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Construction of CQDs-$Bi_{20}TiO_{32}$/PAN electrospun fiber membranes and their photocatalytic activity for isoproturon degradation under visible light

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ABSTRACT

The CQDs-$Bi_{20}TiO_{32}$ photocatalysts exhibited high visible-light responsive photocatalytic activity. To achieve the cyclic utilization of CQDs-$Bi_{20}TiO_{32}$, the novel flexible CQDs-$Bi_{20}TiO_{32}$/PAN fiber membranes were prepared by a simple coaxial electrospinning technique. It was found that the CQDs-$Bi_{20}TiO_{32}$ photocatalyst could be firmly and uniformly fixed on the surfaces of electrospun fibers and the composite fiber membranes possessed the hierarchical macro- and mesoporous structure. The loaded CQDs-$Bi_{20}TiO_{32}$ endowed the composite fiber with an obvious photocatalytic activity for the degradation of the herbicide isoproturon under visible light irradiation. Among these samples, S3 at photocatalyst dosage 15 w/v% had the highest degradation efficiency for isoproturon. Meanwhile, the core-shell structured inorganic-organic hybrid fiber membranes have a significant advantage in the recyclability for photocatalyts. The flexible CQDs-$Bi_{20}TiO_{32}$/PAN electrospun fiber membranes would have potential applications in efficient removal of organic contaminants.

1. Introduction

To date, the water contamination caused by various organic pollutants has aroused worldwide public concern. Semiconductor photocatalysis is one of the most promising technologies for wastewater remediation, due to its sustainability, low pollutants selectivity, high-degree mineralization, and environmentally friendly properties [1–3]. To enlarge the using range of solar light, most researches have been focused on the development of visible-light-responsive photocatalysts, such as Bi-based [4], Ag-based [5], W-based [6], In-based [7,8], and Fe-based [9] photocatalysts. $Bi_{20}TiO_{32}$, a novel visible-light-responsive photocatalyst, has attracted extensive scientific interest in photocatalytic degradation of organic pollutants. Owing to the hybridized valence band by Bi 6s and O 2p orbitals, $Bi_{20}TiO_{32}$ has a relatively narrow band-gap energy 2.36 eV, corresponding to the light absorption edge at 525 nm [10]. Nevertheless, its photocatalytic activity is still inhibited by the high recombination rate of photo-generated electron-hole pairs, resulting in the low utilization efficiency of photons. To solve this issue, carbon quantum dots (CQDs) were introduced into $Bi_{20}TiO_{32}$ photocatalysts via solvothermal synthesis and oil bath reflux method in our previous report [11]. Due to the excellent electron transfer ability and up-converting photoluminescence of CQDs, the separation rate of electron-hole pairs in CQDs-$Bi_{20}TiO_{32}$ composite photocatalyst was obviously enhanced. So CQDs-$Bi_{20}TiO_{32}$ composite exhibited higher photocatalytic activity for the degradation of the herbicide isoproturon than pure $Bi_{20}TiO_{32}$. But it is also a challenge for the photocatalysts in powder form to be reused in practical application.

Electrospinning has received an increasing appeal as a versatile technique to produce fibers with diameters in the range from micrometers to tens of nanometers. The electrospun fiber membranes possess several fascinating features including large surface area, high porosity and light weight [12,13]. By virtue of the merits of such a technique, a variety of one-dimensional (1D) photocatalysts nanofibers have been successfully fabricated, such as ZnO [14], Nb_2O_5 [15], $BiVO_4$ [16,17], In_2S_3/TiO_2 [18], and CuO/TiO_2 [19]. The 1D mesoporous architectures supply more surface active sites for the photocatalytic reaction [20,21], but the inevitable brittleness is another problem for the inorganic photocatalyst fibers in the recycling process. Introduced approximately in 2003 [22,23], coaxial electrospinning technology could combine two different components together to form core-shell

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Table 1
Experimental parameters for the fabrication of CQDs-$Bi_{20}TiO_{32}$/PAN composite fiber membranes.

Sample	Sheath fluid		Core fluid	Flow rate (mL/h)		Average diameter of fiber (nm)	BET surface area (m^2/g)
	C_1[a] (%w/v)	C_2[b] (%w/v)	C_1[a] (%w/v)	Core	sheath		
S1	10	5	15	0.3	0.4	665	7.53
S2	10	10	15	0.3	0.4	687	10.48
S3	10	15	15	0.3	0.4	864	11.18
S4	10	20	15	0.3	0.4	1069	9.41

[a] Concentration of PAN in DMAc.
[b] Concentration of CQDs-$Bi_{20}TiO_{32}$ photocatalyst in DMAc.

structured micro-nanometer scale fibers. If loading the photocatalysts uniformly on the surface of organic polymer fiber by this approach, the resulting flexible composite fiber membranes may get potential applications in environmental purification.

Herein, the flexible CQDs-$Bi_{20}TiO_{32}$/PAN electrospun fiber membranes were successfully prepared through the coaxial electrospinning technology. The CQDs-$Bi_{20}TiO_{32}$ photocatalysts were firmly fixed on the fiber surface and retained good photocatalytic activity. The phase structures, morphologies, optical properties and pore structures of the fiber membranes were well characterized. The visible-light photocatalytic activity and recyclability of the samples were evaluated by the degradation of isoproturon, a phenylurea herbicide with low toxicity. Furthermore, the possible photo-degradation mechanism of isoproturon by the composite fiber membranes was put forward.

2. Experimental

2.1. Materials

Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$), ethylenediamine ($H_2NCH_2CH_2NH_2$), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), benzyl alcohol (C_7H_8O), and absolute ethanol (CH_3CH_2OH) were purchased from the Sinopharm Chemical Reagent Co., Ltd. Tetraisopropyl orthotitanate ($Ti(OC_3H_7)_4$) was procured from the Tokyo Chemical Industry Co., Ltd. *N,N*-Dimethylacetamide (DMAc) was obtained from the Shanghai Lingfeng Chemical Reagent Co., Ltd. All of the above chemicals were of analytical grade and used as received without further purification. Isoproturon (>99.6% pure, HPLC grade) was purchased from the AccuStandard, USA. Polyacrylonitrile (PAN, M_W = 60,000) was supplied by the Zhejiang Shangyu Wuyue Economic and Trade Co., Ltd.

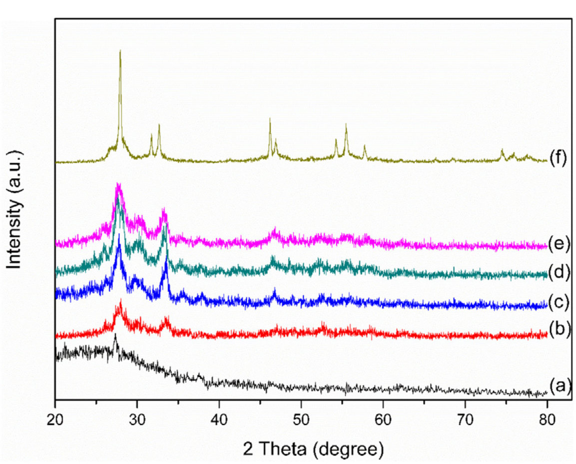

Fig. 1. XRD patterns of (a) PAN electrospun fiber membranes, (b) S1, (c) S2, (d) S3, (e) S4, and (f) CQDs-$Bi_{20}TiO_{32}$ photocatalyat.

2.2. Fabrication of CQDs-$Bi_{20}TiO_{32}$/PAN fiber membranes

The photocatalyst CQDs-$Bi_{20}TiO_{32}$ was prepared according to our previous report [11]. The CQDs-$Bi_{20}TiO_{32}$/PAN fiber membranes were fabricated by coaxial electrospinning technology. The sheath fluid was prepared with PAN, CQDs-$Bi_{20}TiO_{32}$ photocatalyst and DMAc solvent. The concentration of PAN in DMAc was set to 10 w/v% and the contents of CQDs-$Bi_{20}TiO_{32}$ aspect to DMAc were adjusted to 5 w/v%, 10 w/v%, 15 w/v% and 20 w/v%, respectively. The detailed process was described as follows. The fixed amount of PAN powder and appropriate amounts of photocatalysts were added into DMAc. The mixture was vigorously stirred at 75 °C for 6 h to form sheath fluids. The core solution with concentration PAN 15 w/v% was prepared in the same way without using the photocatalyst. Subsequently, the core and sheath solutions were loaded into two syringes connected to a concentric nozzle (inner and outer diameters were 0.8 and 1.2 mm, respectively). A stable voltage of 20 kV was applied to the concentric nozzle by the high voltage supply (ZGF-60KV/5MA, Shanghai Sute Electrical Corp., Ltd. China). The core and sheath fluids were pumped out at rates of 0.3 mL/h and 0.4 mL/h using two syringe pumps (KDS100, Cole-Parmer, USA). The resultant electrospun fiber membranes were collected on the aluminum foil covering on the grounded metallic collector. The distance from the nozzle to collector was set to 20 cm. The temperature and relative humidity during electrospinning processes were maintained at 25 ± 5 °C and 35 ± 5%, respectively. The as-prepared fiber membranes were dried in an oven at 100 °C overnight to remove the residual solvent. To achieve the optimum photocatalyst coating on the PAN fiber, the same electrospinning procedure was carried out using the same core fluid and four different sheath fluids (the contents of CQDs-$Bi_{20}TiO_{32}$ photocatalysts aspect to the solvent were 5 w/v%, 10 w/v%, 15 w/v% and 20 w/v%, respectively). Correspondingly, the obtained fiber membranes were labeled S1, S2, S3 and S4. The detailed preparation parameters and corresponding properties of composite fiber membranes were listed in Table 1. For comparison, bare PAN nanofiber mat was also prepared by the similar method without using photocatalysts.

2.3. Characterization

The phase structures of the prepared samples were characterized using X-ray diffraction (XRD, Rigaku Ltd., Japan) with Cu Ka

Table 2
The contents of CQDs-$Bi_{20}TiO_{32}$ photocatalysts on the electrospun fiber membranes.

Sample	Content of Bi	Content of CQDs-$Bi_{20}TiO_{32}$
PAN fiber membranes	below detectable limit	/
S1	10.9%	12.5%
S2	18.5%	21.2%
S3	24.8%	28.4%
S4	33.5%	38.4%