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3D-3D porous Bi_2WO_6/graphene hydrogel composite with excellent synergistic effect of adsorption-enrichment and photocatalytic degradation

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A novel visible-light 3D-3D Bi_2WO_6/graphene hydrogel (BWO/GH) photocatalyst with the synergistic effect of adsorption and photocatalysis has been successfully synthesized by a facile one-step hydrothermal method and is applied in environment remediation. 3D porous graphene hydrogel, in which 3D-structured flower-like BWO as an efficient photocatalyst is homogenously distributed, not only exhibits the great absorption toward the organic pollution, but also provides multidimensional quality and electron transfer channels. The 3D-3D structure of BWO/GH composite is beneficial to light refraction and reflection, which highly improves the utilization rate of light. The synergistic effect of the 3D-3D BWO/GH composite greatly enhanced the removal rates of organic pollutants and it is ease of separation and recycling in water purification. The removal rate of methylene blue (MB) by BWO/GH composite is about 2.3 times as that of the pure BWO in static systems, and the removal rates of MB and 2, 4-dichlorophenol (2, 4-CDP) are about 1.3 and 3 times as these of the pure BWO in dynamic system. When the irradiation time lasted for 74 h, the removal rate of MB is nearly unchanged and still kept at 36.1%, indicating that the 3D BWO/GH composite has a high stability. The construction of BWO/GH composite resolved the adsorption saturation problem of GH and improved the photocatalytic activity of BWO, thus greatly improved the removal rate of water pollutants.

1. Introduction

Environmental pollution problems have become increasingly serious with the rapid development of human society, especially the water pollution, which seriously affects our daily life [1–3]. It is well known that the adsorption method is one of the widely used strategies for the treatment of water pollution due to its advantages of low cost, high adsorption capacity, high adsorption rate and ease of operation [4–7]. Among diverse of adsorption materials, the 3D network structure of hydrogel [8–10], especially the 3D structural GH [11,12], has attracted much attention because it can reduce the aggregation and provide multidimensional mass transmission channel, and it is easy to separate from the mixture reaction solution. Compared with the traditional adsorption materials such as activated carbon [13,14], silica [15,16] and polymer resins [17], GH shows much higher adsorption activity and adsorption rate for the organic compounds due to its high surface area, particular porous structure and the plane adsorption property, and it is widely used in the field of water pollution [18–21].

Although the absorption method is regarded as an effective method for water treatment, the hazardous water pollutants are just concentrated rather than mineralized to non-polluting substances by adsorption material. It might cause secondary pollution in waste water treatment. Furthermore, the adsorbents are generally difficult to regenerate and need to be treated to release the pollutant when reached their saturations [18,22]. Therefore, it is necessary to develop the new technology to remove the hazardous pollutants from water.

Photocatalysis has been widely used for waste water treatment because photocatalyst possesses excellent oxidation ability and it can decompose refractory organic pollutants and mineralize most toxic compounds completely [23–26]. However, some disadvantages such as the low visible-light absorption, high recombination efficiency of the photo-generated electron-hole pairs and

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ease of agglomeration limit the photocatalysis for industrial application. Therefore, it is believed that the development of novel photocatalytic materials with the synergistic effect of pollutants adsorption-enrichment and photocatalytic degradation undoubtedly has the most significant for the water purification.

The combination of 3D structural hydrogel with photocatalyst to fabricate the 3D porous hydrogel-based composite photocatalyst can not only overcome the adsorption saturation and non-regeneration problems of adsorption material, but also can improve the adsorption property and the separation of powder photocatalysts [27,28]. In addition, photocatalyst can homogenously distribute into the framework of 3D hydrogel, highly reducing the aggregation of powder photocatalyst and expose more active sites. It is beneficial to adsorption and surface photocatalytic reaction [29], thus effectively improves the removal rates of water pollutants. Compared with the other hydrogel-based photocatalyst, the GH-based photocatalyst has attracted much more attention in the field of water purification due to its special 3D porous structure, high surface area and good electrical conductivity [30]. The excellent electrical conductivity of GH can effectively promote the transfer of photo-generated electron, and the 3D porous structure can provide multidimensional quality and electron transfer channels, thus greatly enhance the photocatalytic performance. Until now, a few works about the 3D porous structural graphene aerogels (GA) based photocatalysts with high synergistic removal rates of water pollutants have been reported, such as 3D structural TiO_2/GA composite [31], g-C_3N_4/GA composite [32] and AgX/GA (X = Br, Cl) composite [33]. However, the black graphene hydrogel can absorb the whole UV and visible light and greatly decrease the light absorption of the photocatalyst in porous GH. Therefore, improving the light absorption and utilization of the photocatalyst in GH-based composite is very important for the enhancement of photocatalytic efficiency. Compared to 2D, 1D and 0D photocatalysts, such as g-C_3N_4 nanosheets and TiO_2, 3D hierarchical structural photocatalyst has higher light utilization efficiency due to the light refraction and reflection in the interior structure of photocatalyst. Therefore, the construction of the novel double three-dimensional (3D-3D) structural GH-based photocatalyst composite could greatly improve the light utilization efficiency and the photocatalytic performance of the photocatalyst.

. Bi-based photocatalyst with high photocatalytic performance has attracted great interests [34–36]. Bi_2WO_6 (BWO), as an excellent visible-light-driven photocatalyst with a narrow band gap (~2.8 eV) [37], has a crystal structure composed of accumulated layers of alternating bismuth oxide $(Bi_2O_2)^{2+}$ layers and octahedral $(WO_4)^{2-}$ sheets [38,39]. The layered structure is favorable for electrons and holes transfer in different directions, which effectively inhibits the recombination of electrons and holes, thus leading to the high photocatalytic performance. It has caused extensive concern in the fields of energy conversion [26,40] and pollutants degradation [23,34,41,42] due to its unique molecular structure, reactivity, stability and high photocatalytic activity [43]. In our work, the 3D-3D porous structural BWO/GH composites were successfully synthesized by a facile one-step hydrothermal method. The efficient 3D flower-like BWO photocatalysts were settled in the 3D porous GH network and formed the 3D-3D porous structural BWO/GH composites. This particular structure of BWO/GH composite would improve the light utilization efficiency and absorption of the organic compound, and provide multidimensional quality and electron transfer channels. The photocatalytic performances of BWO/GH composites were evaluated by MB and 2, 4-CDP decomposing under visible light ($\lambda \geq 420$ nm) in both static and dynamic systems. The 3D-3D structural BWO/GH composite may realize the synergistic effect of adsorption-enrichment and photocatalytic degradation. The GH-based photocatalyst composite resolves the problem of adsorption saturation and regeneration, achieving a long term cycle utilization of adsorption material.

2. Experimental

2.1. Synthesis of BWO/GH composites

GO was prepared from graphite powder according to Hummer's method[44]. All other chemicals were of analytical grade and used without further purification. Deionized water was used throughout. In a typical synthesis method: BWO/GH was synthesized by a facile one-step hydrothermal method and then freeze-dried. Ethylene glycol was used to disperse $Bi(NO_3)_3$ and control the morphology of BWO. In details, 0.5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved into 10 mL ethylene glycol after ultrasound for 10 min, then 20 mL GO solution was added with stirring for another 10 min. Here, $Bi(NO_3)_3$ can be dispersed evenly into GO solution. Then, 0.25 mmol $Na_2WO_4{\cdot}2H_2O$ was added and the resultant suspension was stirred for 15 min. Subsequently, the suspension was put into a 50 mL Teflon vessel and then sealed in an autoclave and heated at 180 °C for 24 h. GO was reduced in the process of heating, and 3D porous structural GH was formed by π-π stacking interactions and hydrogen bond interactions between GO nanosheets. The products were treated by freeze-drying after soaking 2–3 days in deionized water. A series of samples were synthesized by changing the molar quantities of $Bi(NO_3)_3{\cdot}5H_2O$ and $Na_2WO_4{\cdot}2H_2O$, and keeping the volume of GO solution unchanged.

2.2. Characterizations

The as-prepared BWO/GH composites were analyzed by the thermogravimetry analysis (TG), the field emission gun scanning electron microscope (FE-SEM, Hitachi SU-8010) and the transmission electron microscopy (TEM, equip a Hitachi HT 7700 electron microscope) with an acceleration voltage of 100 kV. X-ray diffraction (XRD) patterns of BWO/GH samples were recorded by using a Bruker D8 Advance X-ray diffractometer (Cu Kα, λ = 1.5406 Å, 40 kV, 40 mA). Fourier transfer infrared (FT-IR) spectra were performed by using a Bruker V70 spectrometer. Raman spectra were recorded on a microscopic confocal Raman spectrometer (HORIBA HR800, with an excitation of 514.5 nm laser light). The diffuse-reflectance spectrum (DRS) of BWO/GH composites were recorded on an UV–vis spectrophotometer (Hitachi, U-3010, equipped with an integrated sphere, $BaSO_4$ used as the reference). The specific surface area and pore diameter distribution were measured by a MicromeriticsASAP2020 Surface Area and Porosity Analyzer.

2.3. Photocatalytic experiments

The adsorption and photocatalytic performances of different BWO/GH samples in static system were evaluated by degrading methylene blue (MB, 40 ppm) solution in a multi-tube agitated reactor (XPA-7) under visible-light irradiation ($\lambda > 420$ nm). The visible light source was provided by a 500 W xenon lamp (filter, $\lambda = 420$ nm). In the experiment, 25 mg photocatalyst was added into the prepared 50 mL MB solution (40 ppm). At given time intervals, 2.5 mL aliquots were sampled and centrifuged. The MB supernatant liquid was analyzed by recording variations of the maximum absorption peak (664 nm for MB) using a Hitachi U-3010 UV–vis spectrophotometer.

The synergistic effect of adsorption-enrichment and photocatalytic degradation of BWO/GH composites in dynamic system were evaluated by removing MB (1×10^{-5} mol/L) and 2, 4-CDP (5 ppm) in solutions, which conducted in a homemade reactor with a quartz cover[27]. Peristaltic pump provided the power. Visible light source was provided by a xenon lamp (Perfectlight, filter, $\lambda = 420$ nm).