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Review

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.

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 dyestuff 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

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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 Fig. 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 (Fig. 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

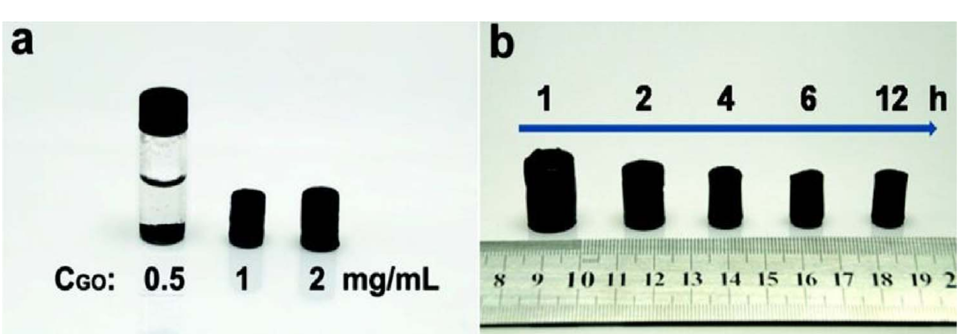

Fig. 1. (a) Photographs of products prepared by hydrothermal reduction with different GO concentrations at 180 °C for 12 h; (b) photographs of the products prepared with 2 mg/mL GO at 180 °C for different times.