



Glucose–TiO₂ charge transfer complex-mediated photocatalysis under visible light



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ARTICLE INFO

Article history:

Received 29 May 2014

Received in revised form 8 July 2014

Accepted 13 July 2014

Available online 19 July 2014

Keywords:

Surface complex

Titanium dioxide

Ligand-to-metal charge transfer (LMCT)

Glucose

Visible light photocatalysis

ABSTRACT

Glucose adsorbed-TiO₂ nanoparticles show photoactivity under visible light ($\lambda > 420$ nm) through the ligand-to-metal charge transfer (LMCT) mechanism. Although glucose has been often utilized as a hole scavenger in TiO₂-based photocatalytic systems, the fact that TiO₂-glucose can form a LMCT complex that absorbs visible light has not been recognized. The TiO₂-glucose LMCT complex induced a marked red-shift in the absorption spectrum which extended to 600 nm, and the visible light absorption gradually decreased with decreasing the concentration of glucose. The TiO₂-glucose complex exhibited remarkable visible light activities for the reduction of Cr(VI) to Cr(III) and the reduction of O₂ to H₂O₂. The observed visible light activities were significantly inhibited when the TiO₂ surface was fluorinated, because the surface fluorides inhibited the formation of LMCT complex of glucose. The electrode coated with TiO₂-glucose complex generated a significant level of photocurrent under visible light. The ATR-FTIR spectra showed that glucose forms a surface complex on TiO₂ through the hydroxyl linkages. The evidences for the formation of the TiO₂-glucose complex and the experimental parameters affecting the visible light-induced activities are discussed in detail.

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1. Introduction

Titania with a wide bandgap (3.0–3.2 eV) has been commonly used as a photocatalyst for environmental remediation and solar energy conversion [1]. Various methods are being investigated intensively to make TiO₂-based photocatalysts work under the visible light. One of the most popular approaches to overcome this problem is the dye sensitization [2]. In the dye sensitization, visible light is absorbed by the dye itself, and the photoexcited electron in the dye is transferred to conduction band (CB) of TiO₂. However, most of successful dye sensitizers are inorganic complexes of expensive/toxic metals such as ruthenium bipyridyl derivatives [3–5].

Another type of sensitization is the surface complexation of ligand-to-metal charge transfer (LMCT). In the LMCT sensitization, electron is photoexcited directly from the highest occupied molecular orbital (HOMO) level of the adsorbate to the TiO₂ CB [6]. Therefore, the light absorption mechanism for the LMCT sensitization is different from that of dye sensitization. LMCT allows

visible light absorption even when the adsorbate itself does not absorb visible light at all. The LMCT complexation is an easy way to extend light response of TiO₂ to the visible region and is versatile because numerous adsorbates are potential candidates for the LMCT sensitization. A variety of organic or inorganic compounds that can form LMCT complexes on TiO₂ has been recently reviewed [6]. The TiO₂-catechol complex, for example, exhibits new absorption band with a tail extending to around 600 nm [7]. A theoretical study revealed that the visible spectral band of TiO₂-catechol complex is resulted from the LMCT and not significantly involved the lowest unoccupied molecular orbital (LUMO) state of catechol [8]. Zhang et al. demonstrated that the use of phenolic resin instead of monomeric phenol for the LMCT complexation on TiO₂ can make a stable LMCT complex that works under visible light [9]. Lao et al. investigated the degradation of persistent organic contaminant, Linuron, in the TiO₂-H₂O₂ system under visible light [10]. Li et al. proved the generation of hydroxyl radical in the visible light-irradiated TiO₂-H₂O₂ system by EPR analysis [11]. Many other compounds that were reported to form the LMCT complexes on TiO₂ include 4-chlorophenol [12], toluene 2,5-diisocyanate (TDI) [13,14], benzylic alcohols [15], fullerol [16], calixarene [17], 8-hydroxyquinoline [18], ascorbic acid [19], dopamine [20], ethylenediaminetetraacetic

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acid (EDTA) [21], aromatic hydrocarbons [22], and gallic acid [23]. All the above examples involve the formation of LMCT complexes on TiO₂ that are responsible for the observed visible light activity.

Glucose is a common bioresource and product of photosynthesis, which is renewable, non-toxic, inexpensive and carbon-neutral in its entire life cycle [24]. Since glucose can be employed as a “green” hole scavenger in photocatalysis, glucose and carbohydrate can be photocatalytically reformed to generate hydrogen over various modified TiO₂ under UV irradiation [25–29]. For instance, Fu et al. investigated the effects of experimental parameters on H₂ evolution in the noble metal-loaded TiO₂ system [26]. Bahruji et al. compared the photocatalytic reactivities of various alcohols on Pd/TiO₂ and showed that glucose has high reactivity in producing H₂ [27]. Xu et al. reported that the photocatalytic activity of H₂ production from biomass (including glucose) reforming can be enhanced by tuning the anatase–rutile phase structure of Pt/TiO₂ [28]. Here we report that the glucose can form a LMCT complex on TiO₂ surface which exhibits the visible light activity. The TiO₂–glucose LMCT complex absorbs visible light significantly and exhibits visible light activity for the photoconversion of Cr(VI) and the production of H₂O₂ via O₂ reduction. In this work, the photocatalytic reactions of TiO₂–glucose complex under visible light were systemically investigated with varying experimental parameters. Evidences for the formation of charge transfer complex are also presented and discussed.

2. Experimental

2.1. Chemicals and catalyst preparation

TiO₂ (P25) with an average surface area of 50 ± m² g⁻¹ and primary particle size of 20–30 nm was used as a base photocatalyst material. Chemical substrates used in this study are as follows: D-(+)-glucose (Sigma-Aldrich), D-(+)-maltose monohydrate (Sigma-Aldrich), cellulose (Sigma-Aldrich), D-(+)-glucosamine hydrochloride (Sigma-Aldrich), 2-deoxy-D-glucose (Sigma-Aldrich), 2-azido-2-deoxy-D-glucose (Sigma-Aldrich), sodium fluoride (NaF, Sigma-Aldrich), chloroplatinic acid (H₂PtCl₆·H₂O, Aldrich), sodium dichromate dihydrate (Aldrich) as Cr(VI) reagent, 1,5-diphenyl carbazide (DPC, Sigma-Aldrich), acetone (Samchun), barium sulfate (Acros), lithium perchlorate (Aldrich), sodium nitrate (Sigma-Aldrich), sodium phosphate monobasic (Sigma-Aldrich), sodium phosphate dibasic (Samchun), *N,N*-diethyl-1,4-phenylene-diamine sulfate (DPD, Aldrich), peroxidase (Aldrich, type VI-A from horseradish). All reagents were used as received. Surface fluorinated TiO₂ (F-TiO₂) was prepared by adding 10 mM NaF to an aqueous suspension of TiO₂. Surface platinumized TiO₂ (Pt/TiO₂) with a typical Pt loading of 1 wt% was prepared by using a photodeposition method as described previously [30]. Ultrapure (18 MΩ cm) deionized water was used and prepared by a Barnstead purification system.

2.2. Characterizations

The UV–visible absorption spectra of bare TiO₂ and glucose-adsorbed TiO₂ powder were obtained by employing a UV–visible spectrophotometer equipped with a diffuse reflectance attachment (Shimadzu UV-2600). The glucose-adsorbed TiO₂ powder was also characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurement. For the ATR-FTIR measurement, the powder samples were simply placed onto the ZnSe crystal and the spectra were collected (referenced against air). The ATR-FTIR spectra were recorded using a Thermo iS50 FT-IR

spectrometer (resolution of 4 cm⁻¹) and 100 interferograms were added for each measurement.

The glucose-adsorbed TiO₂ powder samples for the measurements were obtained as follows. A calculated amount of glucose was added to aqueous TiO₂ suspension and the pH was adjusted at pH 3.5. When F-TiO₂ was used to see the effect of surface fluorination, NaF (10 mM) was added to the TiO₂ suspension. The glucose-adsorbed TiO₂ suspension was filtered, and then the obtained powder was dried in a vacuum oven at room temperature for over 1 day. The prepared samples were used for the diffuse reflectance UV–visible spectra (DR-UVS), ATR-FTIR measurement, and for the analysis of high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2200 FS).

2.3. Photocatalytic activity test and analysis

The TiO₂ powder (1 g L⁻¹) was suspended in a given concentration of glucose solution by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. The pH of the suspension was adjusted with HClO₄ or NaOH standard solution. All photoreactions were done after 30 min of adsorption equilibrium. For the photocatalytic activity tests, a 300-W Xe arc lamp (Oriel) was employed as a light source. Light was filtered through a 10-cm IR water filter and a cutoff filter, and then focused onto a 30-mL Pyrex reactor with a quartz window. During the reaction, the reactor was stirred magnetically. Sample aliquots were withdrawn from the reactor intermittently and filtered through a 0.45-μm PTFE syringe filter (Millipore) for analysis.

Photoconversion of Cr(VI) to Cr(III) was analyzed using a colorimetric method that uses 1,5-diphenylcarbide (DPC) reagent. The color change at 540 nm ($\epsilon = 4 \times 10^4$ L mol⁻¹ cm⁻¹) was monitored using a UV–visible spectrophotometer (Agilent, 8453). Wavelength-dependent photocatalytic activities were investigated with using a set of long-pass cutoff filters ($\lambda > 420, 455, 495, \text{ and } 550$ nm). The photogeneration of H₂O₂ was carried out under the same condition as that for the Cr(VI) reduction experiments except for the absence of Cr(VI) species. The concentration of photogenerated H₂O₂ was determined by a colorimetric DPD method [31]. All experiments were carried out in duplicate or triplicate sets to confirm the reproducibility under the identical experimental condition.

To determine the apparent photonic efficiency (APE) for the glucose-sensitized reduction of Cr(VI) and production of H₂O₂, the photocatalysis experiments were also carried out under the light illumination (from the Xe-arc lamp) filtered through an Oriel monochromator (centered at $\lambda = 430 \pm 10$ nm). The incident photon flux was measured using a Power meter (Newport 1830-C) and then converted into an incident photon flux (I_{in}), which was estimated to be 1.3×10^{-5} Einstein h⁻¹ assuming the monochromatic wavelength of 430 nm. APE was determined as: $APE_{(H_2O_2)}(\%) = (2P_{H_2O_2}/I_{in}) \times 100$ where $P_{H_2O_2}(\text{mol h}^{-1})$ = the rate of H₂O₂ production, $APE_{(Cr(VI))}(\%) = (3P_{Cr(VI)}/I_{in}) \times 100$ where $P_{Cr(VI)}(\text{mol h}^{-1})$ = the rate of Cr(VI) reduction.

Generation of photocurrent was measured with using a TiO₂/FTO electrode immersed in an aqueous solution of glucose. The TiO₂/FTO electrode was fabricated as described elsewhere [32]. The TiO₂/FTO electrode, a Pt wire, and a Ag/AgCl electrode were used as a working, a counter, and a reference electrode, respectively. The electrolyte used was 10 mM LiClO₄, and argon gas was continuously purged through the aqueous solution. The photocurrent was measured with the application of potential bias of 0.5 V (vs. Ag/AgCl) using a potentiostat (Gamry, Reference 600) connected to a computer.

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