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RESEARCH ARTICLE

RESEARCH PROGRESS OF BISMUTH-BASED PHOTOCATALYTIC ANTIBACTERIAL MATERIALS

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ABSTRACT

Antibiotics are a kind of substances which can inhibit or kill some other pathogenic microorganisms. However, the abuse of traditional antibiotics has made the problem of bacterial drug resistance more and more serious.Recently, bismuth based photocatalysis antibacterial materials have attracted much attentiondue to its high activity, long antibacterial duration, good thermal stability, small side effects and low cost. In this paper, In this paper, we focus on reviewing the research progress of bismuth-based composites in photocatalytic antibacterial.

INTRODUCTION

With the continuous development of society, people's health awareness has been continuously improved, and the requirements for environmental quality and living standards have also increased. Pathogenic bacteria widely exist in the environment. they have a great impact on human health because of their wide variety and rapid spread. Although traditional fungicides have good antibacterial and bactericidal properties, there are still problems which are difficult to solve, such as short sterilization time, large doses and do harm to the surrounding environment. Therefore, the research and development of new antibacterial materials is particularly important. Among many antibacterial materials, inorganic photocatalytic antibacterial materials have received much attention due to their unique advantages. As one of the typical representatives of inorganic photocatalytic antibacterial materials, bismuth composite materials have broad development prospects in the field of photocatalysis and antibacterial.

Antibacterial agents and photocatalytic antibacterial principle: Antibacterial agent" refers to a substance that can effectively inhibit the growth, reproduction or kill bacteria of microorganisms, mainly including bactericides and bacteriostatic agents (Chen, 2016). "Fungicide" is a chemical substance that can kill microorganisms."Bacteriostatic agent" is a substance that has little effect on viruses, but can temporarily inhibit the growth and reproduction of microorganisms. According to their chemical structure, antibacterial agents can be subdivided into three categories, namely natural antibacterial agents, organic antibacterial agents and inorganic antibacterial agents (Lu, 2018). Photocatalytic technology refers to the fact that under the condition of light, the catalyst generates active substances with redox ability, which can degrade pollutants or kill germs. The photocatalytic antibacterial mechanism is mainly caused by ROS (active substances) destroying bacterial cell walls through oxidative stress, resulting in bacterial inactivation and eventual death. Oxidative stress is caused by an imbalance between the generated reactive oxygen species and the degradation of ROS by the intracellular antioxidant defense system (Huang, 2015). As shown in Fig. 1, the catalyst is excited when the photocatalyst is irradiated by visible light, and electrons (e-) are excited from the valence band (VB) to the conduction band (CB), leaving the same number of hole (h+) in VB. The redox potential of $O_2/\cdot O^{2-}$ is negative, but the potential of the CB edge of BiOI is more negative than that, so O_2 is reduced to O by electrons located on the CB, which can oxidize organic dye molecules to CO_2 and H_2O , while also decomposing bacterial cells [4]. At the same time, active substances such as H_2O_2 and $\cdot OH$ produced by oxidation can also effectively inactivate bacteria or degrade pollutants.

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Modification of bismuth oxyiodide: Bismuth oxyhalide BiOX (X=Cl, Br, I) is an important ternary structure (V-VI-VII) semiconductor material with unique layered structure, suitable band gap, high stability and strong response to visible light (Di, 2014). The photocatalytic activity of BiOX is generally better than that of commercial TiO_2 (P25), and the

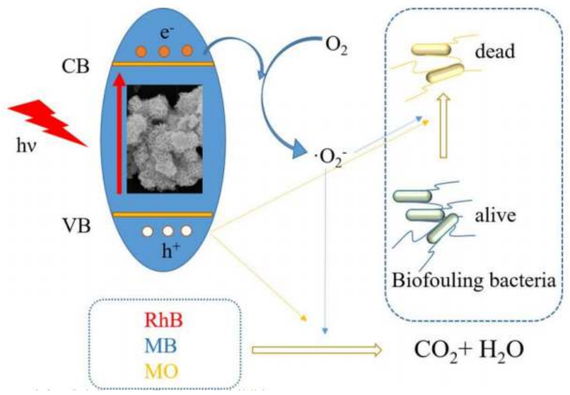

Fig.1. Schematic diagram of photocatalytic process [Montoya, 2011]

Table 1. Propertiesof inorganic and organic antibacterial agents

Properties	Organic antibacterial agents	Inorganic antibacterial agents
Timeliness	Short time and instant effect	Relatively poor
Antibacterial persistence	Poor	Good
Antibacterial range	Narrow	Relatively Wide
Safety	security risk	No security risk
Heat resistance	Above 200°C	Above 500°C

photocatalytic activity gradually increases with the increase of the halogen atomic number. Among of many bismuth oxyhalide materials, bismuth oxyiodide (BiOI) is a widely used visible light responsive photocatalyst with the narrowest forbidden band width of 1.8 eV (Xie, 2016). Besides, BiOI has layered structure and strong built-in electric field, which exhibites promising prospect in photocatalysis and antibacterial. At present, the modification methods of BiOI mainly include semiconductor compounding, metal ion doping, morphology control and carbon material compounding. The absorption of visible light and the photocatalytic activity are enhanced by changing the band gap structure, morphology and surface properties of BiOI (Hou, 2015). Huang *et al*. prepared $BiOI/BiVO_4$ photocatalyst with a core-shell structure by a simple in-situ deposition method, and evaluated its photocatalytic activity by degrading rhodamine B and phenol under visible light. The heterojunction structure realized the migration of photogenerated charges between semiconductors, resulting in the separation efficiency of electrons and holes, thereby the photocatalytic activity of BiOI was greatly improved (Huang, 2017). Liang *et al*. synthesized Ti-doped BiOI microspheres by solvothermal method. The doped BiOI has a larger band gap than pristine BiOI, thus the photocatalytic sterilization activity was also enhanced. Ye and his team used the methods of molecular precursor hydrolysis and calcination to prepare BiOI nanosheets with {100} and {001} exposed faces, respectively. The results showed that exposed side of BiOI has higher catalytic activity (Ye, 2013). In addition, it has also been reported that BiOI combined with graphene can significantly improve the photocatalytic performance (Li, 2015).

Application of bismuth-based composites in photocatalytic antibacterial: Bismuth-based composites are considered to be one of the promising antibacterial materials because of their narrow energy band and strong photocatalytic activity, and have incomparable advantages over other materials. They are widely used in the degradation of water pollutants, sterilization and disinfection. Currently, the most widely studied bismuth-based materials mainly include BiOX (X=Cl, Br, I), Bi_2MoO_6, $g\text{-}C_3N_4/BiOI$, Bi_2WO_6, etc. (Andrieux, 2012). It has been reported that the $Bi_2MoO_6/AgBr$ composites inactivated bacteria with a concentration of 3×10^6 CFU mL^{-1}, and could completely inactivate Escherichia coli (E.coli) within 90 min [(40)]. The polymer semiconductor $g\text{-}C_3N_4/BiOI$ has attracted attention due to its metal-free, low cost, and unique electronic band structure (Wang, 2012; Thomas, 2008). Monomer $g\text{-}C_3N_4$, its photogenerated e^- and h^+ are easy to recombine, while h^+ has a weak oxidative ability on the $g\text{-}C_3N_4$ valence band (VB), which makes it difficult to effectively degrade organic pollutants, and microorganisms cannot be efficiently inactivated. In order to effectively improve the photocatalytic performance of $g\text{-}C_3N_4$, a $g\text{-}C_3N_4/BiOI$ composite material was constructed. 20% $g\text{-}C_3N_4/BiOI$ composite can completely kill E. coli and Staphylococcus aureus (S. aureus) within 30 min, while the monomer $g\text{-}C_3N_4$ and monomer BiOI kill only 84.90% and 77.22% of Staphylococcus aureus (S. aureus), respectively, within 30 min. The bactericidal effect of monomer $g\text{-}C_3N_4$ and BiOI was significantly lower than that of $g\text{-}C_3N_4/BiOI$ composites.

Conclusion

Bismuth-based photocatalytic materials are considered to be a promising nanomaterial. The development of bismuth-based materials with high antibacterial properties is the development direction of photocatalytic antibacterial. This will further promote the practical application of bismuth-based materials in the field of antibacterial.

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