Three-dimensional graphene supported catalysts for organic dyes degradation

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Abstract: Three-dimensional graphene based materials (3D GBMs) as emerging materials have been widely used in various fields. This mini-review selectively highlights the recent research progress in the application of 3D GBMs in organic dyes removal. In particularly, the application potential, catalytic performance, and degradation mechanisms of the 3D GBMs are summarized in this mini-review. The factors affecting the degradation capacity of 3D GBMs are discussed briefly. Furthermore, the possible ongoing researches on 3D GBMs are also put forward. We deem that this mini-review will provide a valuable insight into the design and application of 3D GBMs in environmental field.

Keywords: three-dimensional graphene; catalyst supports; organic dyes; photocatalysis; biodegradation.

1. Introduction

With the rapid growth of population and the growing urbanization and industrialization, the environment pollution and other urgent problems worldwide are becoming increasingly serious.[1-4] The inevitable or unconscionable release of various types of pollutants into water bodies from a wide range of industries and chemical factories has been proposed as the main cause of environment pollution.[5-8] In order to satisfy the better quality of people's living standard, how to ensure the pollutant-free water resources is one of the most difficult challenges that we face in the 21st century.[9,10] Among various contaminants, organic dyes are one of the most widely used chemicals that are mainly discharged from industries of textile,[11,12] cosmetic,[13,14] paper,[15] leather,[16] etc. It is reported that more than 100,000 commercial dyes are available, and over 7×10^5 ton of dye-stuff are estimated to be produced annually.[17] With the large-scale production and wide application, the discharge of organic dyes into waters without treatment has caused public concern. It is a serious challenge to environmental scientists, owing to the ecosystem and health risks and their undesirable diverse colors in waters even at low concentration (less than 1 ppm).[18-20] Unfortunately, the wastewater containing organic dyes is one of the most difficult industrial wastewaters to treat. To date, many treatment technologies, such as adsorption,[21-24] coagulation,[25] photocatalysis,[26] biodegradation,[19] have been applied in dyes removal. Among these approaches, catalysis is a vital subject for purification of water, which has attracted extensive attention in scientific communities due to its ability to transform the organic compounds into inorganic compounds, showing good practical and potential values.[27] Thus, it is necessary to develop efficient catalysis for dyes wastewater treatment.

In the past decades, it has shown that the degradation of organic dyes by photocatalysts (such as TiO_2 nanoparticles) and microorganisms (such as white rot fungi) or their secreted enzymes are promising for organic wastewaters treatment.[26,28,29] Thus, the applications of photocatalysts or biocatalysts in organic dyes removal have been attracted great attentions. As is well known, catalytic reactions are closely related with the structure of catalysts, the distribution of surface active sites and coordination, thus it is key to tune the special composition, morphology, and size of catalyst.[30] Nevertheless, how to enhance the catalytic performance and recovery ability still remains to be solved. Thanks to the development of nanoscience and nanotechnology, the use of advanced materials especially carbon-based nanomaterials in dealing with these problems has grown in importance. Excitingly, graphene, a two-dimensional (2D) single sheet of carbon atoms arranged in a hexagonal network, has been regarded as one of the most promising materials.[31,32] Owing to its remarkable chemical, physical, and mechanical properties, such as large special surface area, excellent electrical and thermal conductivity, high mechanical strength, flexibility, and efficient wide range of light adsorption, graphene-based materials are popular in a broad range of applications.[33-36] Most importantly, the increasing exploration of graphene composites has opened up the opportunities for the application in environmental field.[37,38] Not surprisingly, given the outstanding properties, graphene-based materials have been developed as catalytic supports.[39,40] Unfortunately, it has been found that the combination of the poor dispersion, restacking and multilayer thickness can prevent the practical application of graphene-based materials.[41,42] In addition, the difficult separation from waters also restricts their practical applications.

In recent years, three-dimensional graphene-based materials (3D GBMs) have been attracting increasing attention, since they not only maintain the excellent properties of graphene, but also enhance the practical application potential of graphene. Moreover, another important merit is the integrated morphology of graphene-based monolith, making it easy for manipulation and convenient for separation in the practical application, as well as preventing the release of graphene nanosheets and their environmental risk.[37] Due to these advantages, 3D GBMs have been emerged as promising supports for catalysis. For instance, they have been extensively used as electrocatalysts in energy field to sovle the energy shortage.[43,44] Likewise, they have exhibited great potential in organic pollutants degradation for water pollution treatment.[45,46] What needs to be mentioned is that 3D GBMs have also shown good capacity for organic pollutants adsorption,[42] which is conducive to enhance catalytic degradation performance. In this special review, we mainly highlight their catalytic performance on organic dyes degradation. In order to utilize the potential of 3D GBMs in catalysis for organic dyes removal, it is critical to possess the technologies of large-scale production of graphene monolith. To date, a great deal of work has been done to explore the integration approaches for the fabrication of 3D GBMs. The synthesis and applications of 3D GBMs have been highlighted in several reviews.[41,42,47] However, we note that an all-round overview of the application of 3D GBMs supported catalysts focused on the degradation of organic dyes in environment field is still absent. In order to understand the feasibility of 3D GBMs for organic dyes removal, this review article presents the recent advances related to the synthesis and the dyes degradation of 3D GBMs supported catalysts, as well as the influence factors on the catalytic efficiency. Herein, we deem that this review will provide theoretical basis and valuable insights for the application and special design of 3D GBMs for pollutants removal. Meanwhile, the challenges and outlooks are also offered to expect the better future applications of 3D GBMs in the catalysis field.

2. The potential of 3D GBMs as catalysts support

The catalytic materials play a pivotal role in various fields. Excitingly, they have made significant contributions in environment pollutants removal. So far, a large number of catalytic materials such as transition metals, metal oxides, and hybrid composites have already been widely used for organic pollutants degradation. [48-50] However, the pure catalysts constructed as powder are usually not suitable for the practical applications. In order to overcome the limitations, it is necessary to explore feasible solid surfaces as supports for pure catalysts with the purpose of easy separation and recycling. The superiority of graphene gels such as hydrogels and aerogels (foams or sponges) makes them promising for catalytic materials development.[41,42] In the following sections, the potential of 3D GBMs in environmental application as catalytic materials is discussed.

2.1 Efficient preparation methods

The integration of individual graphene sheets into 3D hierarchical architectures is an effective way to tackle the challenge that graphene materials meet in practical applications. In order to satisfy the requirement of application in pollutants removal, it is imperative to develop simple and efficient preparation methods. Hitherto, the general synthetic strategies reported in the literatures can be mainly classified into three categories, including self-assembly approach, template-directed approach, and other approaches.[37] Among these techniques, the “bottom up” self-assembly approach of graphene oxide (GO) has been regarded as one of the powerful strategies to integrate nanostructure building blocks into macroscopic materials. Since it is cost-effective, high-yield, and adjustable, solution-based reduction of GO is regarded as a well-developed self-assembly approach to induce the gelation.[51] In this part, we will summarize the common synthetic methods, namely, hydrothermal reduction, chemical reduction, and metal ion induced self-assembly that require the GO as precursor.

2.1.1 Hydrothermal reduction

Hydrothermal reduction is an important strategy for the reduction of GO and inducing the self-assembly of GO. Generally, the reaction system is operated in an autoclave under a moderately high temperature. In 2010, Xu et al. [52] prepared a high-performance self-assembly graphene hydrogel (SGH) via a facile one-step hydrothermal process. Briefly, 2 mg/mL GO aqueous dispersion was sealed in a Teflon-lined autoclave and heated to 180°C for 12 h to obtain SGH. After freeze-drying, the well-defined and interconnected 3D porous network with cross-linking sites can be observed by scanning electron microscopy (SEM). GO concentration and reaction time are the key influence factors determining the properties of as-prepared SGH. The formation of SGH is driven by strong hydrophobic and π-π stacking interactions of reduced graphene oxide (rGO), indicating that the concentration of GO should beyond a critical value. The low concentration of GO (0.5 mg/mL) can't form strong hydrophobicity and π-conjugated structures of reduced GO sheets in aqueous solutions, thus the cross-link is difficult to occur. In contrast, the high concentration (2 mg/mL) can provide enough contact opportunities for cross-link to obtain SGH as shown in Figure 1a. With the time increasing, the sizes of as-prepared SGH by hydrothermal reduction of 2 mg/mL GO decreased obviously initially and subsequently changed little (Figure.1b). For fabricating macroporous structures of 3D graphene materials (MGM) with high compression resilience ratio, an improved hydrothermal process is developed by Li's group via reduction of emulsions formed by shaking mixtures of GO and hexane.[53] As the hexane droplets can be stably dispersed in GO dispersion homogeneously, during the hydrothermal process, the 3D network will be formed around the hexane droplets and kept the shape of hexane droplets. Thus, the macroporous structures can be obtained. In comparison with the aerogel made from a pure GO aqueous dispersion, the pore sizes and volume of MGM aerogel are much bigger, and the value of weight density is much lower (8.6 mg cm^{-3} VS 24.4 mg cm^{-3}). In their case, the morphology and weight density of as-prepared 3D graphene materials are also dependent on the concentration of GO. Following the idea and results of this work, this technique can be further explored to fabricate MGM with other hydrophobic organic compounds. In 2014, Shi et al.[54] prepared a 3D graphene hydrogel via hydrothermal treatment of the hydrochloric acid-treated GO solution at 150°C for 5 h, which showed a denser structure with smooth interspace, and assembled many graphene sheets together compared to the traditional hydrothermal treatment. For illuminating the mechanisms of gelation and hydrothermal reduction, Hu et al. [55] reported an in-depth analysis of the reaction products during preparing hydrothermal reduced graphene oxide hydrogels (GHGs) in 2016 as shown in Figure 2, which can deepen the understanding of hydrothermal reduction. It shows obvious differences in the morphology and chemistry between GHGs that reduction under the acidic and basic conditions. For example, the hydrogel with large bulges in its surface is floated under acidic condition (without ammonia addition), whereas the hydrogel sinks in basic conditions. The floatation is ascribed to CO_2 bubbles entrapped inside the hydrogels that can decrease the density of the GHG without ammonia addition. These findings provide important implications on the optimization of the gelation conditions. Overall, the hydrothermal reduction process involves the removal of functional groups on GO (reduction process) and the self-assembly driven by hydrophobic and π-π stacking interactions of rGO (gelation process).

2.1.2 Chemical reduction

Chemical reduction self-assembly methods have been widely used to fabricate 3D GBMs using various reducing agents under mild conditions. In a typical procedure, the reducing agent is added to the GO aqueous dispersion, and heated to 90-95°C for a certain period of time under atmospheric pressure without stirring. Compared with hydrothermal reduction, neither high temperature nor long time is necessary in the mild chemical reduction process. For instance, Chen and Yan[56] reported a mild chemical reduction method to prepare 3D architectures of graphene. They found that the reducing agents such as $NaHSO_3$, Na_2S, vitamin C (VC), HI, and hydroquinone were effective to prepare the 3D graphene hydrogels and aerogels, while the well-known reducing agent hydrazine failed. The as-prepared 3D architectures of graphene also showed high mechanical strength, low-density, thermal stability, high electrical conductivity, etc., making them promising candidates as support for catalysts. The self-assembly mechanism (Figure 3) is driven by hydrophobic and π-π stacking interactions, which is similar with the hydrothermal reduction method. Note that in this procedure, the mass ratio of reducing agent and GO may play important roles in the synthesis of hydrogels. Sui et al.[57] synthesized rGO hydrogel by a simple reduction route with excess VC. In this experiment, they set up a series of mass ratios of VC and GO ranging from 832: 1 to 1: 8. The results showed that the hydrogels could be observed when the mass ratio was higher than 1: 2. In addition, Sheng et al.[58] prepared high-performance SGHs using sodium ascorbate as reducing agent, and they found that the starting concentration of GO, reaction temperature, and reaction time were strongly related to the structure and properties of SGHs as well. Zhang et al.[59] fabricated SGHs using L-cysteine as both templating and reducing agent, which showed high mechanical strength, thermal stability, and large specific surface area. Phenolic acids, the main aromatic secondary metabolites of plants, were also proved to reduce GO and prepare SGHs via in situ self-assembly. The resultant monolithic graphene exhibited high porosity, excellent mechanical strength, and electrical conductivity.[60] Tannic acid as a mild reducing agent was also used to fabricate the 3D graphene materials. The obtained graphene aerogel had high specific surface area and showed good mechanical strength and thermal stability.[61] Although the properties of SGHs are somewhat different using different reducing agents, the differences may extend the scope of applications. In conclusion, chemical reduction self-assembly approach is a simple and rapid synthesis method for 3D GBMs, and the proper reducing agents are important in the chemical reduction for the special design of 3D GBMs.

2.1.3 Metal ion-induced self-assembly

Many researchers have reported that the self-assembly of GO sheets can be obtained by metal ions induction. In 2010, Jiang et al.[62] reported the self-assembly 3D graphene architecture by divalent ion linkage, and suggested that the sufficient divalent ion was critical for the formation of 3D architecture. Moreover, polyvinyl alcohol (PVA) was introduced into the gel to prevent the structure collapse. Graphene/iron oxide hydrogels with 3D interconnected networks can be prepared by ferrous ions induction.[63,64] The initial pH of GO suspension can significantly affect the compositions of as-prepared graphene hydrogels. The magnetic 3D graphene hydrogel can be fabricated when adjusting the pH to 11. If not (such as pH 3–10), the α-FeOOH will be dominated in the products, which is the indication for other studies.[64] Similarly, Co_3O_4 and Mn_3O_4 nanoparticles can grow on the 3D graphene hydrogels uniformly by the induction of Co^{2+} and Mn^{2+}, respectively.[65,66] In the reaction system, metal ions act as both a cross linker and reducing agent to drive the self-assembly and transformation of GO into 3D gel structure.

2.2 High adsorption capacity

High adsorption capacity is recognized as a prerequisite for the catalytic degradation.[37] Thus, it's a feasible approach to increase the catalytic performance of catalysts combining with an ideal adsorbent. Large number of research reports have shown the excellent adsorption capacity of 3D GBMs to various organic dyes removal. For instance, 3D GO sponge showed great adsorption capacity for methylene blue (MB) and methyl violet (MV) removal with high speed and efficiency, due to the strong π-π stacking and anion-cation interaction.[67] Tiwari et al.[68] investigated the removal ability for organic dyes, such as MB and rhodamine B (RhB), using 3D rGO-based hydrogels as adsorbents. The results showed that excellent adsorption efficiency of 3D rGO-based hydrogels for removing MB (~100%) and RhB (~97%) were mainly via π-π stacking and anion-cation interactions. Luo et al.[61] reported the excellent adsorption of monolithic 3D graphene towards dyes. Liu et al.[69] fabricated a 3D reduced graphene oxide (GRGO) aerogel and found the superior adsorption performance towards RhB, MB and crystal violet (CV). Meanwhile, the maximum adsorption capacity of RhB reached 280.8 mg/g, which was better than other adsorbents. Sui et al.[70] found that 3D GO-Polyethylenimine (GEPM) porous materials exhibited an excellent adsorption capacity for amaranth (800 mg/g) due to the pore-rich and amine-rich graphene structure. Kim et al.[71] reported the different adsorption behaviors for cationic and anionic dyes on 3D rGO macrostructure based on the different adsorption mechanisms (Figure. 4), and found that as-prepared 3D rGO macrostructures were more favorable for cationic dyes adsorption. Zhang et al.[72] reported the improved adsorption capacity of TiO_2-graphene hydrogel (TGH), which was significantly higher than the GH and TiO_2 nanoparticles for MB removal. More importantly, the adsorption performance of catalysts is greatly improved after being loaded on 3D porous materials, thus promoting the development of catalyst supports. In addition, the nitrogen and sulphur co-doped 3D graphene hydrogels (N/S-GHs) showed improved adsorption ability for organic dyes (MB, malachite green, and crystal violet), which was ascribed to the surface modification with heteroatoms that can improve the properties of 3D graphene structures, thus enhancing the removal capacities.[73] In summary, the electrostatic interaction and π-π stacking are considered as the main interaction forces for the adsorption behavior. Actually, in addition to dyes, 3D GBMs also show excellent removal performance towards other organic pollutants, oils, and heavy metals,[74-77] exhibiting great application potential in water clean-up.

2.3 Excellent practical application performance

The convenient solid-liquid separation is important for the regeneration of materials. To date, various separation free hybrid hydrogels as catalysts supports have been fabricated for the wastewater treatment.[78,79] For example, separation free C_3N_4/SiO_2 hybrid hydrogels have been used as photocatalysts for the removal of total organic carbon content (TOC) of coking wastewater.[80] C_3N_4-agar hybrid hydrogel photocatalysts could effectively degrade phenol and MB.[81] These reports collectively demonstrated the advantages of 3D materials in high reactivity and separation-free in bulk material, providing facile operation in wastewater treatment.

As reported above, the floatation of 3D graphene gel has been illustrated.[55] The same phenomenon also can be observed in many reports due to their high porosity, low density, and hydrophobicity.[55,73] In addition, high mechanical strength of 3D graphene is another important property for the practical application. For example, Xu et al. [52] prepared SGH (diameter around 0.8 cm) with mechanically strong which can support 100 g weight with little deformation, which can avoid the collapse of materials in practical application. This free separation and high mechanical strength are beneficial for the separation, thereby further enhancing the practical application of 3D GBMs.

3. Degradation of organic dyes pollutants

3.1 Photocatalysis

Photocatalytic degradation is an important advanced oxidation process (AOP) technology to degrade organic pollutants.[82] In the photocatalytic degradation process, organic pollutants are attacked and destroyed by the reactive species such as hydroxyl radicals ($HO^•$) and holes (h^+), which are formed by a multi-step process with the interaction of photocatalyst, energetic light source, and oxidizing agent such as oxygen or air.[83,84] In the past decades, various semiconductor materials have been widely used as photocatalysts in the treatment of the organic pollutants.[85,86] However, the photocatalytic activities of pure photocatalysts are usually impeded by their low adsorption efficiency, limited photocatalytic sensitivity, and fast recombination of photogenerated electron–hole pairs.[87,88] In addition, the difficult separation from the treated water is not beneficial for the practical applications.

3.1.1 Photocatalysis performance

To overcome the limitations mentioned above, 3D graphene materials have been employed as supports in photocatalysis, which can improve the adsorption ability, photocatalytic activity, and recovery. More than those, 3D graphene incorporated semiconductor photocatalysts can exhibit higher catalytic activity over pure photocatalysts due to the synergistic effects between graphene and additives.[72] In addition to the excellent catalytic activity, the as-prepared photocatalysts also show superior durability. The relevant reports presented as follows:

In 2012, Hou et al.[89] investigated the photocatalytic properties of 3D P25-graphene hydrogels, which was obtained by a room-temperature route, in the removal of MB dyes. This hydrogel shows higher decontamination efficiency compared to pure P25 and P25-MWCNTs-graphene. Under UV light irradiation, it needs just 1 h to completely decompose the dyes using this hydrogel, while it takes more than 3 h for pure P25 and P25-MWCNTs-graphene. Meanwhile, the 3D graphene-based composites exhibit good durability and stability, that is, no significant decrease in photocatalytic activities and no significant changes occur in physical structure after four reaction cycles. In addition, they also suggested that the 3D porous stereostructure is responsible for the enhanced adsorption. Similarly, Zhang et al.[72] explored the application of TiO_2-graphene hydrogel (TGH) as adsorbent and photocatalyst in environmental remediation. This hydrogel shows higher photocatalytic activities in comparison with pristine graphene hydrogel and TiO_2 NPs, as well as more excellent adsorption capacity. After the adsorption of MB onto TGH, a photodegradation experiment was conducted under the simulated UV irradiation. It shows that the degradation process can be completed within 30 min in the presence of TGH. In contrast, a part of the initial dye (nearly 33%) still remains in the solution after the same time period for neat TiO_2 nanoparticles. More importantly, TGH still exhibits good reversibility and regeneration after five photocatalytic reaction cycles, and 53% of photocatalytic activity of TGH still remains. 3D graphene aerogels (GAs) also have the potential for photocatalysis. TiO_2/GAs prepared by a hydrothermal method using glucose as linker and dispersant exhibit a highly recyclable photocatalytic activity for methyl orange (MO) pollutant.[90] It shows that the degradation of MO can be up to 90% by this as-prepared TiO_2/GAs after solar light irradiation for 5 h, and 83% of photocatalytic activity of this catalyst still maintains after five reaction cycles. Note that in the wastewater purification process, the recovery of photocatalysts needs to be improved. The superior recyclability is a critical factor for the practical applications. For this reason, Moon et al.[85] studied PVA/poly (acrylic acid)/TiO_2/ graphene oxide (PVA/PAAc/TiO_2/GO) hydrogels for the photocatalytic degradation of organic pollutants. The recycling tests confirmed that more than 90% of photocatalytic activity was maintained after three consecutive cycles. Wang et al. [91] reported a good reusability of 3D-GO/PVA/TiO_2 composite for the photacatalytic degradation of MB and MV. After five runs, the removal efficiency still remained 88.9% and 83.2% for MB and MV, respectively. As is well known, TiO_2 has been widely recognized as one of the most efficient photocatalyst in water purification, due to their non-toxcity, low cost, physical and chemical stability, and high reactivity.[85,92,93] Besides the common TiO_2-based photocatalysts, other semiconductors-based photocatalysts have good pollutants removal ability as well. For example, Cu_2O-RGO composite aerogel shows superior photocatalytic activity for MO degradation. After irradiation for 5 h, nearly 70% MO is degraded with Cu_2O-RGO composite aerogel, while the degradation rate is not higher than 30% with the Cu_2O nanoparticles.[94] 3D G/ZnO exhibits good stability and the degradation rates of MO are 94.25%, 87.5%, and 81.8%, respectively, after 60 min of irradiation in three reaction operations.[95] Compared to bare CeO_2 nanostructures, 3D CeO_2-GAs displays enhanced photocatalytic activity on the degradation of RhB.[96] In addition to metal oxide semiconductor NPs, other semiconductors NPs are also usually incorporated with 3D graphene gels for photocatalysis, such as ZnS-GAs and MoS_2-GO composite hydrogel.[97,98] These photocatalytic materials also achieve the superior photocatalytic performance, owing to the efficient charge transfer from metal sulfide to graphene sheets. BiOBr/RGO aerogel also shows high stability and superior activity for degradation of pollutants in aqueous system.[99] In addition to metal oxide or metal sulfide semiconductor NPs, the combination with metal NPs, such as Ag,[100,101] endows 3D graphene-based materials superior photocatalytic performance as well. For instance, Ag nanoparticles-containing RGO-based composite hydrogel can almost degrade RhB completely with approximately 70 min, and MB with approximately 30 min under UV irradiation.[100]

Overall, the 3D GBMs supported photocatalysts show excellent photocatalytic performance towards organic dyes. The enhanced removal performance may attribute to the synergy of adsorption and photocatalysis via supporting photocatalysts on the 3D graphene gel. It has reported that the synergy of adsorption and photocatalysis can efficiently increase the removal of chromium and bisphenol A by 3D graphene gels.[75,102,103] For dyes removal, the superb adsorption-photocatalysis is also be verified.[72,91] Thus, the combination of superb adsorption capacity of 3D graphene gels and the photocatalysis of photocatalyst is an efficient approach for achieving high dyes removal performance.

3.1.2 Photocatalytic degradation mechanisms

To date, it has been found that the applications of 3D graphene loaded with metal oxide NPs are becoming more and more popular in organic pollutants degradation. Thus, for understanding the photocatalytic degradation pathways of 3D graphene-based photocatalysts, we will take two typical metal oxide-graphene composites (e.g., TiO_2 and ZnO) for examples to explain the photocatalytic process. As mentioned above, the two metal oxide-graphene based composites exhibit excellent photocatalytic performance and good durability and stability in organic pollutants degradation, which is superior to pure catalysts. The reasons for the improved performance of 3D garphene-based materials can be explained by: (a) 3D porous nanostructural graphene possesses higher adsorption capacity for pollutants; (b) the metal oxide NPs, which contribute to the catalytic ability, have a high dispersity on the 3D graphene support; (c) 3D graphene has high carrier mobility, which is beneficial for the charge carriers separation.[37,89,94] Furthermore, compared with 2D graphene sheets, the 3D graphene networks can facilitate the stereoscopic mass electron transfer, which would be confined to a plane in 2D sheets as shown in Figure 5.[89] Generally, the whole photocatalytic process can be described as follows: the metal oxide NPs are excited to generate electron-hole pairs under irradiation, and the photogenerated carriers can be formed on the surface of 3D GBM, then interact with the dye molecules (redox reactions), leading to the decomposition of the dye into CO_2 and H_2O. Taking 3D ZnO/G composite for example,[95] the detail steps can be written as: 1) the activation of ZnO by UV light: $ZnO + h\nu \rightarrow e^- + h^+$; $e^- + O_2 \rightarrow O_2^-$ 2) the oxidative and reductive reaction: $O_2^- + H^+ \rightarrow HO_2^\bullet$; $2HO_2^\bullet \rightarrow H_2O_2 + O_2$; $H_2O_2 + O_2^- \rightarrow HO^\bullet + O_2 + OH^-$; $HO^\bullet$ + organic dyes $\rightarrow CO_2 + H_2O$.

3.2 Biocatalytic degradation

Biocatalytic degradation has been regarded as a feasible route for pollutants removal by microbial reaction and biodegradation enzymes.[104] Enzymes as biocatalysts in microbial biodegradation pathways play key roles in bioremediation, thus having become an attractive and available biological method. However, the practical applications of microorganisms or enzyme catalyzed reactions have numerous challenges including low resistance, catalytic efficiency, stability, and recyclability.[105] Several approaches have been used to deal with the drawbacks, and immobilization is an efficient approach to solve the mentioned problems.[106,107] Since immobilization of active biospecies (such as enzymes and cells) exhibits the advantageous property,[108] this technology opens up the opportunities for the development of effective biocatalysts. Currently, the combination of nano- and bio-technology is already a mature field of research. With the rapid development of nanostructured materials, 3D GBMs as the intriguing supports have attracted intensive interest.

White rot fungi, a class of microorganisms that can decompose a wide range of organic pollutants due to the role of ligninolytic enzymes, have been widely applied in wastewater treatment.[109-112] To date, several researchers have studied the immobilization of microorganisms or enzymes on 3D GBMs. Rodriguez-Couto et al.[113] have explored the immobilization of white rot fungus *Trametes pubescens* using graphene hydrogels and xerogels as supports, the results showed that the laccase activities produced by the fungus were accelerated by immobilization on the 3D graphene gels, and much higher than other inert supports. Following this exciting discovery, their group conducted another work to reinforce the hydrogel by incorporating polymer and test the performance of nanobiocatalysts (laccase immobilized on the hydrogel supports) in the oxidative degradation of the recalcitrant synthetic dye (Remazol Brilliant Blue R, RBBR). The encouraging results showed that nanobiocatalysts exhibited strong catalytic activities and high stability with the completed discoloration of relatively high RBBR concentration in each of the four successive batches, paving the way for the application of nanobiocatalysts in environment remediation.[114] It is worth mentioning that the main degradation action is caused by the immobilized enzymes. The relevant information of laccase can be obtained from other reviews.[115,116] Actually, the as-prepared 3D graphene gels can help the enzyme overcome the main disadvantages such as the fragile nature, and promote the catalytic activity and stability. In another word, the supports play pivotal roles in maintaining the performance of enzymes. Thus, how to enhance the link and synergy between 3D graphene gels and biospecies deserves further research.

In addition to acting as the supports for photo- and bio-catalysts, 3D graphene has also been regarded as one of the promising candidates to support some special catalysts. For example, Zhang's group[117] prepared an iron electrode coating by graphene sponge (GS-Fe electrode), which could significantly improve the decoloration performance of Fe electrode for the decoloration of MB. Their results showed that the decoloration kinetics constant of GS-Fe electrode was five times than that of Fe electrode at the same current density, and its performance remained nearly unchanged in the recycling evaluations. Wang's group[118] fabricated a novel 3D GBM utilizing 3D graphene foam as a matrix to support nanoscale zero-valent iron (nZVI) particles (3DG-Fe) for the degradation of orange IV azo dye. Compared with Fe NPs and Fe beads, the 3DG-Fe composites degraded 94.5% of orange IV within 60 min, showing much higher degradation activity with orange IV. Electrolysis is a widely used technology in water treatment. Luo et al.[119] found that the tannic acid functionalized graphene hydrogel entrapped with gold nanoparticles (Au@TA-GH) exhibited good catalytic activity toward the reduction of MB with the addition of $NaBH_4$. Qiu et al.[120] prepared 3D hierarchical cobalt ferrite/graphene aerogels ($CoFe_2O_4$/GAs), which showed high and recyclable Photo-Feton activity for MO degradation. Furthermore, photoelectrocatalytic technology, a photoelectric synergistic technology in catalytic oxidation, has exhibited great application prospect for organic pollutants degradation.[121,122] Chen et al.[123] reported the efficient photoelectrocatalytic mineralization ability of TiO_2-graphene hydrogel (TGH) electrodes towards MB and phenol. Therefore, it is worthwhile to point out that various 3D GBMs catalysts can be used for organic dyes removal through different degradation pathways, which expand their application potential. Meanwhile, the combination of different technologies for pollutants removal should receive attention.

4. Influence factors on catalytic efficiency

As mentioned above, 3D graphene gels acting as catalyst supports can indeed enhance the catalytic performance of pure catalysts. Nonetheless, the catalytic efficiency will be influenced by some factors, such as the composition of 3D GBMs, solution pH, and initial dye concentration. Herein, we will discuss the main influence factors so as to better design and use the 3D GBMs catalysts for organic pollutants removal.

The catalytic activity of 3D GBMs is attributed to the synergistic effect of 3D self-assembly graphene sheets with the loaded nanoparticles or active biospecies. For photocatalysis, the surface and structural properties of catalysts such as crystal composition, porosity, and surface areas are of great importance.[84] Thus, how to design the incorporation of graphene sheets and catalysts nanoparticles should be taken into consideration. Several studies have reported the effects of the composition of 3D GBMs on photocatalytic activity. For example, Zhang et al.[72] prepared TGH with the ratio of TiO_2 to graphene ranging from 1: 5 to 4: 1, they found that the photocatalytic activities of TGH were enhanced with the increasing ratio of TiO_2 to graphene and reached the maximum value when the ratio increased to 4: 1. Similarly, the increasing TiO_2 proportions in TiO_2/GAs can significantly increase its capacity for MO degradation.[90] Furthermore, PVA/PAAc/TiO_2/GO hydrogel with a higher content of GO can accelerate the photocatalytic decomposition of model pollutant dyes,[85] on account of that the adsorption of pollutants and the interfacial electron-transfer process between TiO_2 and GO are improved by the addition of GO. Actually, a proper content ratio is critical for improving the catalytic performance, because insufficient graphene can't provide enough channels for electrons transfer, while excessive graphene will prevent the UV light from reaching the surface of photocatalysts.[98,124] Therefore, it is evident that the composition of 3D GBMs can affect the decomposition capacity for pollutants removal.

Moreover, the solution pH is also an important influence factor for the degradation of dyes. Moon et al.[85] found that the photocatalytic decomposition behavior of PVA/PAAc/TiO_2/GO nanocomposite hydrogel was pH-sensitive. With the pH increasing from 2 to 10, the photocatalytic activity increased dramatically. Wang et al.[118] found that the degradation efficiency and the rate constant increased with the pH decreasing from 11 to 3, suggesting that the degradation of organic IV by 3 DG-Fe was acid-driven. However, there is no significant change in the catalytic performance of Au@TA-GH during the pH range of 5.0-11.[119] The degradation rate of $CoFe_2O_4$/GAs on MO decreased a little under different pH (range from 3.5 to 9).[120] Obviously, with regard to different organic dyes and catalysts, the solution chemistries will present different effects on their catalytic activity. As shown in Table 1, the catalytic capacity of catalysts was different when respond to different initial pollutants concentrations. Generally, the degradation efficiency of catalysts decreases with the increase of initial pollutants concentration. Cai et al.[95] suggested that more molecules were adsorbed on the 3D graphene/ZnO surface at a high dyes concentration solution, thus leading to the reduction of light intensity on the catalyst surface. Consequently, the degradation rate and capacity were reduced due to the reduction of generated electron-hole pairs. Meanwhile, they also suggested that the optimum dosage of catalyst and light irradiation time were necessary to ensure strong degradation efficiency. Noticeably, various operating parameters will impact the catalytic performance. However, the research on environment conditions that influence the organic dyes removal using 3D GBMs as catalysts is limited. A highlight of the effects of various parameters on the dye degradation may reduce our knowledge gap. Thus, in order to understand the role of main factors, much work is needed to be carried out.

5. Conclusions and Perspectives

In summary, 3D graphene has unique morphology, porous structure, and electronic properties. It has been explored for the design and application as catalysts support for the removal of various organic dyes. Generally, the organic pollutants degradation pathways mainly include photocatalysis, biocatalysis, electrocatalysis, and so on. The coupling of 3D graphene with photoactive semiconductors or active enzymes synergistically improves the removal capacity in wastewater treatment. Additionally, 3D graphene can act as stabilizer, enhancing the durability and stability of catalysts. However, it is worth noting that the composition of 3D GBMs and solution chemistries can influence their removal efficiency, thus more efforts should be devoted to the proper design with optimum catalytic capacity. Furthermore, the research on 3D GBMs is still at early stage. Many technology problems remain to be solved. Therefore, several aspects of 3D graphene as catalytic support in practical environmental organic dyes removal deserve further efforts.

1) Investigate the catalyst morphology-dependent catalysis on organic dyes: It comes to a conclusion that the composition of 3D GBMs plays an important role in the catalysis. However, the controlling morphology of catalysts loaded on graphene gels is usually neglected, which has been explored in the pure catalysts experiments. For example, nanostructured TiO_2 shows various morphologies, such as nanoparticles, nanorods, nanowires, and nanotubes, which can be prepared by different synthesis methods. In addition, the different hierarchical morphologies of TiO_2 (1D nanorods and 3D microspheres) exhibit different photodegradable activities of phenol.[125] Thus, it is a valuable research subject.

2) Seek the potential improving degradation approaches: The high degradation or mineralization efficiency to organic dyes is extremely critical for the colored wastewater cleanup. Till now, researchers have suggested that the combination of multifarious types of nanomaterials is an efficient approach to enhance the catalytic activities.[87, 126] With the development of nano- and bio-technology, the immobilization of microbes on nanomaterials also plays an increasingly vital role in wastewater treatment.[127-129] Therefore, the combination of biocatalyst and photocatalyst or other catalysts on the support of graphene gels is worth of exploring.

3) Understand the effects of co-existing pollutants: Large number of research has shown that 3D GBMs have the great potential in various organic pollutants and heavy metals wastewaters treatment. Theoretically, the adsorption of these pollutants will occupy the active sites of 3D GBMs, which may influence their catalytic performance. Thus, whether and how the co-existing pollutants influence the removal of organic dyes remains to be answered.

4) Research the practical application of 3D GBMs in the real wastewater: Unlike the laboratory experimental study, the conditions of real wastewater are unable to control. The diversity of aqueous solution physicochemical and biological factors may lead to the decrease of catalytic capacity and materials stability. For example, Chen et al.[130] have highlighted the biodegradation of graphene by multiple types of microbes. Overall, the complexity of real wastewater may inhibit the practical application of 3D GBMs. Hence, considerable efforts should be devoted to their application in real wastewater.

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