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The applications of graphene-based materials in pollutant control and disinfection

Chi Him A. Tsang [a], H.Y.H. Kwok [a], Zhanjun Cheng [a, b], D.Y.C. Leung [a, *]

[a] Department of Mechanical Engineering, The University of Hong Kong, Hong Kong
[b] School of Environmental Science and Engineering, Tianjin University, Tianjin, China

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ABSTRACT

Due to their extra-large surface area and porosity, high compression power, hydrophobicity, and strong activity characteristics, there have been increasing interests in applying graphene-based materials for pollutant control and disinfection. The topics covered from photocatalytic reactions in the dye removal and organic conversions in liquid or gas phase, disinfection, oil absorption, and pollutant adsorption. In this manuscript, the characteristics of the photocatalytic reactions for toxins and pollutants like toxic hydrocarbons, carbon dioxides, and dye wastewater, removal of pollutants like oil and heavy metal ions via absorption/adsorption, and disinfection by different graphene-based materials via adsorption inactivation or photocatalytic inactivation will be emphasized. The challenges in pollutant removal research by graphene-based materials, such as the deactivation of graphene-based materials in photocatalytic pollutant removal reactions which was discovered recently and solutions to the corresponding weaknesses were discussed.

Contents

1. Introduction

In a previous submission, the common preparation methods and limitation of raw graphene and their variation products together with the applications in the energy field were introduced [1]. Besides the applications in energy topics, mitigation on environmental pollution problems was the focus on these graphene-based materials in recent years. Aquatic pollution due to industrial activities has been one of the long-lasting problems in the past several decades. Major pollutants include dye from textile factories, chemical from petrochemical plants and waste oil from various oil leakage events. Removal of the dye from sewage usually involves advanced oxidation process and photocatalysis. The use of photocatalyst for photocatalytic decomposition of dye is one of the most effective and economic ways of treatment. At the same time, reduction of CO_2 emission from fossil fuel combustion and toxic

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* Corresponding author.
E-mail address: ycleung@hku.hk (D.Y.C. Leung).

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VOCs from industry and automobile exhaust are also important for alleviating the global warming and air quality problems. On the other hand, disinfection in the water supply and indoor air to remove common harmful pathogens like E-coli, F-solani, and even viruses like EV71 and H9N2 is an important process for public health protection. Such works mostly involve the use of UVC light and photocatalysts. However, the less costly photocatalysis involve the use of UV light, but the solar spectrum only contains 5% of it. Therefore, the rest of the solar irradiation will be wasted. Under this situation, only wide band gap materials, like titania (TiO_2) and zinc oxide (ZnO), can fulfil the activation requirement [2–4]. In order to utilize the solar irradiation effectively during the photocatalytic decomposition, reduction of the band gap of the existing catalysts becomes an important task. In this aspect, graphene offers a good solution to achieve the effective light absorption via band gap reduction by loading with large band gap materials like titania (TiO_2) and zinc oxide (ZnO).

Besides the air and water pollution caused by industrial activity, oil leakage from tanks, ships or oil drilling facilities is one of the most severe environmental problems that occur in the ocean or seashore quite often. In order to reduce the adverse effect on the coastal ecology, absorbing the leaked oils from the contaminated seawater became an important area of research. As an absorbent, good mechanical strength, strong wettability, high porosity, and large specific surface area are important requirements to ensure effective removal of the oils, metal ions, or gas molecules without deformation of the absorbent and subsequent recycling of the absorbed materials (mainly oils). The strong elasticity of absorbent can be beneficial to the collection of absorbed oil from the absorbent through simple squeezing. Huge efforts have been made to develop effective adsorbent in past decades.

From different fundamental studies on various graphene products, especially 3D graphene aerogel (GA)-based products, their mechanical properties, porosity, and wettability (also called superhydrophobicity) were the interest of most studies as such parameters are important indices for the oil absorption process, and the oil recycling from the oil absorbed GA. From different groups of study, the mechanical strength of GA products can be as high as 5 kPa at 50% of the maximum strain to 23.6 kPa in the compression test, with 80–90% recovery after compression [5,6]. They can support a load of 5000–13,000 times of the masses of the GA products without deformation [5,7]. They also exhibit superhydrophobic properties when different GA products were exposed to water, with the resulting water contact angle in the range of 94–142° on the aerogel surface and 155° in the interior of GA [5,6,8]. Pure GA and metal oxide loaded GA products have very high porosity with values as high as 99.6%–99.8% [5,6,9]. The specific surface area of GA, determined by BET characterization, was also large with a range between 322.6 $m^2\ g^{-1}$ and 830 $m^2\ g^{-1}$ [6,7,10]. The above parameters were summarized in Table 1 for different graphene products. Due to the large surface area and easy loading with foreign materials, graphene nanosheets become an alternative choice for oil, dye and metal ion removal from traditional absorbents [11–13].

In this manuscript, a review of the graphene-based materials in the environmental pollutant reduction via the photocatalytic pathway, disinfection, and the pollutant removal via absorption will be emphasized. The challenges of the graphene-based materials in environmental application research due to material limitations and current developments are also in focus.

2. Applications in the environmental area

2.1. Photocatalyst for organic and inorganic pollutant conversion

The 2D metal oxide loaded graphene nanosheets (MO_x/GNs) and 3D metal oxide loaded graphene hydrogel or aerogel (MO_x/GH and MO_x/GA) based hybrid composite is one of the popular materials adopted in recent years as graphene substrate can reduce the chance of charge recombination [3,4,14,15]. ZnO and TiO_2 are commonly used MO_x/GNs photocatalyst for dye removal [2–4,12,14–22], organic conversion [23–26], liquid phase CO_2 reduction [27], H_2 production [2,28], and metal removal [2]. Different results show that the 2D MO_x/GNs and 3D photocatalysts exhibited strong photocatalytic activity under different kinds of light source with efficiency achieving 50% in the photocatalytic Cr^{6+} ion removal [2], 70% to almost 100% in dye removal [2–4,12,14,16–21], and over 93% in the organic compound conversion [23–26]. One of the examples was the photocatalytic activity comparison between ZnO nanorod/GNs and P25 in the methylene blue (MB) photodecomposition under a UV light source. The result from Dai's group showed that the activity and reaction kinetics of ZnO nanorod/GNs was around 2–2.5 times stronger than that of P25, while the kinetics and activity were also affected by the amount of ZnO nanorods loaded with GNs [20]. While the result by Hou et al. [15] reflected that the photocatalytic activity of TiO_2 (P25)-graphene hydrogel in the photo-decontamination of methylene blue, under visible light source, was much stronger than that of bare P25. 3D GH/GA-based materials were also investigated under different conditions [29–31]. Some of the works involved the nitro-benzene conversion into amino-benzene series compounds in the presence of both monometallic Au/GH or bimetallic AuPd/GA and a reducing agent, such as $NaBH_4$. Both the Au/GH and AuPd/GA showed strong activity in the nitro-benzene-based compounds based on the strong reduction (80–90%) in the UV–vis absorption peak of nitro-group in the compound [29–31].

Table 1
List of the selected physical, surface, and mechanical properties of selected 3D graphene-based materials.

GA candidates	Mechanical strength	Specific surface area ($m^2\ g^{-1}$)	Porosity	Water contact angle (Degree)	Elasticity	Ref
ULGA	4 kPa (50%-strain)	N/A	99.7–99.8%	N/A	Recovered to ~100% of original size	[9]
GA	6 kPa (50%-strain)	N/A	99.6%	100° (Surface), 155° (Interior)	Recovered to 80% of original size	[5]
RGO foam	5 kPa (Maximum strain)	N/A	N/A	135°	N/A	[8]
Pure GA	1 kPa (50%-strain)	512	N/A	94°	N/A	[6]
CPFA	10 kPa (50%-strain)	430	N/A	142.2°	Recovered to 90% of original size	[6]
Graphene/FeOOH aerogel	500 kPa (75%-strain), 27.6 kPa (yield stress)	N/A	N/A	N/A	N/A	[56]
NGA	N/A	830	10.8 nm (Pore size)	N/A	N/A	[10]
NGA	Tolerate 5000 times of its own mass	322.6	N/A	132.7°	N/A	[7]

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