



Photocatalytic reduction behavior of hexavalent chromium on hydroxyl modified titanium dioxide



Yali Li¹, Yingying Bian¹, Hongxia Qin, Yaxi Zhang, Zhenfeng Bian*

The Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, PR China

ARTICLE INFO

Article history:

Received 1 December 2016
Received in revised form 12 January 2017
Accepted 17 January 2017
Available online 18 January 2017

Keywords:

Photocatalysis
Titanium dioxide
Hydroxyl modification
Hexavalent chromium reduction

ABSTRACT

The selective adsorption of hexavalent chromium ($\text{Cr}_2\text{O}_7^{2-}$ (Cr(VI))) and the desorption of trivalent chromium (Cr^{3+} (Cr(III))) at the surface of photocatalysts are very important factors in determining the photocatalytic reduction activity of Cr(VI). Here, a homogeneous anchoring of hydroxyl groups on TiO_2 was achieved via a simple soaking method in alkaline solution. The increase of surface hydroxyl groups was confirmed by X-ray photoelectron spectroscopy (XPS) and Fourier transformed infrared spectra (FTIR). Moreover, the zeta potential analysis revealed the positive charged TiO_2 surface in the acid system shown a significant improvement. The surface positive charges had the selective adsorption for Cr(VI) and desorption for Cr(III). Further experimental results revealed that such selective adsorption process played important roles in the photocatalytic reduction of Cr(VI). Finally, a process of selective adsorption/desorption promoted photocatalytic reduction of Cr(IV) was proposed in detail.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Hexavalent chromium (Cr(VI)) from industrial activities (such as electroplating, metal finishing, leather tanning, steel fabricating, photographic, etc.) discharged into water body and resulted in serious environmental pollution [1,2]. Unfortunately, Cr(VI) is known to be mutagenic, carcinogenic and toxic substance, which is harmful to biological systems and can easily enter the food chains [3,4]. Maximum permissible concentration of Cr(VI) in drinking water is 0.05 mg/L [5]. Therefore, it is crucial importance to remove Cr(VI) from wastewater. Many researchers have been done some efforts. The conventional methodologies of removing Cr(VI) such as ion exchange, bioremediation, membrane separation and adsorption or chemical precipitation suffered from limitations like sludge generation, incomplete precipitation, high operating cost, etc [6–9]. Activated carbon, for example, is widely used for the absorption of Cr(VI) [9]. However, the problem is that it can only be used for adsorption of Cr(VI) and desorption of Cr(VI) still needed other treatment. One of the most preferred methods to treat Cr(VI) in wastewater is the transformation of Cr(VI) to Cr(III) [10]. The Cr(III) is considered to be nontoxic and is an essential trace metal in human nutrition [11]. In addition, it can be precipitated out of solu-

tion in the form of $\text{Cr}(\text{OH})_3$ and removed as a solid waste [12]. Therefore, the reduction of Cr(VI) to Cr(III) is regarded as a key process for the treatment of wastewater containing Cr(VI).

Many alternative processes such as chemical reduction and photo-reduction have been proposed for the reduction of Cr(VI) [13,14]. Among these methods, photocatalysis is a promising technique since it achieves the one-step removal of Cr(VI) by utilizing sunlight. TiO_2 , owing to its stability, low cost, and nontoxicity properties, is one of the most important semiconductors being commonly used in heterogeneous photocatalysis [15–21]. It has been reported that TiO_2 can photocatalytic reduce Cr(VI) to Cr(III) where it serves as an electron donor during the reduction of Cr(VI) to Cr(III) [14,22,23].

The photocatalytic reduction activity of TiO_2 is strongly dependent on the interfacial reaction. When Cr(VI) is photocatalytic reduced, it should first adsorb on the surface of TiO_2 . Photogenerated electrons migrate to TiO_2 surfaces and react with Cr(VI). As the Cr(VI) is reduced to Cr(III), the Cr(III) is quickly removed from the surface. This completes the photocatalytic reduction process. Many efforts have been devoted to improve the adsorption capacity and photocatalytic activity of TiO_2 nanomaterials by various strategies, including designing the porous structure to increase specific surface area, combining with adsorbent to improve the adsorption performance, metal or nonmetal doping or modifying with noble metals to promote charge separation [13–15,22–25]. However, increasing specific surface area or combining with adsorbent

* Corresponding author.

E-mail addresses: bianzhenfeng@163.com, bianzhenfeng@shnu.edu.cn (Z. Bian).

¹ Equal contribution as the first author.

focuses on the adsorption performance. In order to efficiently utilize the photocatalytic performance, it is necessary to develop the surface adsorption of Cr(VI) as well as repulsion of Cr(III). However, to the best of our knowledge, no attention has ever been paid to study it.

Herein we report that the hydroxyl group modified TiO₂ was prepared by a simple soaking method in alkaline solution, which was used for photocatalytic reduction of aqueous Cr(VI). The results showed that it can significantly improve the selective adsorption of Cr(VI) as well as desorption of Cr(III). The selectivity greatly improved the performance of the photocatalytic reduction of Cr(VI). The photocatalytic performance on the photocatalytic reduction of Cr(VI) to Cr(III) was investigated in detail, including the concentration of hydroxyl groups, the stability of the catalyst, and the photocatalytic reduction mechanism was also proposed. It is expected that our current work could provide guided information for design and fabricate efficient photoactive materials for photocatalytic reduction of Cr(VI).

2. Experiment section

2.1. Chemicals and materials

TiOSO₄ (15 wt% solution in dilute sulfuric acid, purchased from Sigma–Aldrich) and tert-butyl alcohol, ethanol, NaOH, K₂Cr₂O₇, Cr(NO₃)₃·9H₂O, HCl, Diphenylcarbazide were purchased from aladdin (AR, Shanghai, China). All the chemicals were used as received. Commercial P25 (TiO₂, Degussa) and ST21 (TiO₂, Ishihara Sangyo) were used as received.

2.2. Preparation of the TiO₂ photocatalysts and surface modification

As-prepared TiO₂ were prepared by an alcoholysis route according to our previous work [26]. In a typical synthesis, 2.0 mL TiOSO₄ was slowly added into 40 mL tert-butyl alcohol. The mixture was transferred into a 50 mL Teflon-lined autoclave (48 h, 110 °C). The product was filtered, washed thoroughly with ethanol. The product was subsequently calcined in air (5 °C min⁻¹) at 350 °C for 120 min. The prepared sample was named MT (Mesocrystals TiO₂). Hydroxyl group modified TiO₂ were synthesized by a soaking method in alkaline solutions. 0.5 g TiO₂ (MT, P25, ST21) was slowly added to 50 mL (0.5, 1.0, 2.0 mol/L) NaOH solution and stirred for 0.5 h. Then, the product was washed thoroughly to neutral by deionized water, and finally vacuum drying for 24 h. The prepared sample was named MT (P25, ST21)-x (x = 0.5, 1.0, 2.0), in which x represented the amounts of NaOH solution.

2.3. Characterization

The TiO₂ morphology was characterized by scanning electron microscopy (SEM, HITACHI S4800). The photocatalyst structure was characterized using X-ray diffraction (XRD, D/MAX-2000 with

Cu Kα radiation), Fourier transformation infrared spectrum (FTIR, NEXUS 370) and nitrogen sorption (Micromeritics Instrument Corporation, Tristar II 3020, at 77 K). The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore volume and pore diameter distribution were derived from the adsorption isotherms by the Barrett–Joyner–Halenda (BJH) model. The pH value was measured with a pH meter (Mettler Toledo Delta 320). Surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C, Al Kα). All the binding energies were calibrated by using the contaminant carbon (C1S = 284.6 eV) as a reference. Zeta potential of the TiO₂ were measured by “Malvern Zetasizer Nano ZS”.

2.4. Activity test

2.4.1. Adsorption experiment

In briefly, 20 mg catalyst was added to 20 mL mixture chromium solution (The initial concentration of Cr₂O₇²⁻ ions and Cr³⁺ ions in the mixture solution was 10 mg L⁻¹). The mixture was stirred for 0.5 h under the dark condition to reach adsorption–desorption equilibrium. The Cr(VI) concentration was determined by colorimetrically at 540 nm using the diphenylcarbazide method using a UV–vis spectrophotometer (UV 7502/PC) [27]. The amounts of total chromium were determined by inductively coupled plasma (ICP) emission spectroscopy (VISTA-MPX). The concentration of Cr(III) is equal to the total chromium subtracting the Cr(VI) concentration (Cr(III) = Cr_{total} - Cr(VI)).

2.4.2. Photocatalytic reduction

For typical photocatalytic runs, 50 mL of TiO₂ dispersion (1.0 g/L) containing aqueous solution (Cr(VI), 10 mg/L, pH is about 3 controlled by HCl) using a home-made reactor was stirred for about 30 min to reach adsorption–desorption equilibrium in the dark [28,29]. The photocatalytic reaction was initiated by a LED light (CEL-LED, 365 nm). After stopping the UV illumination, the concentration of Cr(VI) was analyzed by a UV spectrophotometer (UV 7502/PC) at the characteristic wavelength, from which the degradation yield was calculated.

3. Results and discussions

The photocatalytic activity of TiO₂ is strongly dependent on the interfacial reaction. For example, the reduction of Cr(VI) requires three steps, adsorption on surface active sites, photo-reduction and surface desorption process, respectively (Fig. 1). Based on the features of the opposite charge properties of Cr(VI) and Cr(III), if the TiO₂ surface has more positive charge, the selective adsorption of Cr(VI) and desorption of Cr(III) should improve the photocatalytic performance. The TiO₂ surface positive charge density can be increased by increasing the surface hydroxyl groups under the acid

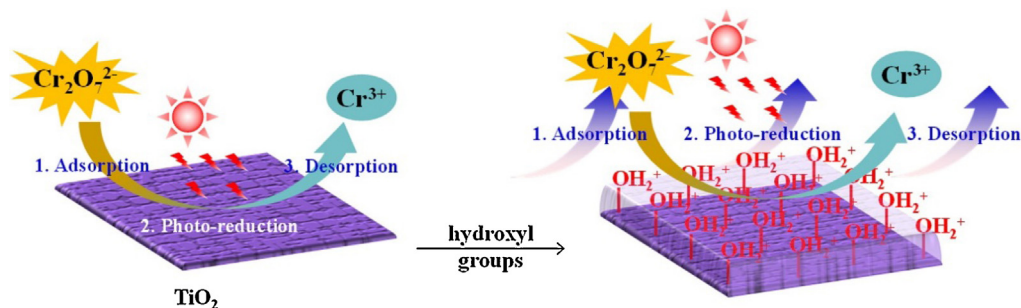


Fig. 1. The process of photocatalytic reduction of Cr(VI) on TiO₂ surface.

Download English Version:

<https://daneshyari.com/en/article/6454686>

Download Persian Version:

<https://daneshyari.com/article/6454686>

[Daneshyari.com](https://daneshyari.com)