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A green approach assembled multifunctional Ag/AgBr/TNF membrane for clean water production & disinfection of bacteria through utilizing visible light

Chengli Tang[a,d,1], Hongwei Bai[a,b,*], Lei Liu[a], Xiaoli Zan[c], Peng Gao[a], Darren Delai Sun[a,**], Wei Yan[d,**]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Energy Research Institute @NTU (ERI@N), Nanyang Technological University, Singapore 737141, Singapore
[c] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[d] Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xianning West Road 28#, Xi'an 710049, China

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ABSTRACT

In order to realize the ideal water treatment in a green and energy saving manner, TiO_2 based multifunctional membrane proved to be a promising approach owing to its capability in utilizing visible light for photocatalytic pollutant degradation and disinfection of bacteria. However, few studies were found about the investigation of antibacterial abilities arising from the intrinsic properties of membrane and its minor composition. Here, a multifunctional membrane was created via a green approach to integrate the merits of hierarchical Ag/AgBr/TNF composites with micro-/-nano porous structures, the intrinsic antibacterial abilities of Ag, and the visible light absorption capability of AgBr. The synergy effects made it being a promising multifunctional membrane for concurrent water filtration and disinfection in a sustainable way. Through a versatile characterization techniques of FESEM, XRD, TES, XPS, and UV-vis spectrometer, the morphology, structure and surface properties of the well prepared Ag/AgBr/TNF multifunctional membrane was thoroughly studied to reveal the deep mechanism behind the high flux, high photocatalytic degradation and disinfection efficiency under visible light. It indicates that the Ag/AgBr/TNF multifunctional membrane exhibited better photocatalytic activity, higher water permeate flux, and higher disinfection abilities over commercial P25 membrane under visible light. Besides the deep mechanism elaborated, the key factors in terms of predominant oxidative species was also exploited in details. This further solidify the broad future of the developed multifunctional membrane. In view of the roaring demand of advanced water treatment and disinfection technology, it is reasonable to believe our developed visible light responsive Ag/AgBr/TNF multifunctional membrane will show great significances to a green and clean future.

1. Introduction

Human beings have been threatened by severe and global water crisis [1,2]: (1) fast depletion of fresh and accessible water resource, (2) dirty, toxic and polluted water raging, and (3) water-borne diseases transmitting [3]. Global water resources are constant through natural cycles or transformation, while the fresh and clean water resources is a minor part and are being depleted or polluted at an unprecedented rate accompanying the fast urbanization and industrialization [4,5]. The increasing global populations further accelerated the consumption of clean water, and the climate change will cause adverse effect on this trend [6,7]. The unstrained and greedy human activities poured lots of toxic and misplaced pollutants into natural fresh water bodies like surface rivers and underground waters resulting in the heavy water pollution [8,9]. Obviously, there is a contradiction between clean water shortage and increasing wastewater, which is not only the cause but also the effect of water crisis [10]. As thus it is an ideal way to solve the conflict through technologically purifying the wastewater in terms

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[*] Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

[**] Corresponding authors.

E-mail addresses: hwbai@ntu.edu.sg, baihw0001@gmail.com (H. Bai), DDSUN@ntu.edu.sg (D.D. Sun), yanwei@mail.xjtu.edu.cn (W. Yan).

[1] Present address: College of Mechanical and Electrical Engineering, Jiaxing University, Jiaxing 314001, P.R. China.

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of pollutants removal and disinfection of bacteria into clean water to guarantee the water security issue [11–15].

In the past years, lots of technologies have been developed for wastewater purifications such as the conventional physical, chemical and biological methods [2]. These traditional methods proved to play a significant role in wastewater treatment and environmental remediation [16–18]. However, these methods are always featured as high energy consumption, low efficiency, low productivity and secondary pollution, which cannot meet the stringent wastewater discharge requirements, high living standards, cost-effective, green and sustainable approaches after considering the even severer global energy crisis [19–21].

Since 1960s, polymer based membrane filtration has become a dominant water treatment technology by rejecting pollutants to produce high quality water at a very competitive cost [22]. However, the intrinsic hydrophobic polymer membrane is easy to be fouled owing to the accumulation of pollutants and bacteria on the surface or in the pores of membrane becomes a bottleneck limiting the broad application of membrane, as it may cause lots of adverse effects such as poorer water quality, lower water productivity, energy-intensive, shorter membrane lifespan and potential secondary pollution [23–25]. To address the membrane fouling issue, our group has developed a novel and sustainable approach in the past years [8,23,26–28]. Basically, two strategies were developed and well proved: (1) change the surface property of hydrophobic membrane into hydrophilic membrane by using inorganic TiO_2 nanofiber materials for high permeate flux [29–31], and (2) multifunctionalize the membrane through incorporating the functions of TiO_2 adsorption/photodegradation of organics matters, and bacteria disinfection for process fouling control and mitigation [32–34]. Following these, we have developed versatile TiO_2 multifunctional membranes and applied them for practical water treatment and disinfections. In particular, well-tailored TiO_2 nanostructure is one of the most successful platform for multifunctional membrane as its unique features in terms of increasing more hierarchical micro-/-nano porous, reducing the intrinsic resistance of membrane and building up more reaction sites for photocatalytic reaction occurring and pollutants adsorption [35–37].

Hierarchically structured TiO_2 membrane is famous for photocatalytic degradation of organic matters, killing bacteria and filtration. However the limiting factor for TiO_2 photocatalytic broad application lies in the limited UV which accounts for less than 4% of full solar spectrum [37], but the only energy source to excite TiO_2 to generate electrons and holes for photocatalysis [33].

Starting from a point of practical engineering application, energy-efficient photocatalysts are highly demanded to effectively utilize the visible light that constitutes 43% of the total sunlight [37]. Hence, it is important to develop a visible light responsive photocatalyst [38–40], and some efforts have been devoted to developing "second-generation" TiO_2 [41] and other narrow band gap semiconductors [42,43] that can absorb visible light. In recent years, numerous interest has been paid to designing Ag/AgX (X = Cl, Br, I) composite materials for specific applications such as bacteria destruction and degradation of organic pollutants in water [44–51].

Although some studies reported the integration of Ag, AgBr with TiO_2 in the form of nanoparticles, spheres, or one dimensional (1D) materials, there is few ideal approach to maximize the best performance of Ag, AgBr and TiO_2 through complete mixing at molecular level. Low temperature hydrothermal reaction provides a good platform to solve this problem by guaranteeing the sufficient and well mixing of Ag, AgBr and TiO_2 precursor from the level of molecular chemistry, this will guarantee the close contact between Ag, AgBr and TiO_2 to promote the fast electrons transfer at a minimal electricity resistance [12,52–54].

Here, we report a tertiary Ag/AgBr/TiO_2 nanofiber (Ag/AgBr/TNF) membrane platform to fully exploit the merits of (1) hierarchical scaffold nanofiber porous structures for high permeate flux, (2) multifunctional pollutants removal and disinfection by adsorption, rejection and degradation by Ag/AgBr/TNF under visible light, and (3) maximizing the advantages of membrane and photocatalysis while completely solving the issues of membrane fouling and catalyst recovery. Because of the close contact and well mixing of AgBr with TiO_2, the visible light absorbing capability and high photocatalytic efficiency of AgBr/TiO_2 will be further accelerated by Ag [50]. While, the intrinsic antibacterial ability of Ag will also enhance the disinfection of bacteria simultaneously. All these unique merits will lead to a sharp weapon to solve the wastewater treatment, clean water production and disinfection of bacteria issues in practical engineering applications.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB), silver nitrate ($AgNO_3$), dimethylsulfoxide (DMSO), ethylenediaminetetraacetic acid (EDTA), and salicylic acid (SA) were purchased from Sigma Aldrich. Commercial TiO_2 powder (Degussa P25) (P25 NP) was obtained from Germany Degussa Corporation (BET surface area, *ca.* 50 m^2/g; particle size, 25 nm). All the above reagents were of AR grade and used as received. Deionized (DI) water was used throughout this study. *Escherichia coli* (*E. coli*) K12 ER2925 was purchased from New England Biolab.

2.2. Fabrication of TiO_2 nanofibers (TNF) and synthesis of Ag/AgBr/TNF composites

A facile low temperature hydrothermal method was used to synthesize TNF with dissolving P25 NPs into 10 mol/L NaOH [55]. The resultant solution was transferred into a Teflon-lined autoclave and stored in the electronic oven for 48 h at 180 °C. After naturally cooling down, white precipitation formed at the bottom was recovered and repeatedly washed by 0.1 mol/L HCl solution and then DI water with the assistance of ultrasound. The TNF was gained after calcination of the neutralized product at a temperature of 600 °C.

The product of Ag/AgBr/TNF was synthesized by a modified deposition-precipitation method as mentioned in literature [56]. Typically, 0.1 g of TNF was ultrasonicated in 50 mL of DI water to disperse it evenly. Then, 0.12 g of CTAB was added to this suspension, and the mixture was stirred magnetically for 2 h to get a homogeneous solution. After that, 2 mL of 0.6 mol/L diamminesilver(I) hydroxide($Ag(NH_3)_2OH$) was quickly added to the mixture. This solution was aged with stirring for 20 h and then filtered, washed with water, and dried at 60 °C. The final Ag/AgBr/TNF photocatalysts were obtained by calcination at 500 °C in air for 3 h.

2.3. Fabrication of multifunctional Ag/AgBr/TNF membrane

With referring to our previous studies [27], identical amount of as-synthesized Ag/AgBr/TNF composite materials were suspended in DI water and then filled into a filtration cup at the bottom of which a commercial cellulose acetate (CA) membrane from Millipore was mounted [8,37]. The substrate CA membrane is 47 mm in diameter and has a pore size of 0.45 μm. By using a dead-end filtration setup as described in Fig. S1 (Supporting information (SI)), the synthesized Ag/AgBr/TNF composite were uniformly assembled onto the surface of CA and formed a hierarchically structured new functional layer. Under the given operating pressure, the Ag/AgBr/TNF is well assembled onto the CA membrane and is stable for concurrent water purifications.