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Invited feature article

Mechanisms on the enhanced sterilization performance of fluorocarbon resin composite coatings modified by g-C_3N_4/Bi_2MoO_6 under the visible-light

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ABSTRACT

Photocatalysts, which are produced by strong oxidizing groups ($^{\bullet}OH$, h^+, $^{\bullet}O_2^-$), could solve marine biofouling problems efficiently. A number of studies showed that the microbial attachment was the original of marine biological attachment, and oxidizing groups inhibit the bacterial activity. In present work, the hybrid g-C_3N_4/Bi_2MoO_6 photocatalysts were synthesized via a sonochemical method. The successful combination of g-C_3N_4 and Bi_2MoO_6 was characterized by various physicochemical techniques, such as XRD, SEM, TEM, UV–vis and EIS test. As the results showed, the sterilization performance of the PEVE composite coatings was enhanced after adding g-C_3N_4/Bi_2MoO_6 under the visible-light irradiation. When the content of g-C_3N_4 in Bi_2MoO_6 was 7%, the sterilization performance of composite coatings was prominent under visible light irradiation for 4 h. This finding was attributed to the increased separation efficiency of the photogenerated electron-hole pairs of Bi_2MoO_6 by g-C_3N_4, which contributed to the generation of superoxide radicals ($^{\bullet}O_2^-$). Meanwhile, we also tested the stability and sterilization performance of 7% g-C_3N_4/Bi_2MoO_6/PEVE coating, the results demonstrated that the g-C_3N_4/Bi_2MoO_6/PEVE coating has good stability and cycle performance. This work has great significance in the photocatalyst technology as a coating for killing marine bacteria to address marine biofouling problems.

1. Introduction

With the development of internal trade, the ships play indispensable roles in trade contracts. However, the marine biofouling is one of the worldwide problems in marine systems, which results from the accumulation of algae, marine plants, and colonization of marine microorganisms, causing a series of serious economical and safety problems [1]. Traditionally, the application of antifouling coatings for releasing toxic substances and polluting marine environment has been banned [2], thus, many researches are focusing on novel, efficient methods and technologies to solve the marine problems.

Semiconductor-based photocatalysis technology is a novel and green technique, which uses sunlight as the energy source to degrade pollutants and kill bacteria [3]. Existing studies showed that many researches focus on evaluating the photocatalytic antibacterial activity of TiO_2, confirming its effective antibacterial performance for *Escherichia coli*, and *Staphylococcus aureus* [4]. Under light irradiation, the electrons (e^-) and holes (h^+) generated by the semiconductor will react with water or air to generate active oxidizing radicals (h^+, $^{\bullet}OH$, $^{\bullet}O_2^-$), which directly contact and decompose the pollutants or bacteria [5]. However, TiO_2 can only absorb ultraviolet light because of its large band gap (Eg = 3.2 eV) [6–8], resulting in low photocatalytic activity under sunlight conditions. Hence, its application is limited. Therefore, numerous kinds of visible light active photocatalysts have been developed.

Bismuth molybdate compounds are catalysis materials, and among the various bismuth-based materials, recent research studies have shown that Bi_2MoO_6 possess excellent visible light photocatalytic properties because of its small band gap (Eg = 2.5–2.8 eV) [9,10]. Ma et al. reported that the Bi_2MoO_6 photocatalysts were synthesized by a facile impregnation method for the highly improved photoelectrochemical (PEC) property related to water oxidation [11]. Li et al. found that Bi_2MoO_6 could be used to kill bacteria under visible light [12]. However, compared with other semiconductor materials, the photocatalytic performance of Bi_2MoO_6 is limited by the high recombination rate of photoinduced electrons and holes and by the relatively poor

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quantum yield [11]. Among the numerous methods of improving the photocatalytic performance of Bi_2MoO_6, the use of π structural material to modify Bi_2MoO_6 is efficient [11,12]. The g-C_3N_4 has a narrow band gap (Eg = 2.7 eV), thus, it can absorb visible light, thereby increasing the separation efficiency of electron-hole pairs by forming electronic interactions with photocatalysts during the catalytic reaction [13–15]. Liang et al. reported that the Bi_2MoO_6-g-C_3N_4 composite photocatalysts were synthesized by a facile impregnation method [16]. Lv et al. reported that g-C_3N_4/Bi_2MoO_6 composite photocatalysts have the significant photocatalytic performance than that of g-C_3N_4 and Bi_2MoO_6 photocatalyst, respectively [17]. Ma et al. synthesized g-C_3N_4/Bi_2MoO_6 composite photocatalysts by a hydrothermal deposition method and the composite photocatalysts photocatalytic activity was improved [18]. Yan et al. Used the template-free solvothermal method to synthesize the g-C_3N_4/Bi_2MoO_6 photocatalysts, and they got the results that the as-prepared samples exhibited superior photocatalytic activity towards the degradation of dyes (Rhodamine B and Methyl blue) under visible light irradiation [19]. But, in addition, almost no studies on g-C_3N_4/Bi_2MoO_6 composites for photocatalytic disinfection of bacteria have been reported so far.

Hence, we proceeded a successful attempt to synthesize the hybrid g-C_3N_4/Bi_2MoO_6 photocatalysts via a sonochemical method [20], to enhance the sterilization performance of fluorocarbon resin (PEVE) coatings. The photocatalytic sterilization test was performed to evaluate the antibacterial activity of g-C_3N_4/Bi_2MoO_6/PEVE coatings under visible light (λ > 420 nm) irradiation. As the results showed, the sterilization performance of PEVE coatings was enhanced after adding g-C_3N_4/Bi_2MoO_6 under visible-light irradiation. Meanwhile, we also tested the stability and sterilization performance of g-C_3N_4/Bi_2MoO_6/PEVE coatings, the results demonstrated that the g-C_3N_4/Bi_2MoO_6/PEVE coatings have good stability and cycle performance. Moreover, possible mechanisms for the enhanced sterilization performance of fluorocarbon resin (PEVE) coatings was discussed. This work has great significance in the photocatalysis technology as a coating for killing marine bacteria to address marine biofouling problems.

2. Experiments

2.1. Synthesis of Bi_2MoO_6 and g-C_3N_4

All chemicals used were of analytical grade and were not purified further. Pure Bi_2MoO_6 was synthesized through hydrothermal method [21,22]. First, 0.004 mol of $Bi(NO_3)_3{\cdot}5H_2O$ and 0.002 mol of $Na_2MoO_4{\cdot}2H_2O$ were dissolved in 50 ml of deionized water and stirred at room temperature for 1 h with a speed of 500 rpm. Then, the resultant mixture was processed hydrothermal at 180 °C for 24 h. After funnel separation, the Bi_2MoO_6 powder (noted as BMO) was rinsed with distilled water and ethanol, and then dried at 80 °C in a vacuum oven.

The g-C_3N_4 was synthesized through melamine thermolysis [23]. A certain amount of melamine was added in a crucible and then heated to 550 °C at a rate of 3 °C/min for 4 h in air [24]. Then the obtained solid was ground into powder, to produce g-C_3N_4.

2.2. Preparation of g-C_3N_4/Bi_2MoO_6 composites

The g-C_3N_4/Bi_2MoO_6 composites were prepared as follows: 0.046 g g-C_3N_4 was dissolved into 30 ml of methanol solution and was subjected to ultrasound for 30 min (40 kHz, 150 W). Then 0.915 g Bi_2MoO_6 was added into the g-C_3N_4 solution, and the suspension was stirred for 6 h to ensure better performance after ultrasonication for 30 min (40 kHz, 150 W). Finally, the composites were centrifuged, washed with water and ethanol, and dried at 80 °C for 6 h to obtain the 5% g-C_3N_4/Bi_2MoO_6 photocatalyst (noted as 5% CN/BMO). Following the above method, other g-C_3N_4/Bi_2MoO_6 composite photocatalytic samples with different weight content of g-C_3N_4 in composite of 3%, 7% and 15% were prepared (noted as 5% CN/BMO, 7% CN/BMO, and 15% CN/BMO).

2.3. Preparation of g-C_3N_4/Bi_2MoO_6/PEVE coatings

Initially, the g-C_3N_4/Bi_2MoO_6 sample prepared by the above-mentioned method was mixed with fluorocarbon resin (PEVE) paint at a ratio of 3:100 (mass fraction) [23]. In addition, the polyvinylpyrrolidone (PVP) was blended with the g-C_3N_4/Bi_2MoO_6 at a ratio of 3:10 [25]. Then, the mixed solution was subjected to ultrasound for 1 h (40 kHz, 150 W), and the composite paints were uniformly coated on previously prepared sheet of glass (25 mm × 76 mm × 1 mm) and dried in air. Following the above methods, different g-C_3N_4/Bi_2MoO_6/PEVE coatings were prepared (noted as BMO/PEVE, 3% CNBP, 5% CNBP, 7% CNBP, and 15% CNBP).

2.4. Photocatalytic antifouling experiments

The photocatalytic antifouling experiments were performed using a 500 W Xe lamp (λ > 420 nm) as the light source, and the antibacterial activities of the coatings were tested by counting colony-forming units (CFUs) on the culture dishes [26]. 2216E Solid medium (peptone, 5 g; yeast extract, 1 g; $FePO_4$, 0.01 g; agar, 18 g; sea water, 700 ml; pH 7.4–7.8) was prepared before the experiment [5]. The process of bacterial cultivation under visible light irradiation is as follows. First, the prepared CNBP coatings were sterilized under UV light. Then, the coatings were immersed in certain amount of seawater and lit for 4 h [26]. The bacterial membrane was scraped from the coating surface using a sterilized cotton sign and diluted the sample in 50 ml sterilized seawater every once in a while. Then, we inoculated 0.1 ml of the resulting suspension to the solid medium by sterile pipettes [27]. The process was accomplished in a biological sterilization box. Finally, we maintained the vaccinal solid medium in the box at constant temperature box (28 °C) for 24 h and observed the colony distribution on the medium.

2.5. Characterizations

The antibacterial activities of the coatings were tested by counting colony-forming units (CFUs) on the culture dishes. Crystallographic properties were characterized by powder X-ray diffraction (XRD, Rigaku DMAX- Ultima+ diffractometer) with Co target in the range of 10°–90°. Fourier transform infrared spectroscopy spectra (FT-IR) was performed on Perkin Elmer Frontier with a range of 4000–400 cm^{-1}, and infrared transmission spectra were recorded for KBr discs containing the powder sample. The microstructures were acquired by scanning electron microscope (SEM) with SUPRA 55 SAPPHHIRE and field emission on high-resolution transmission electron microscopy (HRTEM) with JEOL JEM-2100 instrument, and X-ray spectroscopy (EDX) was also performed. The UV–vis diffuse reflectance spectra (DRS) were measured with TU-1901 UV–vis spectrophotometer.

Moreover, to test the transfer efficiency of the photogenerated electrons of the samples, photoelectrochemical measurements (EIS) were carried out in three electrode quartz cell, the reference and the counter electrodes were calomel electrode (SCE saturated with KCl) and platinum electrodes, respectively. The working electron was selected (Bi_2MoO_6 and g-C_3N_4/Bi_2MoO_6). The electrolyte was 0.1 mol/L $NaSO_4$ solution, and all the photoelectrochemical measurements were carried out under visible light irradiation from a 500 W Xe lamp with 420 nm cutoff filters.