Evaluation and suppression of Microcystis aeruginosa by photocatalyst coatings with visible light photocatalytic activity

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Abstract. Photocatalyst coatings had been successfully fabricated by molten salt treatment at 673 K for 3 h for titanium (Ti) coatings, which coated on alumina (Al2O3) balls by mechanical coating technique with Ti powder. The influence of molten salt treatment on the formed compounds, surface morphology and photocatalytic activity under visible light irradiation on degradation of MB solution and suppression of Microcystis aeruginosa of photocatalyst coatings was investigated. XRD results show that potassium titanate (K2Ti4O9) forms on the surface of Ti coatings during molten salt treatment. The visible light photocatalytic activity of photocatalyst coatings has been effectively enhanced by molten salt treatment.

Introduction

Nowadays, cyanobacterial blooms have increasingly occurred on a global level as a result of eutrophication. Such blooms are of particular concern due to their impacts on water quality, since several genera can produce toxins, called cyanotoxins that are harmful to human health. Consequently, research on new methods for water purification develops in different ways, including chemical, electrochemical and photochemical processes. Among all kinds of water purification techniques, oxidative degradation methods, using electromagnetic radiation have been receiving increased attention for the detoxification of the aquatic environment. They are generally referred to as advanced oxidation processes and mainly involve ultraviolet (UV) irradiation in the presence of hydrogen peroxide or ozone, and UV or near visible light in the presence of titanium dioxide (TiO2) [1-3]. Previous studies have demonstrated that TiO2 is a potential photocatalyst for many years, because of its excellent chemical stability, low-cost and high photocatalytic activity [4-6]. TiO2 photocatalyst can be applied to the degradation of organic/inorganic pollutants, purification of air and water, and so on. Due to its wide band gap (>3 eV) and fast electron-hole recombination, the photoreaction efficiency of TiO2 is severely limited [7-9]. Therefore, an enormous amount of research has been devoted to enhancing the visible light photocatalytic activity of TiO2, mainly by narrowing the band gap via elemental doping and sensitization with semiconductor possess narrowed band gap [10-13].

Recently, these materials of crystalline layered titanate compounds, including K2Ti6O13 and K2Ti4O9, are characterized by high adsorptivity relative to the parent TiO2 powder. However, the main disadvantage of layered titanate as a photocatalyst is that its activity in the visible light range is lower than that of TiO2 [14,15]. Tretyachenko et al. studied the synthesis, adsorption,
photocatalytic activity of semiconductor materials based on amorphous potassium titanate powder modified with transition metal oxides/hydroxides. The powder was found to exhibit high photocatalytic activity under simulated solar radiation [15]. Titanates, particularly potassium titanate, exhibit attractive physical-chemical properties owing to their distinct crystal structures, which show great potential for photocatalysis. Numerous potassium titanates with unique crystal structures (i.e., layered and tunnel structures) have been synthesized. Potassium titanates can be fabricated in the form of whiskers or fibers, and have been used as photocatalysts for water cleavage [16-18].

In this work, photocatalyst coatings were fabricated by molten salt treatment for Ti coatings, formed on Al$_2$O$_3$ balls by mechanical coating operation. The influence of molten salt treatment on phase structure, surface morphology and photocatalytic activity under visible light irradiation on degradation of methylene blue (MB) solution and suppression of Microcystis aeruginosa of photocatalyst coatings was investigated and characterized. The relationship between the photocatalytic activity under visible light irradiation on suppression of *Microcystis aeruginosa* and the formed compounds as well as the surface morphology is discussed.

**Experimental**

**Fabrication of photocatalyst coatings.** Ti coatings were coated on Al$_2$O$_3$ balls (average diameter of 1 mm) by mechanical coating technique [19], with Ti powder (average diameter of 30 μm) and named as "M10-Ti". Then Ti coatings were subjected to molten salt treatment with KNO$_3$ at 673 K holding for 3 h [20], and named as "K-673".

**Characterization and photocatalytic activity.** The crystal phases of the formed compounds were analyzed by X-ray diffraction (XRD, JDX-3530, JEOL) with Cu-Kα radiation. The surface morphology was examined by scanning electron microscopy (SEM, JSM-5300, JEOL). The photocatalytic activity of the samples was evaluated for decomposition of MB solution under visible light irradiation (wavelength > 420 nm) with an intensity of 5000 lx for 24 h [19]. While before the evaluation and suppression of *Microcystis aeruginosa*, the samples were also dried under UV irradiation for 24 h. The relationship between absorption and cell density of *Microcystis aeruginosa* (UTEX LB 2061) had been investigated and proposed to the following equation:

$$y = 9.0 \times 10^7 \times x$$

where $y$ is the cell density (cells/mL) and $x$ is the absorption. The suppression of *Microcystis aeruginosa* (12 mL) was carried out under visible light irradiation for 7 days.

**Results and discussion**

**Phase structure and surface morphology.** Fig. 1 shows XRD patterns of the M10-Ti and K-673 samples by molten salt treatment. From the M10-Ti sample, it can be found that Ti coatings
formed on the surface of Al₂O₃ balls, and the color shows metallic. While the K-673 sample shows the potassium titanate of K₂Ti₆O₁₃ forms on the surface of Ti coatings and the color is light-gold, under molten salt treatment at 673 K for 3 h. This indicates that the amorphous potassium titanate crystallizes and forms 6-potassium titanate [21]. The surface morphology of the M10-Ti and K-673 samples is shown in Fig. 2. In general, the K-673 sample is not as smooth as that of the M10-Ti sample. Moreover, with increasing the temperature to 773 K, the XRD results are almost same as that of K-673, but the nano structure obviously forms on the surface of Ti coatings [22]. Therefore, it hints that the nano structure formed on the surface of Ti coatings is too small to be detected.

![Image](a) ![Image](b)

Fig. 2. Comparison of surface morphology of the M10-Ti (a) and K-673 (b) samples.

**Photocatalytic activity.** The photocatalytic activity of the K-673 sample is evaluated by degradation of MB solution under visible light irradiation at room temperature, as shown in Fig. 3. In general, the M10-Ti sample could not show any photocatalytic activity, even under UV irradiation [22]. The K-673 sample shows the visible light photocatalytic activity, according to the concentration change of MB solution. It hints that photocatalytic activity is related with the formed compounds of potassium titanate (Fig. 1) and the suitable accessible surface (Fig. 2).

![Graph](MB solution concentration, c/μmol L⁻¹ vs. Visible irradiation time, t/h)

Fig. 3. Comparative photocatalytic degradation of MB solution of the M10-Ti and K-673 samples under visible light irradiation.

The photocatalytic activity on suppression of Microcystis aeruginosa of the M10-Ti and K-673 samples is evaluated under visible light irradiation at room temperature, as shown in Fig. 4. Fig. 4a shows the cell density of Microcystis aeruginosa exposed to the M10-Ti and K-673 samples. For the M10-Ti sample, it does not show any suppression of Microcystis aeruginosa. While the K-673 sample shows effective suppression of Microcystis aeruginosa under visible light irradiation. The suppression of Microcystis aeruginosa of the K-673 sample could be owing to the generated hydroxyl radicals by the photocatalyst coatings [24]. At the same time, Fig. 4b and 4c show the change with presence of the M10-Ti and K-673 samples.

**Summary**

The photocatalyst coatings were successfully fabricated by molten salt treatment for Ti coatings, which coated on Al₂O₃ balls by mechanical coating technique with Ti powder. The potassium titanate
of K₂Ti₆O₁₃ forms on the surface of Ti coatings and the color shows light-gold, during molten salt treatment at 673 K holding for 3 h. The photocatalytic activity on degradation of MB solution and its suppression of Microcystis aeruginosa of photocatalyst coatings has been effectively enhanced by molten salt treatment.

Fig. 4. Relationship between the cell density and incubation time of the M10-Ti and K-673 samples under visible light irradiation (a). Photographs of evaluation test before the test (b) and after the test for 7 days (c).

References