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Degradation of microcystin-LR by highly efficient $AgBr/Ag_3PO_4/TiO_2$ heterojunction photocatalyst under simulated solar light irradiation

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ABSTRACT

A novel photocatalyst $AgBr/Ag_3PO_4/TiO_2$ was developed by a simple facile *in situ* deposition method and used for degradation of mirocystin-LR. TiO_2 (P25) as a cost effective chemical was used to improve the stability of $AgBr/Ag_3PO_4$ under simulated solar light irradiation. The photocatalytic activity tests for this heterojunction were conducted under simulated solar light irradiation using methyl orange as targeted pollutant. The results indicated that the optimal Ag to Ti molar ratio for the photocatalytic activity of the resulting heterojunction $AgBr/Ag_3PO_4/TiO_2$ was 1.5 (named as 1.5 BrPTi), which possessed higher photocatalytic capacity than $AgBr/Ag_3PO_4$. The 1.5 BrPTi heterojunction was also more stable than $AgBr/Ag_3PO_4$ in photocatalysis. This highly efficient and relatively stable photocatalyst was further tested for degradation of the hepatotoxin microcystin-LR (MC-LR). The results suggested that MC-LR was much more easily degraded by 1.5 BrPTi than by $AgBr/Ag_3PO_4$. The quenching effects of different scavengers proved that reactive h^+ and •OH played important roles for MC-LR degradation.

1. Introduction

Worldwide blue–green algal bloom results in microcystins (MCs) pollution that needs urgent remediation solution. There are more than 90 microcystin variants, among which, microcystin-LR (MC-LR) possesses the most toxic effect [1,2]. As a result, a guideline value of 1 $\mu g\,L^{-1}$ for MC-LR in drinking water has been issued by the World Health Organization [3]. In general, MC-LR exhibits a stable property against physicochemical and biological factors such as temperature, sunlight and enzymes [4–6]. Advanced oxidation processes (AOPs) including chlorination, ozonation, hydrogen peroxide disinfection and photocatalysis have been proved efficient to remove MC-LR [6–9], but the cost of continuous input of expensive chemical reagents is prohibitive. Therefore, photocatalysis which only uses solar light has attracted a great attention as a MC-LR remediation approach as solar light is a cost-free, durable and pollution-free resource.

As an essential element in photocatalysis, developing photocatalyst materials, UV and UV-Vis absorbing materials, has drawn great attention in recent years. This is particular true for UV-Vis absorbing materials because visible light account for around 45% of solar light energy [10–12]. For example, Ag_3PO_4, which can absorb the light shorter than 530 nm, was more active for water oxidation than traditional catalyst such as TiO_2, WO_3 and TiO_2-N [13]. However, this material is self-photocorrosive due to excessive electrons accumulation on the conductive band resulting from incapable of converting hydrogen ion to hydrogen on the surface of the catalyst. This incapability is caused by the lower electrode potential of Ag/Ag_3PO_4 than the reduction potential of H^+ (Ag/Ag_3PO_4 = +0.42 V) [13]. Eventually, this leads to reduced photocatalytic oxidation capacity of especially when $AgNO_3$ is not used as electron trapper. The photocatalytic activity and stability of other silver salts such as AgCl or AgBr can be greatly enhanced by doping an appropriate amount of Ag nanoparticles (Ag NPs) [14,15]. Our previous studies revealed the role of Ag NPs on the photocatalytic activity and stability of Ag_3PO_4 under simulated solar light condition. The results indicated that doping a small amount of Ag on the surface of Ag_3PO_4 greatly accelerated the oxide activity of Ag_3PO_4. However, the photo-corrosivity of Ag_3PO_4 cannot be prevented unless a significant amount of Ag is doped on the surface of the catalyst, which would enviably decrease the photocatalytic activity of Ag/Ag_3PO_4 [16]. On the other hand, Ag_3PO_4 is

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slightly soluble in aqueous solution, which is inferred as a main reason for the unstable state of Ag_3PO_4 during photocatalysis process ($K_{sp} = 1.4 \times 10^{-16}$, 0.02 g L^{-1} 25 °C). Researchers have successfully prevented Ag_3PO_4 from dissolving and achieved a much more photocatalytically efficient catalyst, $AgBr/Ag_3PO_4$, through doping an insoluble AgBr nanoshell around Ag_3PO_4 particle [17,18]. However, the photo-corrosion still cannot be avoided after several cycles of photocatalysis as AgBr itself is also a type of photo-corrosive silver salt [18]. Therefore, developing a stable catalyst as a dopant for $AgBr/Ag_3PO_4$ is highly desired in order to accelerate photocatalysis by Ag^0 and to counteract the decrease of photocatalytic capacity due to the loss of AgBr. In addition, reducing the cost of silver materials serving as dopant is another challenge as to reduce the overall cost of the photocatalyst.

Recent studies have shown TiO_2 as the most stable photocatalyst capable of reacting with Ag^0 to achieve a more efficient photocatalytic activity under UV–Vis light [19–21]. The aim of this study is to develop a new catalyst $AgBr/Ag_3PO_4/TiO_2$ (BrPTi) by combining TiO_2 with $AgBr/Ag_3PO_4$ and to investigate the photocatalytic activity of BrPTi.

2. Materials and methods

2.1. Preparation of catalyst

The BrPTi heterojunction catalysts were synthesized by *in situ* deposition of $AgBr/Ag_3PO_4$ onto TiO_2 (P25) surface. TiO_2 (P25) powder was sonicated in distilled water for 10 min to form homogenous TiO_2 suspension. An appropriate dosage of $AgNO_3$ was then added into the TiO_2 dispersed water (pH = 7). After magnetic stirring for 20 min, appropriate dosage of $Na_3PO_4{\cdot}12H_2O$, dissolved in 25 mL distilled water, was dropwise added into the solution. The theoretical molar rate of added Ag/original Ti was controlled to be 0.3, 0.9, 1.5 and 2.4, respectively. After the Ag_3PO_4/TiO_2 reaction mixture was magnetically stirred for 3 hours, NaBr solution was slowly added into the above suspension with the theoretical molar percentages of added Br/P being controlled to be 60%. The mixture was vigorously stirred for 3 h. The precipitates were collected, washed with distilled water for 4 times, and dried at 60 °C for 24 h. The $AgBr/Ag_3PO_4$ (molar percentage (Br/P) = 60%) was prepared following the procedure reported by Cao et al. [18].

2.2. Characterization of the catalyst

The crystalline phases of the samples were determined by powder X-ray diffraction (XRD) (Rigaku RINT2200, Japan). The morphology of the samples was obtained by scanning electron microscopy (SEM) (JEOL, JSM-5600, Japan). UV–vis diffuse reflectance spectra (DRS) of different samples were recorded on a Shimadzu UV-3100PC Scan UV–vis-NIR spectrometer with $BaSO_4$ as the background and at 200–800 nm. The specific surface area of the samples were determined using Brunauer–Emmett–Teller (BET) specific surface analysis device (Coulter SA3100, US). The XPS measurements were conducted using PHI1800 (PH1800, Japan).

2.3. Experimental design

2.3.1. Optimization of the photocatalytic activity of $AgBr/Ag_3PO_4/TiO_2$

The photocatalytic activities of these heterojunctions were measured using methyl orange (MO) as targeted pollutant. The measurement was carried out by adding the MO stock solution and the catalyst in distilled water to achieve MO concentration of 8.2 mg L^{-1}. The total volume of the solution for the reaction was adjusted to 60 mL. A simulated solar lamp (XC-100B, SERIC Ltd., Japan) positioned axially at the centre was used to simulate solar light. The light intensity was measured with a photometer (LI-250A, LI-COR Inc., USA) and set as 6 W m^{-2}. The photometer consists of two modules, display module and light sensor module. The light sensor was positioned horizontally in the middle of magnetic stirrer. The light intensity can be read on the display module till the number on it kept stable. The light intensity was adjusted by changing the relative position between stirrer and light source. Before irradiation, the suspension (60 mL) was magnetically stirred for 30 min in the dark to achieve equilibration. The irradiation was then start to maintain the photocatalytic reaction for 50 min. During irradiation, samples were taken at an interval of 10 min. A 2 mL suspension was collected and centrifuged to remove the photocatalyst particles. The catalyst-free MO solution was analyzed using a UV–VIS spectrophotometer (Shimadzu, UV-MINI-1240-100V, Japan). The concentration of MO was determined from its maximum absorption at a wavelength of 464 nm with deionized water as a reference sample.

2.3.2. Evaluation of the stability of $AgBr/Ag_3PO_4/TiO_2$

The stability of BrPTi was evaluated under the best photocatalytic activity with MO being used as target pollutant. Three reaction dishes were prepared for once, two and three times photocatalysis runs, respectively. For each run, the total volume of the solution for the reaction was adjusted to 6 mL in the glass dish of 5 cm diameter with an initial MO concentration of 8.2 mg L^{-1}. For each dish, the catalyst dosage was initially set to be 0.001 g. The resulting suspensions from the last run were washed with distilled water and centrifuged to remove the remaining organics from the previous run as well as to retrieve the catalyst for the following run. During the photocatalysis period, samples were taken at appropriate time intervals, and measured by a spectrophotometer at 464 nm.

2.3.3. Evaluation of MC-LR degradation by the $AgBr/Ag_3PO_4/TiO_2$ heterojunction

The BrPTi with the best photocatalytic activity was tested for its ability to degrade the MC-LR. MC-LR standard (90% purity, Wako Pure Chemical Industries, Ltd., Japan) stored at −20 °C, was used to prepare a stock solution with a concentration of 50 mg L^{-1}. The degradation experiment was performed in a 100 mL beaker placed on a magnetic stirrer. A simulated solar lamp (XC-100B, SERIC Ltd., Japan) positioned axially at the centre was used as a simulated solar light source. The MC-LR stock solution and catalyst (0.01 g) dissolved in distilled water was mixed to produce MC-LR concentration a desirable level. The total volume of the solution for reaction was adjusted to 30 mL and the light intensity was set at 4 W m^{-2}. Before irradiation, the suspension was magnetically stirred for 60 min in the dark to achieve adsorption equilibration. The lamp was then switched on to initiate the photocatalytic reaction for a period of 25 min. During irradiation, sampling was performed periodically and centrifuged.

2.3.4. Investigation of the roles of the reactive oxygen species in MC-LR degradation

A series of tests were conducted to study the mechanism responsible for the solar light-induced photocatalysis. Sacrificial agents including ammonium oxalate (AO), *tert*butanol (TBA), benzoquinone (BQ) and catalase (CAT), were added to the degradation system to ascertain the active species, h^+, •OH and $\bullet O_2^-$ and H_2O_2, respectively for the degradation process. The dosages of these scavengers were based on the levels reported previously [22–25].

Hydroxyl radicals (•OH) formed were detected by photoluminescence (PL) technique [26]. Terephthalic acid, which reacts readily with •OH to produce a highly fluorescent product, 2-hydroxyterephthalic acid, was used as a probe molecule to detect •OH. The fluorescence intensity at 425 nm, which can be ascribed