Assembly and enhanced elimination performance of 3D graphene aerogel-zinc oxide hybrids for methylene blue dye in water

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ABSTRACT

The hybrid consisting of ZnO nanocrystals and graphene aerogel (GA) are facilely assembled with a one-pot hydrothermal method combined with freeze-drying process. Their adsorption capacity and photocatalytic degradation performance in the removal of methylene blue (MB) under visible and UV light irradiation are evaluated in details. The results show that the hybrids exhibit much better adsorptivity and higher photocatalytic activity than pristine ZnO and most of the ZnO-based materials reported previously. Meanwhile, the hybrids also possess excellent photochemical stability. Among them, GA-ZnO(5) displays the highest adsorptive efficiency (94.2%) and the best total removal efficiency for MB dye (95.9%) under visible light irradiation. And GA-ZnO(3) exhibits the best total removal efficiency (97.6%) irradiated by UV light under the harsh conditions. A possible photocatalytic mechanism is also proposed. As a result, the 3D GA-ZnO hybrids are confirmed to be a promising functional material in field of wastewater remediation.

1. Introduction

With the rapid industrial development, water contamination caused by organic dyes becomes a seriously global problem. Most of the dyes are resistant to biodegradation and highly toxic and hazardous, which leads to harms toward aquatic organisms, humans, plants, and animals [1–3]. Till now, various strategies have been employed to alleviate the contamination. Among them, adsorption by various porous adsorbents [4–14] and photo-degradation over semiconductor-based photocatalysts are extensively focused on by many researchers, such as TiO_2 [15,16], ZnO [17–19], CdS [20–22], WO_3 [23–25], and SnO_2 [26–28].

As a typical n-type semiconductor photocatalyst, ZnO has outstanding advantages, such as high photosensitivity, chemical stability, non-toxicity, and low-cost preparation [29]. Furthermore, ZnO may exhibit higher photocatalytic activity than TiO_2 for the photo-degradation of organic pollutants. This can be ascribed to the high electron mobility of ZnO (200–300 cm^2 V^{-1} s^{-1}) which is much higher than that of TiO_2 (0.1–4.0 cm^2 V^{-1} s^{-1}) [30]. Even so, the wide band gap (3.37 eV) and high exciton binding energy (60 meV) allow ZnO only to absorb UV light (~4% of solar spectrum) [2]. Therefore, it is necessary to extend the solar radiation response and restrain the recombination of e-–h$^+$ pairs of ZnO. Literatures revealed that this is

expected to be realized by incorporation of metals [31–33], constructing heterojunctions [34–37], or coupling carbon-based materials, such as carbon or carbon-dots [18,38], carbon nanotube (CNT) [39], as well as graphene [40–42].

As an excellent dopant for the semiconductor photocatalysts, graphene possesses a π-conjugated planar structure, which is beneficial to increase the dye absorption through the π–π stacking. Its unpaired π electrons could also reduce the bandgaps of these hybrid materials. In addition, it can provide conductive electron channels for the separated charge carriers and then inhibit the recombination of electrons and holes [43]. Noticeably, as compared with traditional 2D graphene, graphene aerogel (GA) with a 3D macroscopic architecture possesses much higher porosity and electrical conductivity, as well as larger specific surface area. The porosity can improve the utilization of solar lights because the lights entering the pores can be repeatedly reflected until they are possibly absorbed. In addition to the higher adsorptive capacity, the large surface area ensures GA to adsorb more organic dye molecules than graphene, leading to the enhanced photocatalytic efficiency. Hence, GA-based composites provide exceptional potential in water remediation [44–48]. Even so, to the best of our knowledge, there is scarce literature about the hybrids consisting of ZnO nanocrystals and GA for the removal of organic dyes in water so far.

In the present work, we report the assembly of GA-ZnO hybrids with 3D architecture via a one-pot hydrothermal method combined with freeze-drying process. The resultant hybrids are found to possess excellent adsorptivity and high photocatalytic activity for the elimination of methylene blue (MB) in water both under visible and UV light irradiation. A possible photocatalytic mechanism is also illustrated and analyzed in details. The results confirm that the hybrids to be promising in the future water remediation applications.

2. Experimental methods

2.1. Assembly of GA-ZnO hybrids

Graphene oxide (GO) solution was synthesized from graphite powder with the modified Hummers' method [49]. Then, the GO solution was used to assemble GA-ZnO hybrids by a one-pot hydrothermal method combined with freeze-drying process. In brief, a uniform mixture solution was obtained by ultrasonic 30 mL of deionized (DI) water and 30 mL of GO solution (3.3 mg mL^{-1}) for 2 h. The pH value was adjusted to about 10 with ammonia, and then 30 mL of $Zn(NO_3)_2 \cdot 6H_2O$ solution with various concentrations was added. Whereafter, the as-prepared solution was ultrasonicated for 2 h and stirred for another 4 h before it was sealed evenly into Teflon-lined autoclaves and maintained at 180 °C for 24 h, following by freeze-drying process. The resultant materials were denoted as GA-ZnO(x) (where x referred to the mass ratio of $Zn(NO_3)_2 \cdot 6H_2O$ to GO in precursors, which was 1, 3, 5, and 10, respectively).

For comparison, pristine GA and ZnO were also prepared with the same procedure without the addition of $Zn(NO_3)_2 \cdot 6H_2O$ and GO solutions, respectively.

2.2. Characterization of the materials

The materials were characterized by thermogravimetric (TG) analysis, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS), fourier-transform infrared (FT-IR) spectroscopy, nitrogen adsorption-desorption and Raman spectroscopy (see the Supplementary Materials in detail).

2.3. Adsorption and photocatalytic activity

The adsorption capacity as well as the UV and visible light-driven photocatalytic activity of the resultant materials were measured by comparing the concentrations of MB dye with an air flow of 40 mL min^{-1} at room temperature. In each experiment, the slurry containing 5.0 mg of catalyst and 25 mL of MB solution (20.0 mg L^{-1}) was stirred in a 50 mL cylindrical quartz vessel in the dark, UV and visible light irradiation, respectively. In these experiments, the visible and UV light sources were provided by a 300 W Xe-lamp equipped with a cutoff filter ($\lambda \geq 420$ nm) and a 300 W Hg-lamp equipped with a cutoff filter ($\lambda \leq 380$ nm). At given time intervals of 30 min, about 2 mL of the suspension liquid was taken out and the filtered clear solution was analyzed with a UV–vis spectrophotometer at the maximal absorption wavelength for MB (664 nm).

The removal efficiency of MB was evaluated using C/C_0 and the kinetics study of the removal performance was discussed according to Eq. (1).

$$Ln\left(\frac{C_0}{C}\right) = kt \tag{1}$$

where $C_0 = 20.0$ mg L^{-1} was the initial concentration of MB, C was the concentration of MB in the desired time interval (mg L^{-1}), k was the removal rate constant, and t was the operating time (min).
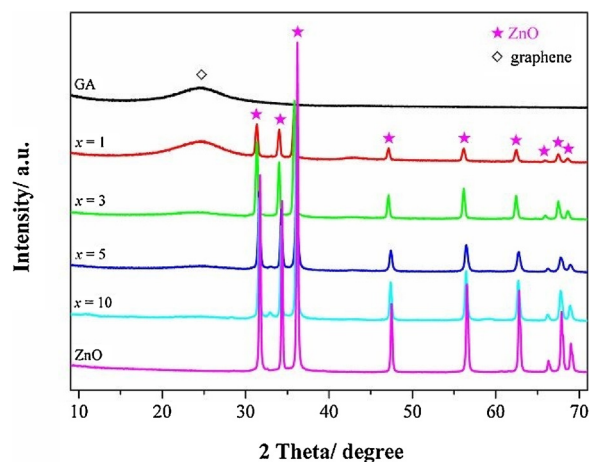

Fig. 1. XRD patterns of GA, ZnO, and the GA-ZnO(x) hybrids.

3. Results and discussion

3.1. Characterization

Fig. 1 showed the X-ray diffraction (XRD) patterns of GA, ZnO, and GA-ZnO(x) hybrids. The typical peaks appeared at 31.6°, 34.4°, 36.1°, 47.4°, 56.4°, 62.7°, 66.4°, 67.9° and 69.1° can be assigned to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes, respectively [50], which are the characters of hexagonal wurtzite ZnO (JPCDS 41-1487) and could be found in both ZnO and GA-ZnO hybrids. In addition, an extremely broadening (002) diffraction peak was observed at 24.8° for GA, whose intensity was gradually decreased with the increasing x in GA-ZnO(x) hybrids. And it even disappeared in the case of GA-ZnO(10) ascribed to the limited amount and the destroyed regular stacks of GA in the hybrid. No other impurity peaks were detected, indicating that the GA-ZnO hybrids were successfully assembled. Additionally, the diffraction peaks of ZnO in the GA-ZnO(x) hybrids shift slightly to lower angle with decreasing x, implying that the doping of GA increases the lattice parameters of ZnO to some extent.

At high temperature, GA can react with oxygen to produce CO_2 and H_2O gases and the corresponding weight loss may be used to estimate its percentage in the hybrids. Therefor TG curve of the GA-ZnO(3) hybrids was conducted and analyzed, as shown in Fig. S1. The gradual weight loss below 200 °C ($\sim$2.84%) was caused by desorption of the surface adsorbed water. The further loss in the temperature range of 200–550 °C ($\sim$50.17%) was ascribed to the removal of oxygen-containing groups and the decomposition of carbon framework of GA. According to the TG analysis, the weight percentage of ZnO in GA-ZnO (3) hybrids was about 47%, which was in accordance with the mass ratio of 3 for $Zn(NO_3)_2 \cdot 6H_2O$ to GO in the precursors.

Raman spectroscopy is one of the most effective techniques in characterization of the structure of carbonaceous-based materials [51]. In Fig. 2, two Raman bands appeared at 1330 and 1587 cm^{-1} could be obviously observed in GA and GA-ZnO(3) hybrids, which were ascribed to the disordered (D) band and graphitic (G) band, respectively [15]. Meanwhile, the intensity ratio of the D and G band (I_D/I_G) for GA-ZnO (3) was 1.26, which was slightly higher than that of GA ($I_D/I_G = 1.20$). It is known that the D band is related to the defects and the G band originates from the in-plane vibration of sp^2 carbon atoms. The result demonstrated that the incorporation of ZnO increased the defect degree of GA to some extent. Additionally, compared with that of GA at 1324 cm^{-1}, a Raman shift in the D band of GA-ZnO(3) was observed (1349 cm^{-1}), suggesting that an intensive chemical interaction between ZnO and GA may be already existed.

The fourier-transform infrared (FT-IR) spectra were also carried out to characterize the structure of GA, ZnO, and GA-ZnO(x) hybrids