Visible light photocatalysis of fullerol-complexed TiO$_2$ enhanced by Nb doping

Jonghun Lim[a], Damián Monllor-Satoca[a], Jum Suk Jang[a], Seockheon Lee[b], Wonyong Choi[a],*

[a] School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea
[b] Center for Water Resources Cycle Research, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

ARTICLE INFO

ABSTRACT

Visible light photocatalysis by TiO$_2$ nanoparticles modified with both fullerol complexation and Nb-doping (fullerol/Nb-TiO$_2$) demonstrated an enhanced performance. Nb-doped TiO$_2$ (Nb-TiO$_2$) was firstly prepared by a conventional sol–gel method, and subsequently fullerol was adsorbed on the surface of Nb–TiO$_2$. The physicochemical and optical properties of as-prepared fullerol/Nb-TiO$_2$ were analyzed by various spectroscopic methods (TEM, EELS, XPS, and DRS). The adsorption of fullerol on Nb–TiO$_2$ surface increased the visible light absorption through a surface-complex charge-transfer (SCCT) mechanism. Nb-doping enhanced the charge transport and induced the Ti cation vacancies that retarded the recombination of photo-generated charge pairs by trapping the electrons injected from the HOMO level of fullerol. Due to the advantage of simultaneous modification of fullerol and Nb-doping, the visible light photoactivity of fullerol/Nb–TiO$_2$ was more enhanced than either Nb–TiO$_2$ or fullerol/TiO$_2$. The photocatalytic activities of fullerol/Nb–TiO$_2$ for the reduction of chromate (Cr^{VI}), the oxidation of iodide, and the degradation of 4-chlorophenol were all higher than bare TiO$_2$ and singly modified TiO$_2$ (i.e., Nb–TiO$_2$ and fullerol/TiO$_2$) under visible light ($\lambda > 420$ nm). A similar result was also confirmed for their photoelectrochemical behavior: the electrode made of fullerol/Nb–TiO$_2$ exhibited an enhanced photocurrent under visible light. On the other hand, the decay of open-circuit potential of the fullerol/Nb–TiO$_2$ electrode after turning off the visible light was markedly slower than either that of Nb–TiO$_2$ or fullerol/TiO$_2$, which implies the retarded recombination of photo-generated charge pairs on fullerol/Nb–TiO$_2$. In addition, the electrochemical impedance spectroscopic (EIS) data supported that the charge transfer resistance is lower with the fullerol/Nb–TiO$_2$ than either Nb–TiO$_2$ or fullerol/TiO$_2$. This specific combination of the bulk (Nb-doping) and surface (fullerol complexation) modifications of titanium dioxide might be extended to other cases of bulk + surface combined modifications.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide (TiO$_2$) is a well-known wide bandgap photocatalyst that has been extensively studied for solar energy conversion (fuels, solar cells) [1,2] and a great variety of photocatalytic processes [3,4]. However, its photoactivity is mostly limited to the UV region because of its wide bandgap (3.0–3.2 eV). For many years, researchers have tried to expand its activity to the visible light region, as visible light accounts for 45% of incident solar energy. Various strategies have been attempted to induce visible light absorption [5–13]. One of the most popular methods is to modify the TiO$_2$ surface by attaching visible light-absorbing adsorbates (e.g., dyes, surface complexes). In the case of dye sensitization, the photo-generated electrons are transferred from the excited dye LUMO (lowest unoccupied molecular orbital) level to the semiconductor (normally, conduction band states). On the other hand, the sensitization by surface complexes proceeds through a charge transfer (CT) mechanism between the surface adsorbate and semiconductor, in which the electron is photoexcited directly from the adsorbate ground-state (HOMO: highest occupied molecular orbital) to the semiconductor conduction band (CB). Such CT-complex formation on TiO$_2$ has been previously reported with catechol [14], fullerol (C$_{60}$(OH)$_x$) [15], 2,4-diisocyanate (TDI) [16], EDTA [17], metal cyanide [18], phenolic resin [19], to name a few examples. The visible light activation of wide bandgap semiconductors by the surface complex CT mechanism has been recently reviewed [20]. Although the mechanism of photoinduced electron transfer is different between the CT-surface complex (HOMO to TiO$_2$ CB) and dye sensitization (LUMO to TiO$_2$ CB), there are some similarities. For example, the CT-complex and dye should have the proper anchoring groups such as hydroxyl or carboxyl groups so that the chemical binding between the adsorbate

---

molecule and the semiconductor surface is strong enough to induce the electronic coupling between the adsorbate orbital and the semiconductor CB states [21]. However, because of this strong electronic coupling, both CT-complexation and dye sensitization on TiO$_2$ suffer from the fast recombination between the injected electron and the oxidized adsorbate, which limits the overall photocatalytic activity [22].

The electrons injected into CB should be rapidly transported to reactive surface sites and the electron transport in metal oxide can be enhanced by doping foreign elements in the lattice of base materials. In this respect, Zn-, Al- and Nb-doped TiO$_2$ have been studied as base electrodes for dye-sensitized solar cells (DSSC) [23–25] and photocatalysts [26]. In particular, Nb doping in TiO$_2$ increases the electron concentration, conductivity and transport efficiency with enhancing the photocurrent because the additional electron is introduced through a charge compensation mechanism upon the ionic substitution of Nb^{5+} in a Ti^{4+} position (with reducing some Ti^{4+} to Ti^{3+}) [27,28]. Alternatively, the charge compensation can be achieved by creating Ti^{4+} vacancies in the lattice, which may serve as electron traps [25,29]. Furthermore, it has been proposed that the driving force for charge injection from the excited dye to Nb-TiO$_2$ in DSSC is enhanced and the recombination between the injected electron and the oxidized dye radical is retarded by a positive shift of flat band potential (V_{fb}), which is induced by Nb doping [25,29,30].

This study aimed to apply the Nb-doping effect to the CT-sensitization of TiO$_2$ under visible light. As a model system of CT-sensitization, fullerol (C$_{60}$(OH)$_x$) complexed on Nb-TiO$_2$ surface was selected. The CT-sensitization mechanism of fullerol/TiO$_2$ and its photocatalytic and photoelectrochemical (PEC) properties were previously investigated [15]. The activity of fullerol/Nb-TiO$_2$ sample was evaluated under ambient condition for the photocatalytic conversion of various substrates as well as its PEC performance under visible light. Significant improvements in the photocatalytic and PEC activities of fullerol/Nb-TiO$_2$ were observed compared with either fullerol/TiO$_2$ or Nb-TiO$_2$. The fullerol sensitization through surface complexation and the Nb doping effect on the interfacial charge transfer and recombination are discussed in detail to understand the advantage of modification of the dual components (fullerol and Nb dopant) in the CT-type visible light photocatalysis.

2. Experimental

2.1. Chemicals and materials

The chemicals used in this study were titanium tetraisopropoxide (TTIP, Ti(OCH(CH$_3$)$_2$)$_4$, Aldrich), Fullerol (polyhydroxyfullerene, C$_{60}$(OH)$_x$, x = 10–15, MER corporation), ethanol (Aldrich), niobium chloride (NbCl$_5$, Aldrich) and nitric acid (HNO$_3$, Shinyo). 4-chlorophenol (4-CP, Sigma), Na$_2$Cr$_2$O$_7$ (Cr^{VI}, Aldrich) and KI (Aldrich) were used as chemical substrates for photocatalytic activity tests. All chemicals were used as received without further purification. Deionized water used for solution preparation was ultrapure (14 MΩ cm) and prepared by a Barnstead purification system.

2.2. Preparation of photocatalysts

Bare TiO$_2$ and Nb-TiO$_2$ were prepared by a sol–gel method. For bare TiO$_2$, 1.25 mL of TTIP was dissolved in 25 mL of ethanol. This aqueous solution was then added dropwise to 250 mL of distilled water and its pH was subsequently adjusted to 1.5 with nitric acid. The resulting sol was stirred for 24 h, evaporated at 50 °C using a rotary evaporator, dried at 70 °C, calcined at 400 °C (heating ramp,

1 °C/min) and kept at this temperature for 3 h. As for the preparation of Nb-TiO$_2$, niobium chloride (NbCl$_5$) at various concentrations was added to the solution of TTIP and ethanol and the same procedure described above was followed.

Fullerol was adsorbed on the surface of bare TiO$_2$ and Nb-TiO$_2$ by following a reported method [15]. In brief, the as-prepared catalyst powder (0.1 g) was dispersed in an aqueous fullerol solution (100 mL, 45 μM) and buffered at pH 3 with HClO$_4$. The solution was stirred for 3 h, and then the catalyst was collected by filtering. After drying in an open-air oven (80 °C), a brownish powder was obtained.

2.3. Characterization of photocatalysts

The crystalline phase identification of as-made bare-TiO$_2$ and Nb-TiO$_2$ was carried out by X-ray diffraction (XRD) using the Cu $K\alpha$ radiation (Mac Science Co. M18XHF). Diffuse reflectance UV/visible absorption spectra (DRS) of powder samples were recorded using a spectrophotometer (Shimadzu UV-2401PC) with an integrating sphere attachment and BaSO$_4$ was used as the reference. The electron energy loss spectroscopy (EELS) analysis was obtained using a JEM-2100F microscope with Cs-corrected line. The surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, XSAM 800 pci) with using Mg $K\alpha$ as an excitation line (1253.6 eV). The binding energy calibration was performed using the impurity C 1s peak present in the prepared sample as the reference energy (284.6 eV).

2.4. Photocatalytic activity tests

The visible light photoactivities of the synthesized samples were tested using the photocatalytic oxidation of 4-chlorophenol (4-CP), and iodide and the photoreduction of hexavalent chromate (Cr^{VI}). The as-prepared samples were dispersed in distilled water (0.5 g/L). An aliquot of substrate stock solution was added to the suspension and then the initial pH of the suspension was adjusted to 3.0 with a standard solution of HClO$_4$. The solutions were equilibrated in the dark for 30 min prior to visible light irradiation. Photo-irradiation was performed using a 300-W Xe arc lamp (Oriel) as a light source. Light passed through a 10-cm IR water filter and a cut-off filter (λ > 420 nm for visible light irradiation), and then the filtered light was focused onto a 30 mL Pyrex reactor with a quartz window. Sample aliquots were intermittently withdrawn from the reactor every 30 min during visible light irradiation and filtered through a 0.45 μM PTFE syringe filter (Millipore) to remove the photocatalyst particles. Multiple photocatalytic activity measurements were carried out under the identical experimental conditions to confirm the reproducibility. When the photocatalytic oxidation of iodide to triiodide (I$_3^-$) was tested, the triiodide production was monitored by measuring the spectrophotometric absorbance at 352 nm (ε = 26,400 M^{-1} cm^{-1}). The degradation of 4-CP and the concurrent production of chloride were monitored using a high performance liquid chromatography (HPLC, Agilent 1100 series) and an ion chromatograph (IC, Dionex DX-120), respectively. The concentration of Cr^{VI} was analyzed using a colorimetric method with 1,5-diphenylcarbazide (DPC) reagent [31]. The color change was monitored at 540 nm (ε = 6,850 M^{-1} cm^{-1}) using a UV/Visible spectrophotometer (Agilent 8453).

2.5. Photoelectrochemical measurements

All PEC measurements were carried out using a standard three-electrode cell connected to a computer-controlled potentiostat (Gamry, Reference 600). The PEC cell consisted of a photoanode of fullerol/Nb-TiO$_2$, a Ag/AgCl (saturated KCl) reference electrode and a platinum wire (for Mott–Schottky plot and electrochemical