakeyama, K., Tateishi, H., Watanabe, Y., Taniguchi, T., Gezuhara, K., Hayami, S., Funatsu, A., Sakata, M., Kuwahara, Y., Kurihara, S., Matsumoto, Y., 2012. Photochemical engineering of graphene oxide nanosheets. J. Phys. Chem. C 116 (37), 19822–19827.
Kong, Q., Preis, S., Li, L., Luo, P., Wei, C., Li, Z., Hu, Y., Wei, C., 2020. Relations between metal ion characteristics and adsorption performance of graphene oxide: a comprehensive experimental and theoretical study. Separ. Purif. Technol. 232, 115956.
Krishnamoorthy, K., Veerapandian, M., Zhang, L.-H., Yun, K., Kim, S.J., 2012. Antibacterial efficiency of graphene nanosheets against pathogenic bacteria via lipid peroxidation. J. Phys. Chem. C 116 (32), 17280–17287.
Kryuchkova, M., Fakhrullin, R., 2018. Kaolin alleviates graphene oxide toxicity. Environ. Sci. Technol. Lett. 5 (5), 295–300.
Kuang, Y., Shang, J., Zhu, T., 2020. Photoactivated graphene oxide to enhance photocatalytic reduction of CO2. ACS Appl. Mater. Interfaces 12 (3), 3580–3591.
Kuznetsov, D.A., Chen, Z.X., Kumar, P.V., Tsoukalou, A., Kierzkowska, A., Abdala, P.M., Safonova, O.V., Fedorov, A., Muller, C.R., 2019. Single site cobalt substitution in 2D molybdenum carbide (MXene) enhances catalytic activity in the hydrogen evolution reaction. J. Am. Chem. Soc. 141 (44), 17809–17816.
Li, H.J., Song, X.D., Shi, Y.T., Gao, Y., Si, D.H., Hao, C., 2019a. Role of water oxidation in the photoreduction of graphene oxide. Chem. Commun. 55 (12), 1837–1840.
Li, M., Gu, M.M., Tian, X., Xiao, B.B., Lu, S.Y., Zhu, W., Yu, L., Shang, Z.F., 2018a. Hydroxylated-graphene quantum dots induce DNA damage and disrupt microtubule structure in human esophageal epithelial cells. Toxicol. Sci. 164 (1), 339–352.
Li, Q., Huang, H., Chen, Z.W., Huang, X., Deng, K.R., Luo, S.P., Wang, Z.W., Yu, X.F., Quan, Z.W., 2019b. Thickness-dependent structural stability and anisotropy of black phosphorus. Advanced Electronic Materials 5 (3), 1800712.
Li, X.K., Mu, L., Hu, X.G., 2018b. Integrating proteomics, metabolomics and typical analysis to investigate the uptake and oxidative stress of graphene oxide and polycyclic aromatic hydrocarbons. Environmental Science-Nano 5 (1), 115–129.
Li, Y., Yang, N., Du, T.T., Wang, X.Z., Chen, W., 2016. Transformation of graphene oxide by chlorination and chloramination: implications for environmental transport and fate. Water Res. 103, 416–423.
Li, Y., Zhang, M., Hao, R.J., Wang, H.H., He, X.Z., Du, T.T., Yang, X., Wang, Y.Y., 2019c. Influence of (photo) bromination on the transformation, aggregation and sedimentation of graphene oxide. Chem. Eng. J. 355, 487–497.
Liao, K.-H., Lin, Y.-S., Macosko, C.W., Haynes, C.L., 2011. Cytotoxicity of graphene oxide and graphene in human erythrocytes and skin fibroblasts. ACS Appl. Mater. Interfaces 3 (7), 2607–2615.
Liu, C., Kong, D.S., Hsu, P.C., Yuan, H.T., Lee, H.W., Liu, Y.Y., Wang, H.T., Wang, S., Yan, K., Lin, D.C., Maraccini, P.A., Parker, K.M., Boehm, A.B., Cui, Y., 2016a. Rapid water disinfection using vertically aligned MoS2 nanofilms and visible light. Nat. Nanotechnol. 11 (12), 1098–1104.
Liu, F., Zhang, F.W., Liu, H., Zhang, J.Y., Guo, S.W., 2016b. Graphene quantum dots with Zn2+ and Ni2+ conjugates can cleave supercoiled DNA. J. Coord. Chem. 69 (22), 3395–3402.
Liu, M.M., Zhang, M., Hao, R.J., Du, T.T., Li, T., Li, Y., 2019a. Disinfection byproduct formation and toxicity of graphene oxide in water treatment system. Chemosphere 217, 68–75.
Liu, P.D., Shao, H.M., Kong, Y., Wang, D.Y., 2020a. Effect of graphene oxide exposure on intestinal Wnt signaling in nematode Caenorhabditis elegans. J. Environ. Sci. 88, 200–208.
Liu, S., Zeng, T.H., Hofmann, M., Burcombe, E., Wei, J., Jiang, R., Kong, J., Chen, Y., 2011. Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress. ACS Nano 5 (9), 6971–6980.
Liu, S.B., Hu, M., Zeng, T.H., Wu, R., Jiang, R.R., Wei, J., Wang, L., Kong, J., Chen, Y., 2012a. Lateral dimension-dependent antibacterial activity of graphene oxide sheets. Langmuir 28 (33), 12364–12372.
Liu, T., Wang, C., Gu, X., Gong, H., Cheng, L., Shi, X.Z., Feng, L.Z., Sun, B.Q., Liu, Z., 2014. Drug delivery with PEGylated MoS2 nano-sheets for combined photothermal and chemotherapy of cancer. Adv. Mater. 26 (21), 3433–3440.
Liu, Y., Huang, L., Guo, G.L., Ji, L.C., Wang, T., Xie, Y.Q., Liu, F., Liu, A.Y., 2012b. Pulsed laser assisted reduction of graphene oxide as a flexible transparent conducting material. J. Nanosci. Nanotechnol. 12 (8), 6480–6483.
Liu, Y., Zheng, S.X., Gu, P., Ng, A.J., Wang, M.N., Wei, Y.Y., Urban, J.J., Mi, B.X., 2020b. Graphene-polyelectrolyte multilayer membranes with tunable structure and internal charge. Carbon 160, 219–227.
Liu, Z.L., Rios-Carvajal, T., Andersson, M.P., Ceccato, M., Stipp, S.L.S., Hassenkam, T., 2019b. Ion effects on molecular interaction between graphene oxide and organic molecules. Environmental Science-Nano 6 (7), 2281–2291.
Long, W.J., Fang, C.L., Wei, J.J., Li, H.D., 2018a. Stability of GO modified by different dispersants in cement paste and its related mechanism. Materials 11 (5), 834.
Long, W.J., Li, H.D., Fang, C.L., Xing, F., 2018b. Uniformly dispersed and Re-agglomerated graphene oxide-based cement pastes: a comparison of rheological properties, mechanical properties and microstructure. Nanomaterials 8 (1), 31.
Lu, J., Zhu, X.S., Tian, S.Y., Lv, X.H., Chen, Z.H., Jiang, Y.L., Liao, X.S., Cai, Z.H., Chen, B.Y., 2018. Graphene oxide in the marine environment: toxicity to Artemia salina with and without the presence of Phe and Cd2+. Chemosphere 211, 390–396.
Lu, X.L., Feng, X.D., Werber, J.R., Chu, C.H., Zucker, I., Kim, J.H., Osuji, C.O., Elimelech, M., 2017. Enhanced antibacterial activity through the controlled

alignment of graphene oxide nanosheets. Proc. Natl. Acad. Sci. U.S.A. 114 (46), E9793–E9801.
Lu, X.Y., Lu, T.T., Zhang, H.J., Shang, Z.B., Chen, J.Y., Wang, Y., Li, D.L., Zhou, Y.M., Qi, Z.C., 2019. Effects of solution chemistry on the attachment of graphene oxide onto clay minerals. Environmental Science-Processes & Impacts 21 (3), 506–513.
Malina, T., Marsalkova, E., Hola, K., Tucek, J., Scheibe, M., Zboril, R., Marsalek, B., 2019. Toxicity of graphene oxide against algae and cyanobacteria: nanoblade-morphology-induced mechanical injury and self-protection mechanism. Carbon 155, 386–396.
Markovic, M., Andelkovic, I., Shuster, J., Janik, L., Kumar, A., Losic, D., McLaughlin, M.J., 2020. Addressing challenges in providing a reliable ecotoxicology data for graphene-oxide (GO) using an algae (Raphidocelis subcapitata), and the trophic transfer consequence of GO-algae aggregates. Chemosphere 245, 125640.
Martin-de-Lucia, I., Campos-Manas, M.C., Aguera, A., Leganes, F., Fernandez-Pinas, F., Rosal, R., 2018. Combined toxicity of graphene oxide and wastewater to the green alga Chlamydomonas reinhardtii. Environmental Science-Nano 5 (7), 1729–1744.
Matsumoto, Y., Koinuma, M., Ida, S., Hayami, S., Taniguchi, T., Hatakeyama, K., Tateishi, H., Watanabe, Y., Amano, S., 2011. Photoreaction of graphene oxide nanosheets in water. J. Phys. Chem. C 115 (39), 19280–19286.
Mi, B.X., Zheng, S.X., Tu, Q.S., 2018. 2D graphene oxide channel for water transport. Faraday Discuss 209, 329–340.
Mu, Q.X., Su, G.X., Li, L.W., Gilbertson, B.O., Yu, L.H., Zhang, Q., Sun, Y.P., Yan, B., 2012. Size-dependent cell uptake of protein-coated graphene oxide nanosheets. ACS Appl. Mater. Interfaces 4 (4), 2259–2266.
Nogueira, P.F.M., Nakabayashi, D., Zucolotto, V., 2015. The effects of graphene oxide on green algae Raphidocelis subcapitata. Aquat. Toxicol. 166, 29–35.
Ou, Y.N., Wu, J.W., Meyer, J.R., Foston, M., Fortner, J.D., Li, W.L., 2019. Photoenhanced oxidation of nC(60) in water: exploring H2O2 and hydroxyl radical based reactions. Chem. Eng. J. 360, 665–672.
Ouyang, S.H., Li, K.W., Zhou, Q.X., Hu, X.G., 2019. Widely distributed nanocolloids in water regulate the fate and risk of graphene oxide. Water Res. 165, 114987.
Paital, B., Guru, D., Mohapatra, P., Panda, B., Panda, N., Rath, S., Kumar, V., Saxena, P.S., Srivastava, A., 2019. Ecotoxic impact assessment of graphene oxide on lipid peroxidation at mitochondrial level and redox modulation in fresh water fish Anabas testudineus. Chemosphere 224, 796–804.
Perreault, F., de Faria, A.F., Nejati, S., Elimelech, M., 2015a. Antimicrobial properties of graphene oxide nanosheets: why size matters. ACS Nano 9 (7), 7226–7236.
Perreault, F., Fonseca de Faria, A., Elimelech, M., 2015b. Environmental applications of graphene-based nanomaterials. Chem. Soc. Rev. 44 (16), 5861–5896.
Qiu, B.C., Xing, M.Y., Zhang, J.L., 2018. Recent advances in three-dimensional graphene based materials for catalysis applications. Chem. Soc. Rev. 47 (6), 2165–2216.
Rasool, K., Helal, M., Ali, A., Ren, C.E., Gogotsi, Y., Mahmoud, K.A., 2016. Antibacterial activity of Ti3C2Tx MXene. ACS Nano 10 (3), 3674–3684.
Reina, G., Gonzalez-Dominguez, J.M., Criado, A., Vazquez, E., Bianco, A., Prato, M., 2017. Promises, facts and challenges for graphene in biomedical applications. Chem. Soc. Rev. 46 (15), 4400–4416.
Ren, H.L., Wang, C., Zhang, J.L., Zhou, X.J., Xu, D.F., Zheng, J., Guo, S.W., Zhang, J.Y., 2010. DNA cleavage system of nanosized graphene oxide sheets and copper ions. ACS Nano 4 (12), 7169–7174.
Ren, X.M., Li, J., Chen, C.L., Gao, Y., Chen, D.Y., Su, M.H., Alsaedi, A., Hayat, T., 2018. Graphene analogues in aquatic environments and porous media: dispersion, aggregation, deposition and transformation. Environmental Science-Nano 5 (6), 1298–1340.
Reynosa-Martinez, A.C., Tovar, G.N., Gallegos, W.R., Rodriguez-Melendez, H., Torres-Cadena, R., Mondragon-Solorzano, G., Barroso-Flores, J., Alvarez-Lemus, M.A., Montalvo, V.G., Lopez-Honorato, E., 2020. Effect of the degree of oxidation of graphene oxide on As(III) adsorption. J. Hazard Mater. 384, 121440.
Ruiz, O.N., Fernando, K.A.S., Wang, B.J., Brown, N.A., Luo, P.G., McNamara, N.D., Vangsness, M., Sun, Y.P., Bunker, C.E., 2011. Graphene oxide: a nonspecific enhancer of cellular growth. ACS Nano 5 (10), 8100–8107.
Shams, M., Guiney, L.M., Huang, L.J., Ramesh, M., Yang, X.N., Hersam, M.C., Chowdhury, I., 2019. Influence of functional groups on the degradation of graphene oxide nanomaterials. Environmental Science-Nano 6 (7), 2203–2214.
Shao, Y.L., El-Kady, M.F., Wang, L.J., Zhang, Q.H., Li, Y.G., Wang, H.Z., Mousavi, M.F., Kaner, R.B., 2015. Graphene-based materials for flexible supercapacitors. Chem. Soc. Rev. 44 (11), 3639–3665.
Souza, J.P., Baretta, J.F., Santos, F., Paino, I.M.M., Zucolotto, V., 2017. Toxicological effects of graphene oxide on adult zebrafish (Danio rerio). Aquat. Toxicol. 186, 11–18.
Souza, J.P., Mansano, A.S., Venturini, F.P., Santos, F., Zucolotto, V., 2019. Antioxidant metabolism of zebrafish after sub-lethal exposure to graphene oxide and recovery. Fish Physiol. Biochem. 45 (4), 1289–1297.
Souza, J.P., Venturini, F.P., Santos, F., Zucolotto, V., 2018. Chronic toxicity in Ceriodaphnia dubia induced by graphene oxide. Chemosphere 190, 218–224.
Sun, B.B., Zhang, Y.Q., Chen, W., Wang, K.K., Zhu, L.Y., 2018. Concentration dependent effects of bovine serum albumin on graphene oxide colloidal stability in aquatic environment. Environ. Sci. Technol. 52 (13), 7212–7219.
Sun, B.B., Zhang, Y.Q., Liu, Q., Yan, C.R., Xiao, B.W., Yang, J., Liu, M.L., Zhu, L.Y., 2020. Lateral size dependent colloidal stability of graphene oxide in water: impacts of protein properties and water chemistry. Environmental Science-Nano 7 (2), 634–644.
Syngouna, V.I., Giannadakis, G.I., Chrysikopoulos, C.V., 2020. Interaction of graphene oxide nanoparticles with quartz sand and montmorillonite colloids. Environ. Technol. 41 (9), 1127–1138.
Takenaka, S., Yamashita, K., Takagi, M., Hatta, T., Tsuge, O., 1999. Photo-induced DNA cleavage by water-soluble cationic fullerene derivatives. Chem. Lett. (4), 321–322.
Tan, Z.Q., Wang, B.W., Yin, Y.G., Liu, Q., Li, X., Liu, J.F., 2020. In situ tracking photodegradation of trace graphene oxide by the online coupling of photoinduced chemical vapor generation with a point discharge optical emission spectrometer. Anal. Chem. 92 (1), 1549–1556.
Tang, L.H., Chang, H.X., Liu, Y., Li, J.H., 2012. Duplex DNA/graphene oxide bio-interface: from fundamental understanding to specific enzymatic effects. Adv. Funct. Mater. 22 (14), 3083–3088.
Tashan, H., Khosravi-Darani, K., Yazdian, F., Omidi, M., Sheikhpour, M., Farahani, M., Omri, A., 2019. Antibacterial properties of graphene based nanomaterials: an emphasis on molecular mechanisms, surface engineering and size of sheets. Mini-Reviews Org. Chem. 16 (2), 159–172.
Tomaszewski, M., Cema, G., Ciesielski, S., Lukowiec, D., Ziembinska-Buczynska, A., 2019. Cold anammox process and reduced graphene oxide - varieties of effects during long-term interaction. Water Res. 156, 71–81.
Tong, Y.C., Feng, A.Q., Hou, X., Zhou, Q.X., Hu, X.G., 2019. Nanoholes regulate the phytotoxicity of single-layer molybdenum disulfide. Environ. Sci. Technol. 53 (23), 13938–13948.
Tu, Y., Lv, M., Xiu, P., Huynh, T., Zhang, M., Castelli, M., Liu, Z., Huang, Q., Fan, C., Fang, H., 2013. Destructive extraction of phospholipids from Escherichia coli membranes by graphene nanosheets. Nat. Nanotechnol. 8 (8), 594–601.
Wang, C., Wu, C.Y., Zhou, X.J., Han, T., Xin, X.Z., Wu, J.Y., Zhang, J.Y., Guo, S.W., 2013. Enhancing cell nucleus accumulation and DNA cleavage activity of anti-cancer drug via graphene quantum dots. Sci. Rep. 3, 2852.
Wang, D.Y., Sun, L.L., Liu, W., Chang, W.W., Gao, X., Wang, Z.X., 2009. Photoinduced DNA cleavage by alpha-, beta-, and gamma-cyclodextrin-bicapped C-60 supramolecular complexes. Environ. Sci. Technol. 43 (15), 5825–5829.
Wang, F.F., Wang, F., Gao, G.D., Chen, W., 2015. Transformation of graphene oxide by ferrous iron: environmental implications. Environ. Toxicol. Chem. 34 (9), 1975–1982.
Wang, H., Hu, B., Gao, Z., Zhang, F., Wang, J., 2020. Emerging role of graphene oxide as sorbent for pesticides adsorption: experimental observations analyzed by molecular modeling. J. Mater. Sci. Technol. https://doi.org/10.1016/j.jmst.2020.02.033.
Wang, K., Ruan, J., Song, H., Zhang, J., Wo, Y., Guo, S., Cui, D., 2011. Biocompatibility of graphene oxide. Nanoscale Res Lett 6, 8.
Wang, S.H., Shao, J.D., Li, Z.B., Ren, Q.Z., Yu, X.F., Liu, S.J., 2019a. Black phosphorus-based multimodal nanoagent: showing targeted combinatory therapeutics against cancer metastasis. Nano Lett. 19 (8), 5587–5594.
Wang, W., Xu, H., Ren, X.M., Deng, L.P., 2019b. Interfacial interaction of graphene oxide with Na-montmorillonite and its effect on the U(VI) retention properties of Na-montmorillonite. J. Mol. Liq. 276, 919–926.
Wang, X.X., Yu, S.J., Jin, J., Wang, H.Q., Alharbi, N., Alsaedi, A., Hayat, T., Wang, X.K., 2016a. Application of graphene oxides and graphene oxide-based nanomaterials in radionuclide removal from aqueous solutions. Sci. Bull. 61 (20), 1583–1593.
Wang, Z.Y., von dem Bussche, A., Qiu, Y., Valentin, T.M., Gion, K., Kane, A.B., Hurt, R.H., 2016b. Chemical dissolution pathways of MoS2 nanosheets in biological and environmental media. Environ. Sci. Technol. 50 (13), 7208–7217.
Wei, D.L., Zhao, C.F., Khan, A., Sun, L., Ji, Y.F., Ai, Y.J., Wang, X.K., 2019. Sorption mechanism and dynamic behavior of graphene oxide as an effective adsorbent for the removal of chlorophenol based environmental-hormones: a DFT and MD simulation study. Chem. Eng. J. 375, 121964.
Whitby, R.L.D., Gun'ko, V.M., Korobeinyk, A., Busquets, R., Cundy, A.B., Laszlo, K., Skubiszewska-Zieba, J., Leboda, R., Tombacz, E., Toth, I.Y., Kovacs, K., Mikhalovsky, S.V., 2012. Driving forces of conformational changes in single-layer graphene oxide. ACS Nano 6 (5), 3967–3973.
Wu, J.W., Alemany, L.B., Li, W.L., Benoit, D., Fortner, J.D., 2017a. Photoenhanced transformation of hydroxylated fullerene (fullerol) by free chlorine in water. Environmental Science-Nano 4 (2), 470–479.
Wu, J.W., Benoit, D., Lee, S.S., Li, W.L., Fortner, J.D., 2016. Ground state reactions of nC(60) with free chlorine in water. Environ. Sci. Technol. 50 (2), 721–731.
Wu, J.W., Li, W., Fortner, J.D., 2017b. Photoenhanced oxidation of C-60 aggregates (nC(60)) by free chlorine in water. Environmental Science-Nano 4 (1), 117–126.
Xin, H.J., Tang, Y.L., Liu, S.L., Yang, X., Xia, S.J., Yin, D.Q., Yu, S.L., 2018. Impact of graphene oxide on algal organic matter of Microcystis aeruginosa. ACS Omega 3 (12), 16969–16975.
Xin, Q., Shah, H., Nawaz, A., Xie, W.J., Akram, M.Z., Batool, A., Tian, L.Q., Jan, S.U., Boddula, R., Guo, B.D., Liu, Q., Gong, J.R., 2019. Antibacterial carbon-based nanomaterials. Adv. Mater. 31 (45), 1804838.
Xu, L., Zhao, J., Liu, Z.M., Wang, Z.Y., Yu, K.Q., Xing, B.S., 2019. Cleavage and transformation inhibition of extracellular antibiotic resistance genes by graphene oxides with different lateral sizes. Sci. Total Environ. 695, 133932.
Yao, H.Y., Huang, Y., Li, X., Li, X.H., Xie, H.B., Luo, T.L., Chen, J.W., Chen, Z.F., 2020. Underlying mechanisms of reactive oxygen species and oxidative stress photoinduced by graphene and its surface-functionalized derivatives. Environmental Science-Nano 7 (3), 782–792.
Yin, Z.F., Cui, C.J., Chen, H., Duoni, Yu X., Qian, W.Z., 2019. The application of carbon nanotube/graphene-based nanomaterials in wastewater treatment. Small 16 (15), 1902301.

Yu, Q.L., Zhang, B., Li, J.R., Du, T.T., Yi, X., Li, M.C., Chen, W., Alvarez, P.J.J., 2017. Graphene oxide significantly inhibits cell growth at sublethal concentrations by causing extracellular iron deficiency. Nanotoxicology 11 (9–10), 1102–1114.
Yu, Y.F., Nam, G.H., He, Q.Y., Wu, X.J., Zhang, K., Yang, Z.Z., Chen, J.Z., Ma, Q.L., Zhao, M.T., Liu, Z.Q., Ran, F.R., Wang, X.Z., Li, H., Huang, X., Li, B., Xiong, Q.H., Zhang, Q., Liu, Z., Gu, L., Du, Y.H., Huang, W., Zhang, H., 2018. High phase-purity 1T'-MoS2- and 1T'-MoSe2- layered crystals. Nat. Chem. 10 (6), 638–643.
Yuan, X.Y., Peng, D., Jing, Q.Y., Niu, J.W., Cheng, X., Feng, Z.J., Wu, X., 2018. Green and effective removal of aqueous graphene oxide under UV-light irradiation. Nanomaterials 8 (9), 654.
Zeng, Z.Y., Wang, Y.L., Zhou, Q.B., Yang, K., Lin, D.H., 2019. New insight into the aggregation of graphene oxide in synthetic surface water: carbonate nanoparticle formation on graphene oxide. Environ. Pollut. 250, 366–374.
Zhang, C.D., Wang, Y.Q., Zhao, H.R., 2020a. Is graphene oxide a chemoattractant? Nano Lett. 20 (2), 1455–1460.
Zhang, F., Li, S., Zhang, Q., Liu, J., Zeng, S., Liu, M., Sun, D., 2019a. Adsorption of different types of surfactants on graphene oxide. J. Mol. Liq. 276, 338–346.
Zhang, S., Li, B.F., Wang, X.X., Zhao, G.X., Hu, B.W., Lu, Z.H., Wen, T., Chen, J.R., Wang, X.K., 2020b. Recent developments of two-dimensional graphene-based composites in visible-light photocatalysis for eliminating persistent organic pollutants from wastewater. Chem. Eng. J. 390, 124642.
Zhang, S.Y., Zhang, X.J., Lei, L., Yu, X.F., Chen, J.W., Ma, C.X., Wu, F.C., Zhao, Q., Xing, B.S., 2019b. pH-dependent degradation of layered black phosphorus: essential role of hydroxide ions. Angew. Chem. Int. Ed. 58 (2), 467–471.
Zhang, X.L., Zhou, Q.X., Zou, W., Hu, X.G., 2017. Molecular mechanisms of developmental toxicity induced by graphene oxide at predicted environmental concentrations. Environ. Sci. Technol. 51 (14), 7861–7871.
Zhang, X.Y., Gong, C.C., Akakuru, O.U., Su, Z.Q., Wu, A.G., Wei, G., 2019c. The design and biomedical applications of self-assembled two-dimensional organic biomaterials. Chem. Soc. Rev. 48 (23), 5564–5595.
Zhang, Y., Meng, T.T., Guo, X., Yang, R.X., Si, X.H., Zhou, J.T., 2018. Humic acid alleviates the ecotoxicity of graphene-family materials on the freshwater microalgae Scenedesmus obliquus. Chemosphere 197, 749–758.
Zhang, Y., Meng, T.T., Shi, L., Guo, X., Si, X.H., Yang, R.X., Quan, X., 2019d. The effects of humic acid on the toxicity of graphene oxide to Scenedesmus obliquus and Daphnia magna. Sci. Total Environ. 649, 163–171.
Zhao, F.F., Wang, S.C., Zhu, Z.L., Wang, S.G., Liu, F.F., Liu, G.Z., 2019. Effects of oxidation degree on photo-transformation and the resulting toxicity of graphene oxide in aqueous environment. Environ. Pollut. 249, 1106–1114.
Zhao, H.R., Zhang, C.D., Wang, Y.Q., Chen, W., Alvarez, P.J.J., 2018. Self-damaging aerobic reduction of graphene oxide by Escherichia coil: role of GO-mediated extracellular superoxide formation. Environ. Sci. Technol. 52 (21), 12783–12791.
Zhao, J., Ning, F.Y., Cao, X.S., Yao, H., Wang, Z.Y., Xing, B.S., 2020a. Photo-transformation of graphene oxide in the presence of co-existing metal ions regulated its toxicity to freshwater algae. Water Res. 176, 115735.
Zhao, J., Wang, Z.Y., White, J.C., Xing, B.S., 2014. Graphene in the aquatic environment: adsorption, dispersion, toxicity and transformation. Environ. Sci. Technol. 48 (17), 9995–10009.
Zhao, J.F., Zhang, B.W., Li, J.Y., Liu, Y.C., Wang, W.F., 2016a. Photo-enhanced oxidizability of tetrazolium salts and its impact on superoxide assaying. Chem. Commun. 52 (77), 11595–11598.
Zhao, J.F., Zhang, B.W., Yu, C.H., Liu, Y.C., Wang, W.F., Li, J.Y., 2016b. Graphene oxide: a potential bodyguard protecting proteins from photosensitive damage. Carbon 109, 487–494.
Zhao, Y.C., Hsieh, H.S., Wang, M., Jafvert, C.T., 2017. Light-independent redox reactions of graphene oxide in water: electron transfer from NADH through graphene oxide to molecular oxygen, producing reactive oxygen species. Carbon 123, 216–222.
Zhao, Y.C., Jafvert, C.T., 2015. Environmental photochemistry of single layered graphene oxide in water. Environmental Science-Nano 2 (2), 136–142.
Zhao, Y.L., Chen, H., Yang, Y.H., Wu, Q.L., Wang, D.Y., 2020b. Graphene oxide disrupts the protein-protein interaction between Neuroligin/NLG-1 and DLG-1 or MAGI-1 in nematode Caenorhabditis elegans. Sci. Total Environ. 700, 134492.
Zheng, B., Wang, C., Xin, X.Z., Liu, F., Zhou, X.J., Zhang, J.Y., Guo, S.W., 2014. Electron transfer from graphene quantum dots to the copper complex enhances its nuclease activity. J. Phys. Chem. C 118 (14), 7637–7642.
Zheng, J., Li, J.C., Zhang, L.H., Chen, X.J., Yu, Y.D., Huang, H., 2020. Post-graphene 2D materials-based antimicrobial agents: focus on fabrication strategies and biosafety assessments. J. Mater. Sci. 55 (17), 7226–7246.
Zheng, M., Lu, J.G., Lin, G.M., Su, H.L., Sun, J.Y., Luan, T.G., 2019. Dysbiosis of gut microbiota by dietary exposure of three graphene-family materials in zebrafish (Danio rerio). Environ. Pollut. 254, 112969.
Zhou, W.H., Pan, T., Cui, H.D., Zhao, Z., Chu, P.K., Yu, X.F., 2019. Black phosphorus: bioactive nanomaterials with inherent and selective chemotherapeutic effects. Angew. Chem. Int. Ed. 58 (3), 769–774.
Zhou, X.J., Zhang, Y., Wang, C., Wu, X.C., Yang, Y.Q., Zheng, B., Wu, H.X., Guo, S.W., Zhang, J.Y., 2012. Photo-fenton reaction of graphene oxide: a new strategy to prepare graphene quantum dots for DNA cleavage. ACS Nano 6 (8), 6592–6599.
Zhu, X.B., Ji, X.Y., Kong, N., Chen, Y.H., Mahmoudi, M., Xu, X.D., Ding, L., Tao, W., Cai, T., Li, Y.J., Gan, T., Barrett, A., Bharwani, Z., Chen, H.B., Farokhzad, O.C., 2018. Intracellular mechanistic understanding of 2D MoS2 nanosheets for anti-exocytosis-enhanced synergistic cancer therapy. ACS Nano 12 (3), 2922–2938.
Zou, W., Zhou, Q.X., Zhang, X.L., Hu, X.G., 2019. Dissolved oxygen and visible light irradiation drive the structural alterations and phytotoxicity mitigation of single-layer molybdenum disulfide. Environ. Sci. Technol. 53 (13), 7759–7769.
Zou, W., Zhou, Q.X., Zhang, X.L., Mu, L., Hu, X.G., 2018. Characterization of the effects of trace concentrations of graphene oxide on zebrafish larvae through proteomic and standard methods. Ecotoxicol. Environ. Saf. 159, 221–231.