



# Photocatalytic reduction of Cr(VI) with TiO<sub>2</sub> film under visible light<sup>☆</sup>



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## ABSTRACT

The performance of photocatalytic reduction of chromium (VI) via a new TiO<sub>2</sub> film and a platinum anode was systematically evaluated. The as-prepared TiO<sub>2</sub> film is composed of a dye-sensitized zone and a catalysis zone. Charge separation was accomplished with electron transferring to the catalysis zone and positive charge transforming to an anode. A powerful reduction ability of the reaction system was achieved in the absence of any organics under visible light irradiation. Several parameters including pH, dissolved O<sub>2</sub>, the primary active species, the durability of the as-synthesized film and so on were investigated.

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## 1. Introduction

Chromium is a toxic and mobile pollutant mainly originating from industrial processes like electroplating, leather tanning, and metallurgy [1,2]. It mainly occurs in two common oxidation states in aquatic environment, Cr(III) and Cr(VI). Cr(VI) species are known acutely toxic and carcinogenic, and one hundred times higher toxic than Cr(III) [3,4]. In addition, Cr(VI) is mobile in nature because of its weak absorption to inorganic surfaces [5]. In contrast, Cr(III) is readily precipitated at near-neutral pH, and it is much less mobile in the environment due to its highly “particle reactive” [6]. Removal of chromium from the environment has been actively investigated through many techniques such as cross flow microfiltration [7], reverse osmosis [8], ion exchange [9,10]. These methods were sometime expensive and often inefficient at low concentrations. Therefore, the preferred treatment of chromium pollutant in water is reduction of Cr(VI) to less harmful Cr(III), then readily occurs precipitation as Cr(OH)<sub>3</sub> in neutral or alkaline solutions [11].

Recently, photocatalytic reduction of Cr(VI) to Cr(III) using the semiconductor photocatalysis technology has received considerable attention [12–18]. Of all semiconductors, TiO<sub>2</sub> is the most frequently used photocatalyst due to its favorable chemical

property, high stability, and relatively low cost [19]. Electron (e<sup>-</sup>) and hole (h<sup>+</sup>) are generated during the photolysis proceed of TiO<sub>2</sub>. These photoelectrons and photoholes either recombine or become involved in redox reactions. The photo-excited electrons in DSC zone under light irradiation can arrive at catalysis zone rapidly [20], promoting the reduction of Cr(VI). During degradation of organics, the photoelectrons can attack O<sub>2</sub> to produce active species O<sub>2</sub><sup>•-</sup>, H<sub>2</sub>O<sub>2</sub> and •OH [21]. The photoholes with highly oxidizing ability can directly participate in oxidative degradation of organics or oxidizing water to produce •OH. These generated active species O<sub>2</sub><sup>•-</sup>, H<sub>2</sub>O<sub>2</sub> and •OH can degrade organics fully to CO<sub>2</sub> and water. Therefore, both photoelectrons and holes can play a role in the degradation of organic pollutants. For photocatalytic reduction of Cr(VI), electrons at the conduction band (CB) of TiO<sub>2</sub> reduce Cr(VI) to Cr(III). But the photoholes can not be used to reduce Cr(VI), and even produce •OH from oxidation of water, which will oxidize Cr(III) to Cr(VI). In addition, the photoholes can not be used to reduce Cr(VI) similarly, and produce •OH from oxidation of water, which will oxidize Cr(III) to Cr(VI). Meanwhile the serious electron-hole recombination causes its very slow reduction. Thus, organic compounds [22–26], such as methanol, ethanol, and acid, are often added as scavenger to suppress charge recombination and avoid the formation of •OH, thus leading to enhancement of the photoreduction. Alternatively, the photocatalytic reduction of Cr(VI) can be conducted in couple with the oxidation of organics by adding some organic pollutants in solution. Inorganic heavy metal ions and organic pollutants generally exist concurrently in actual pollution systems. Recently, the suspended TiO<sub>2</sub> powder has been proved to be an efficient photocatalyst for treatment of Cr(VI) waste

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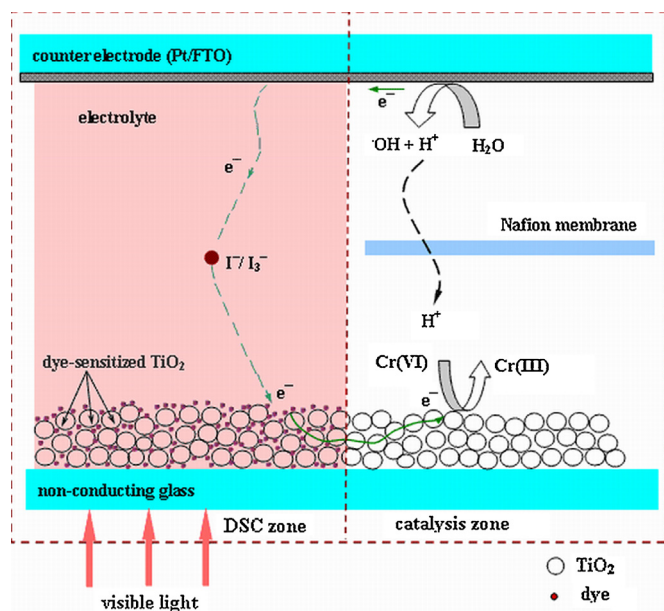


Fig. 1. Working mechanism for the photocatalytic reduction of Cr(VI).

water with organics. However, its UV light response of band gap 3.2 eV, penetration depth of UV light, filtration and re-suspension of these powders limit its practical application [27]. Moreover, it is evident that TiO<sub>2</sub> is not suitable for the treatment of single Cr(VI) waste water, which contains no or trace amount of organics at all. Hence, developing efficient and durable systems under visible light response for reduction of Cr(VI) becomes necessary.

Herein, we used a new TiO<sub>2</sub> film for photocatalytic reduction of Cr(VI) in aqueous solution under visible light irradiation. The as-prepared TiO<sub>2</sub> film was a composite of two zones, dye-sensitized (DS) zone and catalysis zone. In DS zone, a similar structure of dye-sensitized solar cells (DSCs) was fabricated, which was composed of a dye-sensitized TiO<sub>2</sub> film, electrolyte, and a counter electrode [28]. Light absorption and charge separation are finished in the DS zone. Electrons injected from dyes into CB of TiO<sub>2</sub> can diffuse from the DS zone to the catalysis zone along the network of TiO<sub>2</sub> nanoparticles. Any species with a reduction potential more positive than the CB of TiO<sub>2</sub> can consume these electrons in catalysis zone, among which the reduction of Cr(VI) to Cr(III) is inclined to be realized (Fig. 1). Besides, the high work efficiency through the TiO<sub>2</sub> film inspired us to verify the possibility of photocatalytic reduction of Cr(VI) in the absence of any organics [29–31].

## 2. Experimental

### 2.1. Apparatus

The new TiO<sub>2</sub> film was prepared according to the previous work [29]. The photocatalytic reduction of Cr(VI) experiment was implemented in a H-type reactor (Fig. 2). The catalysis zone with an activated area of 1.96 cm<sup>2</sup> was inserted into solution A containing K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> aqueous solution (20 mg L<sup>-1</sup>, 50 mL, pH 2). An electrode (Pt/FTO) with the same area acted as anode was inserted into solution B with 50 mL of distilled water. The two solutions were separated by Nafion membrane. The counter electrode of the TiO<sub>2</sub> was connected with the anode through a copper wire. A 300 W Xe lamp ( $\lambda_{\max}$  = 500 nm) was used as the visible light source, which irradiated at a distance of 20 cm to the TiO<sub>2</sub> film surface through 420 nm cutoff filters. Light intensity, as measured by a visible-irradiance meter, was about 40 mW cm<sup>-2</sup> at the position of the dye-sensitized region located. Air was bubbled through the pipe

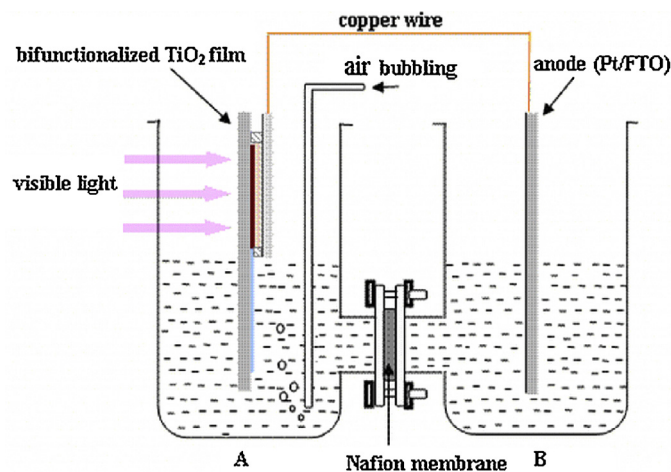


Fig. 2. Photocatalytic reduction of Cr(VI) in H-type reactor.

at a rate of 25 L h<sup>-1</sup>, and gas flow was continued during irradiation. The initial pH in solution was adjusted by 2 M NaOH or 2 M H<sub>2</sub>SO<sub>4</sub>.

### 2.2. Chemical analysis

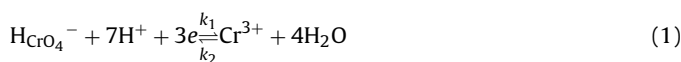
During the given time intervals, 1.0 mL of the sample was taken from the solution, and was analyzed for Cr(VI) using a 1,5-diphenylcarbazide (BDH) colorimetric method [32], determined spectrophotometrically by measuring the absorbance at 540 nm in acid solution with a UV–vis spectrophotometer (Varian). The concentration of phenol was determined by a HPLC using an Agilent 1100 chromatograph equipped with a ZORBAX Eclipse XDB-C18 reversed phase column. HPLC was detected by a UV detector adjusted to 270 nm. The mobile phase was a mixture of water and methanol (20:80 v/v) with a flow rate of 1.0 mL/min. The amounts of H<sub>2</sub> and O<sub>2</sub> was determined by GC/TCD. The concentration of Methyl orange (MO) in aqueous solution was monitored by UV/vis spectrophotometric measurements at given time intervals. Hydrogen peroxide concentration was determined by a spectrophotometric method using the potassium titanium (IV) oxalate method [33], and then the absorbance was measured at 400 nm in a 1 cm quartz cell. The fluorescence emission

Of 7-hydroxycoumarin was measured at 332 nm excitation using a spectro fluorometer.

## 3. Results and discussion

### 3.1. Effect of pH on the photoreduction of Cr(VI)

The pH of the solution is an important parameter in photocatalytic process. The reduction of chromium at different initial pH was shown in Fig. 3. The variation of pH had an obvious influence on the reduction of chromium (VI). Higher degradation efficiency was obtained when experiments were occurred in acidic solutions than that in alkaline solutions. The photoreduction efficiency dropped markedly with the increase of pH. For example, 99.5% of reduction efficiency was achieved at pH 2 after 60 min of visible light illumination, whereas 77% of Cr(VI) was reduced at pH 10 within the same time period. The effect of the acidified pH is in agreement with the reported results [34,35]. The dominant chromium species in the solution of pH 2 is HCrO<sub>4</sub><sup>-</sup>. The overall reduction reaction of HCrO<sub>4</sub><sup>-</sup> can therefore be written as follows:



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