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Photochemical oxidation mechanism of microcystin-RR by p-n heterojunction Ag/Ag₂O-BiVO₄

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ABSTRACT

Microcystin-RR (MC-RR), a form of microcystin with two arginine moieties, is a cyanobacterial toxin that has been detected across a wide geographic range. It is a great concern globally because of its potential liver toxicity. Herein, the abilities of BiVO₄, Ag-BiVO₄, Ag₂O-BiVO₄ and Ag/Ag₂O-BiVO₄ to photocatalytically degrade MC-RR under visible-light irradiation ($\lambda \geq 420$ nm) were investigated and compared. The possible degradation pathways were explored through analysis of the reaction intermediates by high-performance liquid chromatography-mass spectrometry. The results showed that the presence of Ag⁰ enhanced the photocatalytic efficiency of Ag/Ag₂O-BiVO₄ via a synergetic effect between Ag₂O and Ag⁰ at the p-n heterojunction. Moreover, the presence of Ag⁰ also greatly promoted the adsorption of MC-RR on the photocatalyst surface. Toxicological experiments on mice showed that the toxicity of MC-RR was significantly reduced after photocatalytic degradation.

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1. Introduction

The growth of blue-green algae as a result of eutrophication promotes the formation of microcystins, a class of toxins, which has become an issue of global concern[1]. In addition to poisoning wild animals, livestock and poultry, microcystins can also contaminate drinking water, leading to liver damage in humans and an increased incidence of liver cancer [2–5]. Toxicological research has found that microcystins inhibit mammalian liver function by binding to 1A (PP1) and 2A (PP2), thus

causing liver-tissue necrosis and resulting in primary tumors [6–9].

A variety of conventional water-treatment methods, including flocculation, activated-carbon adsorption and membrane separation, have been employed to purify water contaminated by microcystins. However, because of the low concentrations and stable structures of the microcystins, the purification efficiencies were far from satisfactory [10–12]. In recent years, the uses of advanced oxidation technologies for the removal of microcystins has received wide attention. Of the various mi-

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microcystins identified to date, MC-LR, MC-RR and MC-YR are the most toxic and abundant [13–15]. Microcystin-RR (MC-RR) has been found to be widespread in water bodies polluted by blue-green algae in China [16]. In addition, further studies have revealed that MC-RR is the most resistant to photocatalytic degradation by TiO_2 under Ultraviolet irradiation [17].

Photocatalysis has been established as an effective technique for the removal of microcystins. For MC-RR, the study of photocatalytic degradation has particularly focused on photocatalysts such as Bi_2WO_6 [18] and TiO_2 [19,20] under UV irradiation. Because only a very small portion of sunlight (about 4%) is ultraviolet, it is important to extend the response of these photocatalysts to the more abundant visible region. However, little work has been done on the visible-light-induced photocatalytic degradation of MC-RR. In our previous study, we reported an Ag-BiVO₄ composite photocatalyst prepared by a one-step hydrothermal method [21]. In this catalyst, both Ag and Ag₂O coexisted on the surface of BiVO₄, forming a p-n heterojunction and thus greatly improving the photocatalytic efficiency [22–31]. As a result, the composite photocatalyst exhibited excellent photocatalytic activity for the degradation of the dye rhodamine B and colorless salicylic acid under visible-light irradiation ($\lambda \geq 420 \text{ nm}$) [21]. In the present study, we extended the application of this composite photocatalyst to the degradation of the geographically widespread toxin MC-RR to realize its visible-light degradation. In addition, to fabricate more efficient heterojunction structures between the Ag species and the BiVO₄, a two-step hydrothermal method was employed. It was found that the Ag/Ag₂O-BiVO₄ could be used as an efficient photocatalyst for the photodegradation of MC-RR under visible-light irradiation. The degradation pathway was investigated in some detail, and the mechanism of the photocatalytic degradation on the surface of the heterojunction catalyst was proposed.

2. Experimental

2.1. Materials

MC-RR was purchased from Express Technology Co. Chromatographically pure trifluoroacetic acid (TFA), methanol and acetonitrile were obtained from Merck Co. Other chemicals were of reagent grade and used without further purification. Deionized and doubly distilled water was used throughout the study.

2.2. Preparation of the catalyst

A hydrothermally synthesized sample of monoclinic BiVO₄ was immersed in an aqueous solution of AgNO₃ and the mixture was stirred for 30 min and subsequently filtered. Then, the solid was calcined at 300 °C to obtain the Ag₂O-BiVO₄ composite. Ag⁰-BiVO₄ was prepared by adding BiVO₄ into a methanol solution of AgNO₃ and removing the dissolved oxygen by bubbling nitrogen gas into the solution. The solution was then irradiated with visible light and filtered to obtain the Ag⁰-BiVO₄. Ag⁰/Ag₂O-BiVO₄ was prepared in a similar way to Ag⁰-BiVO₄,

except that the BiVO₄ was displaced by the above-obtained Ag₂O-BiVO₄.

2.3. Characterization of the catalyst

The crystallinity of the samples was characterized by X-ray diffractometry (XRD; Ultima IV, Rigaku, Japan) with Cu K α radiation. The surface morphologies of the composite photocatalysts were observed by field-emission scanning electron microscopy (FE-SEM; JSM-7500F, JEOL, Japan) and transmission electron microscopy (TEM; JEM-1011 microscope, JEOL, Japan, operating at 100 kV). The Brunauer-Emmett-Teller (BET) specific surface areas were determined using an ASAP 2020 surface area and pore size analyzer (Micromeritics, USA).

2.4. Photocatalytic degradation of MC-RR

The reaction solutions were prepared by mixing 5 mL of MC-RR (3 mg/L) and 2 mg of the catalyst in a Pyrex vessel without adjusting the pH. The initial pH was 6.8. A 100 W Hg lamp (75 mW/m²) with a 400 nm cut-off filter was used to ensure the admittance of only visible light. The suspensions were magnetically stirred in the dark for 2 h to ensure that the adsorption/desorption equilibrium was established. At defined time intervals, 0.3 mL of the reaction mixture was collected, centrifuged and filtered through a Millipore filter (0.22 μm) to remove photocatalyst particles.

2.5. MC-RR toxicological tests

A group of male and female mice weighing between 20 and 25 g were kept at room temperature, under natural light conditions, with feeding, for several days to adapt to their environment. One week after the start of the experiment, the mice were randomly divided into two groups, A and B. The mice in group A were injected with 3 mL of the 10 mg/L stock solution of MC-RR, and those in group B were injected with the photodegraded MC-RR solution (10 mg/L, 3 mL). Both groups were given the same amount of food and water. Mice were sacrificed after 3 h injection and anatomical photographs of their livers were taken.

2.6. Analysis of intermediates

High-performance liquid chromatography (HPLC) analysis was performed using a Waters 600 HPLC (Waters, USA) equipped with a Waters 2998 photodiode array (PDA) detector and C₁₈ reverse-phase column (5 μm , 4.6-mm i.d. $\times$ 250 mm, Kromasil). The mobile phase consisted of (1) water containing 0.05% TFA (v/v) and (2) methanol, at a ratio of 35:65 (v/v). The injection volume of the samples was 20 μL and the flow rate was 0.6 mL/min. The detection wavelength was 238 nm. The detection limit for MC-RR was 0.13 $\mu\text{g/L}$.

Liquid chromatography-mass spectrometry (LC/MS; Agilent, USA) was used to monitor the reaction intermediates with full scanning from $m/z = 300$ –1200 in positive-ion mode. A workstation equipped with the LC/MSD Trap software was

used to control the instrument, analyze the data and quantitate the results. The mobile phase was varied by gradient elution with formic acid (pH = 2.6) and acetonitrile. Gradient elution was programmed as follows: 0–10 min, 0–20% acetonitrile; 10–20 min, 35% acetonitrile; 20–35 min, 60% acetonitrile; 35–45 min, 80% acetonitrile.

A dissolved-oxygen analyzer (Thermo Orion, USA) was used to measure oxygen consumption during the photodegradation of MC-RR. The reaction vessel was completely filled with the reaction solution, fully aerated, and the initial dissolved oxygen (DO) was recorded. Then, the bottle was sealed during photocatalysis and the final DO was recorded.

3. Results and discussion

3.1. XRD analysis of the samples

The XRD patterns of BiVO_4 , Ag-BiVO_4 , $\text{Ag}_2\text{O-BiVO}_4$ and $\text{Ag/Ag}_2\text{O-BiVO}_4$ are shown in Fig. 1. Sharp diffraction peaks were observed for all the samples, indicative of the good degree of crystallinity. Comparison with the standard cards of the XRD software jade5.0 revealed that the prepared BiVO_4 samples were monoclinic scheelite (JCPDS 14-0688, $a = 5.195$, $b = 11.701$, $c = 5.092$, $Z = 4$). For $\text{Ag}_2\text{O-BiVO}_4$, in addition to the peaks from BiVO_4 , a characteristic diffraction peak at $2\theta = 15.85^\circ$ appeared, implying the presence of Ag_2O . By comparison with the standard data, the diffraction peaks at $2\theta = 34.5^\circ$ and 35.2° in $\text{Ag/Ag}_2\text{O-BiVO}_4$ and Ag-BiVO_4 were attributed to the presence of metallic Ag.

3.2. SEM, TEM and BET analysis of samples

SEM images in Fig. 2 shows that all the prepared photocatalysts consisted of particles with sizes of several hundred nanometers. In the BiVO_4 , the particles exhibited polyhedral geometry with non-uniform size. Following the generation of metallic Ag by photoreduction, fine Ag particles were observable on the surface of BiVO_4 , indicative of the successful loading of Ag. However, in $\text{Ag}_2\text{O-BiVO}_4$, some small, seemingly amorphous particles appeared on the surface of the BiVO_4 , and many

Fig. 1. XRD patterns of the catalysts.

Fig. 2. SEM images of BiVO_4 (a), Ag-BiVO_4 (b), $\text{Ag}_2\text{O-BiVO}_4$ (c) and $\text{Ag/Ag}_2\text{O-BiVO}_4$ (d).

of the surface sites became uneven. These observations indicated that the Ag_2O was successfully loaded onto the surface of BiVO_4 , with an intimate contact between the two species. In the sample of $\text{Ag/Ag}_2\text{O-BiVO}_4$, small particles, evidently formed of $\text{Ag/Ag}_2\text{O}$, also appeared on the surface of the truncated octahedral bipyramids of BiVO_4 . In addition, porous microspheres with diameters of around 500 nm were observed, probably formed by the $\text{Ag/Ag}_2\text{O}$ during the loading of that species. However, these microspheres presumably played only a minor role in the enhanced photocatalytic activity because of their small quantity. Consistent with the TEM results, it showed that $\text{Ag/Ag}_2\text{O-BiVO}_4$ (Fig. 3(a)) consisted of particles with a size of about 100 nm. However, the sample proved heavily unstable under the TEM process, probably because of the reduction of Ag_2O and BiVO_4 by the probe electron beam. Therefore, no diffraction pattern was observed in the SAED images (Fig. 3(b)).

The specific surface area of a photocatalyst is an important factor influencing its adsorption capacity and photocatalytic activity. Analysis of the BET specific surface areas of BiVO_4 , Ag-BiVO_4 , $\text{Ag}_2\text{O-BiVO}_4$ and $\text{Ag/Ag}_2\text{O-BiVO}_4$ yielded values of 4.0, 8.39, 5.27 and 6.02 m^2/g , respectively. These results suggested that the presence of Ag or Ag_2O did not strongly influence the specific surface areas of the composites.

3.3. Photocatalytic degradation of MC-RR under visible-light irradiation

The adsorption experiments (Fig. 4) showed that the presence of metallic Ag^0 or Ag_2O on the surface of BiVO_4 significantly enhanced the adsorption of MC-RR onto the photocata-

Fig. 3. TEM (a) and SAED (b) images of the $\text{Ag/Ag}_2\text{O-BiVO}_4$ sample.

Fig. 4. Kinetic curves for degradation of MC-RR under visible-light irradiation. $C_{\text{cata}} = 1.0 \text{ g/L}$, $C_{\text{MC-RR}} = 3 \text{ mg/L}$.

lysts, implying strong interactions between the Ag^0 or Ag_2O and the MC-RR molecules. Moreover, the ability of $\text{Ag/Ag}_2\text{O-BiVO}_4$ to adsorb MC-RR was greater than that of the photocatalysts modified by either Ag^0 or Ag_2O separately. Under visible-light irradiation, all the photocatalysts exhibited some capacity for the photodegradation of MC-RR. The degradation reactions proceeded much more rapidly on both the Ag-BiVO_4 and $\text{Ag}_2\text{O-BiVO}_4$ photocatalysts than on the pure BiVO_4 . For example, after 30 min of irradiation, 17%, 63% and 77% removal of the original MC-RR was achieved by the BiVO_4 , Ag-BiVO_4 and $\text{Ag}_2\text{O-BiVO}_4$ systems, respectively. For the binary modified photocatalyst, $\text{Ag/Ag}_2\text{O-BiVO}_4$, the photocatalytic degradation efficiency was further enhanced relative to the singly modified systems. After 80 min of visible-light irradiation, complete degradation of the MC-RR was achieved by the $\text{Ag/Ag}_2\text{O-BiVO}_4$ photocatalyst.

3.4. Mechanism for the enhanced photocatalytic activity of $\text{Ag}^0/\text{Ag}_2\text{O-BiVO}_4$

Ag_2O is a narrow-band-gap semiconductor, with conduction band and valence band potentials of -0.12 eV and 1.23 eV (vs. NHE), respectively [32]. On the other hand, BiVO_4 is a typical n-type semiconductor (n-SC), with valence band and conduction band potentials of 0.32 and 2.78 eV (vs. NHE), respectively [33]. When the two semiconductors come into physical contact, a heterojunction interface is formed between them [34]. The relative potentials noted above give rise to an internal electric field at the heterojunction. Under visible-light irradiation, photo-generated electron-hole pairs are produced in the system comprising Ag_2O and BiVO_4 . Because of the presence of the heterojunction, the electrons are trapped in the BiVO_4 , while the holes are captured by the Ag_2O . Thus, charge separation is greatly enhanced. Subsequently, the photogenerated electrons are captured by surface-adsorbed O_2 , while the photogenerated holes are transferred directly to the adsorbed MC-RR species, whereupon they oxidize water to form hydroxyl radicals. Moreover, the metallic Ag^0 species act as a electron receptors, capturing electrons from the surface both BiVO_4 and Ag_2O , and

thereby further extending the lifetime of the photogenerated holes[35–40]. Therefore, the heterojunction composed of $\text{Ag/Ag}_2\text{O}$ and BiVO_4 facilitates the separation of photo-generated electrons and holes. This in turn greatly enhances the photocatalytic activity for the oxidative degradation of MC-RR. Moreover, the presence of metallic Ag also alters the surface composition of BiVO_4 and enhances the adsorption between the MC-RR and the catalyst surface, which improves the photocatalytic degradation of MC-RR. In addition to capturing electrons and changing the catalyst surface properties, metallic Ag has also been reported to promote the charge separation of semiconductors by inducing local electromagnetic fields under irradiation [41]. Above the three effects improve the activity of the photocatalyst. Therefore, both the presence of metallic Ag and the formation of heterojunction in the $\text{Ag/Ag}_2\text{O-BiVO}_4$ catalyst gives rise to enhance photocatalytic degradation of MC-RR under visible-light irradiation (Fig. 5).

3.5. Degradation pathway of MC-RR over $\text{Ag/Ag}_2\text{O-BiVO}_4$ under visible-light irradiation

The intermediates that formed during the photodegradation of MC-RR over $\text{Ag/Ag}_2\text{O-BiVO}_4$ were detected by LC/MS. Based on the results, two possible degradation pathways for the photocatalytic degradation of MC-RR over $\text{Ag/Ag}_2\text{O-BiVO}_4$ were proposed, i.e., peroxidation and hydroxylation, as depicted in Fig. 6. The evidence suggested that the initial photodegradation occurred via both pathways. In the peroxidation pathway, the formation of a peroxidation intermediate with $m/z = 1025.57$ is the first step, presumably resulting from decarboxylation by photogenerated holes. Subsequently, the peroxides are transformed into ketones or hydroxylated intermediates with m/z values of 1009.57 , 995.56 and 1007.56 . The second oxidation pathway involves reactions at the Adda residue, which contains unsaturated double bonds that are attacked by $\bullet\text{OH}$, as indicated by the formation of hydroxylated intermediates ($m/z = 1071.57$). After hydroxylation, the unsaturated double bonds are evidently cleaved to generate an intermediate with $m/z = 911.45$. This intermediate can undergo hydrolysis to other products.

3.6. Toxicological effect of MC-RR in mice

Fig. 7(a) and (b) displayed the extent of liver damage in

Fig. 5. Mechanism for the enhanced photocatalytic activity of $\text{Ag}^0/\text{Ag}_2\text{O-BiVO}_4$.

Fig. 6. Possible photocatalytic degradation pathways of MC-RR over Ag/Ag₂O-BiVO₄ under visible-light irradiation.

mice treated with MC-RR and MC-RR after photodegraded, respectively. The livers of the mice injected with MC-RR showed significant congestion and swelling, discoloration (purple, brown and even black), blunted edges and lobes adhering together. The deep black color of the intestines was an obvious symptom of poisoning. By contrast, the mice injected with the photodegraded MC-RR solution showed no significant swelling or color change of the liver, and no obvious symptoms of poisoning. From these results it was evident that MC-RR was toxic, and affected the synthesis and detoxification function of the liver, while MC-RR after photodegraded over Ag/Ag₂O-BiVO₄ under visible-light irradiation significantly reduced its toxicity.

4. Conclusions

Ag/Ag₂O-BiVO₄ was used as a visible-light photocatalyst for the degradation of MC-RR. Structural characterization of the catalyst showed that Ag₂O and BiVO₄ formed an effective heterojunction interface, which played an important role in the degradation process. In this heterojunction structure, Ag and

Ag₂O acted as electron acceptors that extending the charge-carrier lifetime and thus enhanced the photocatalytic activity. Based on the structure of the reaction intermediates of MC-RR degradation, two possible degradation pathways, i.e. peroxidation and hydroxylation, were suggested, in which the visible-light-induced photocatalytic degradation of MC-RR over Ag/Ag₂O-BiVO₄ involved oxidation either by hydroxyl radicals, photogenerated holes or superoxide radicals. The degradation

Fig. 7. Toxicological effects of MC-RR on mouse livers.

Graphical Abstract

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Photochemical oxidation mechanism of microcystin-RR by p-n heterojunction Ag/Ag₂O-BiVO₄

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The Ag/Ag₂O-BiVO₄ composite photocatalyst with heterojunction structure exhibit perfect photoactivity for the degradation of microcystin MC-RR under visible light irradiation, relative to those of BiVO₄, Ag-BiVO₄ and Ag₂O-BiVO₄. The high activity steps from the charge separation due to the presence of heterojunction.

of MC-RR thus predominantly involved the cleavage of unsaturated C=C bonds in the Adda residue and a decarboxylation reaction. Acute-toxicity tests in mice showed that after the photocatalytic treatment, the toxicity of MC-RR was significantly reduced.

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p-n型异质结催化剂Ag₂O-BiVO₄对微囊藻毒素(MC-RR)的光化学氧化机理研究

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摘要: 微囊藻毒素(MC-RR)是一种具有两个精氨酸结构的微囊藻毒素, 它是由蓝藻细菌产生的一种能普遍被检测到的细胞毒素, 近由于其潜在的肝毒性受关注. 在可见光($\lambda \geq 420$ nm)照射条件下, 以MC-RR为光催化降解污染物, 对BiVO₄, Ag-BiVO₄, Ag₂O-BiVO₄和Ag/Ag₂O-BiVO₄光催化降解性能进行了比较研究. 通过HPLC-MS测定了其降解中间产物, 并分析了其可能的降解途径. 结果表明, Ag的存在通过构筑p-n异质结光催化剂而提高了Ag/Ag₂O-BiVO₄的光催化效率. 此外, Ag⁰的存在极大地促进了MC-RR在光催化剂表面上的吸附作用. 小鼠的毒理学实验表明, MC-RR经过光催化降解后毒性显著降低.

由于水体富营养化形成的蓝绿藻促进微囊藻毒素的形成, 这已成为全球关注的问题. 被微囊藻毒素污染的饮用水除了会毒害野生动物, 家畜和家禽外, 还会损害人类肝脏, 这也是肝癌的发病率高的原因. 毒理学研究发现, 微囊藻毒素通过结合到1A(PP1)和2A(PP2)上强烈地抑制蛋白磷酸酶的活性, 从而导致肝细胞的损伤, 引发原发性肿瘤.

目前对光催化降解MC-RR的研究主要集中在紫外光催化氧化领域. 采用太阳光中的紫外区或者近紫外区, 利用传统的TiO₂光催化剂对MC-RR的光催化氧化研究; 太阳光中只有极少部分(约4%)的紫外光, 大部分(约43%)是可见光, 因此, 如何将光催化剂的吸收光谱拓宽至可见光区域, 提高催化剂对可见光的利用率, 进一步提高光催化降解MC-RR的能力, 具有一定的理论和实际意义.

钎酸铋是一类新型的p型可见光光催化剂, 将其与n型半导体Ag₂O材料选择性的复合制备出p-n型异质结复合光催化剂能够显著提高其光催化性能. 本文将这种复合光催化剂的应用扩展到广泛检测到的毒素MC-RR的降解中, 以实现可见光降解. 发现Ag/Ag₂O-BiVO₄可以在可见光照射下有效光催化降解MC-RR. 跟踪其降解中间产物, 研究了其可能降解途径, 并提出了在异质结催化剂表面上的光催化降解机理.

催化剂表征结果表明, Ag₂O和BiVO₄形成有效的异质结界面, 在降解中发挥重要作用. 在该异质结结构中, Ag和Ag₂O作为电子受体以增强电荷载流子寿命并提高光催化活性. 依据MC-RR氧化产物的结构、化学性质和降解体系中所检测到的产物, 推测其可能的机理: Ag-Ag₂O-BiVO₄可见光光催化降解MC-RR是一个涉及到羟基自由基和超氧自由基的共同氧化作用, 同时根据液相质谱对中间产物的鉴定, 得到MC-RR两条主要的可能降解途径, 其中主要涉及到Adda中不饱和碳碳双键和Mdha中烯键的氧化, 以及各氨基酸之间肽键的水解. 小鼠急性毒理实验表明, 经光催化反应后MC-RR的毒性明显减小.

关键词: 光催化; p-n异质结; 银; 氧化银; 钎酸铋; 微囊藻毒素(MC-RR); 机理

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