Discussion on the reaction mechanism of the photocatalytic degradation of organic contaminants from a viewpoint of semiconductor photo-induced electrocatalysis

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ABSTRACT

Up to now, the well-known mechanism on the photocatalytic degradation of contaminants is mainly based on the reactions derived from the photogenerated electron-hole pairs and their subsequent oxidizing species, and the degradation of organic dyes are especially focused. Whereas, it is rarely concerned the relationship of the oxidation ability of photocatalysts with the oxidative behaviors of contaminants. In this paper, a semiconductor photo-induced electrocatalysis model is proposed to clarify the photocatalytic mechanism by correlating the band structures of BiOI, $Bi_4O_5I_2$, and $Bi_4O_5Br_2$ with their visible-light photocatalytic reactivity to phenol, bisphenol A, methylparaben, and propylparaben. It is revealed that the essential condition for degrading a certain contaminant is the valence band potential of photocatalyst is positive than the oxidation potential of contaminant. The valence band position of a photocatalyst can be determined by its optical absorption and electrochemical flat band potential measurement, and the oxidation potential of a contaminant can be measured by cyclic voltammetry technique. In particular, it is indicated that the oxidation potential of contaminants are generally correlated with their molecular orbital energy, which can be predicted by density functional theory (DFT) calculation. And the band positions of photocatalysts evaluated by an empirical equation based on the element electronegativity is in accordance with the actual band potentials. In addition, the bands composition calculated using DFT not only matches the experimental results but also provides the related information on the band structure with the chemical composition of catalysts. Thus, from the viewpoint of photo-induced electrocatalysis and with the help of experimental and theoretical analysis, the most photocatalytic reactions can be predicted and designed, which is universal for the environmental photocatalysis.

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1. Introduction

In the past few decades, a large number of studies have focused on the semiconductor photocatalysis of environmental remediation [1,2]. Up to now, the mechanism for the photocatalytic degradation of organic contaminants has attracted significant attention and various hypotheses have been suggested [3–5]. It is widely accepted that the mechanism involves semiconductor absorbs photons when the photocatalyst is irradiated by sunlight or illuminated light, and if the energy of incident light is high enough, the electrons in the valence band (VB) of the semiconductor can

be excited to its conduction band (CB) to generate electron (e^-) and hole (h^+) pairs. The photogenerated carriers then react with water or dissolved oxygen to produce reactive oxidizing species (ROS) such as hydroxyl radicals ($^\bullet OH$) and superoxide anions radicals ($^\bullet O_2^-$), and incorporate with the photogenerated holes to decompose pollutants into small molecules. However, although tens of thousands of papers have reported on the successful degradation of various pollutants [6–8], to the best of our knowledge, there is almost no study predicting whether these photocatalysts are able to degrade other kinds of contaminants or not. In other words, no research has answered the basic question of photocatalysis about what is the essential condition for the degradation of a particular contaminant. For instance, a photocatalyst has good catalytic activity for the photodegradation of typical pollutants such as rhodamine B (RhB) and methyl orange (MO) would imply it is

a good catalyst with extensive and practical application to other organic contaminants? Obviously, it is doubtful. This reveals the limited understanding of photocatalysis, which greatly weakens the research significance and environmental applications, and hinders an in-depth understanding of the photocatalytic mechanism as well.

In recent years, our group has worked continuously on bismuth-based photocatalysts for the visible-light photocatalytic degradation of pollutants with specific structures, especially phenolic pollutants [9–14]. And we have found: (1) The band structures of bismuth-based semiconductor, including bismuth oxyhalides and Bi-based double metal oxides, could be easily regulated by tailoring with bismuth, oxygen, type of halogen (or another metal), and their proportion. (2) Majority of narrow-band semiconductor materials, in particular bismuth-based semiconductors, are difficult to generate hydroxyl radicals through the reaction of the photogenerated holes with H_2O or OH^- under visible-light irradiation. Thus, the primarily oxide species are the photogenerated holes and superoxide radicals. Considering to the oxidizing power of $\bullet O_2^-$ is not very strong, the oxidizing activity of these semiconductors will be determined by the oxidation ability of photogenerated holes. These findings inspire us to find out the relationships between the band structure of photocatalysts (especially for the valence band potential) and the molecular structure of pollutants (especially for the oxidation behaviors of organic contaminants), and subsequently to predict the essential conditions for the possibility of a photocatalytic degradation reaction.

To solve the above problems, herein, a series of photocatalytic experiments have been carried out using a variety of photocatalysts with different band structures to degrade varied pollutants. By combining the experimental results, basic theories of photocatalysis, and principles of physical chemistry (particular for the electrochemistry and computational chemistry), we summarize a new model called "semiconductor photo-induced electrocatalysis" (SPEC) to expatiate the reaction mechanism of the photocatalytic degradation and to better interpret what happens during photocatalytic process. More importantly, it is expected to predict the possibility of the reactions before the photodegradation experiments. From the viewpoint of photo-induced electrocatalysis, we can be more intuitive in the realization of different photocatalysis systems and easily predict, design, and develop effective photocatalysts for the degradation of a specific target contaminant.

2. Experimental

2.1. Materials

Bisphenol-A(BPA) and phenol were purchased from Sinopharm Group Chemical Reagent Co. Ltd. Methylparaben (MPB), propylparaben (PPB), and 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) were obtained from J&K Chemical Ltd. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), potassium iodide (KI), potassium bromide (KBr), sodium oxalate, were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Ethylene glycol (EG) was bought from Chinasun Specialty Products Co., Ltd. Rhodamine B (RhB), tetracycline (TC), acetaminophen (APAP), isopropanol (IPA), and propionic acid (PA) were obtained from Aladdin Reagent Co., Ltd. All reagents were of analytical grade and used as-received without further purification.

2.2. Synthesis of the photocatalysts

The $Bi_4O_5I_2$ nanoflakes were synthesized using a solvothermal route according to the process described in our previous report [11]. Briefly, 1.5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 3 mmol KI were dissolved in 35 mL EG, and the solution pH was adjusted to ~9 by a NaOH solution (2 mol L^{-1}). Afterwards, the mixture was transferred into a Teflon-lined stainless-steel autoclave and kept inside an electric oven at 140 °C for 12 h. After completion of the reaction, the precipitate was collected, washed with deionized water and ethanol, and finally dried at 60 °C. The BiOI nano-microspheres were produced using the same process but without adding the NaOH solution. The $Bi_4O_5Br_2$ nanoflakes were also synthesized using the same procedure, but KI was replaced by 1.5 mmol KBr.

2.3. Computational methods

The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of selected contaminants were calculated by density functional theory (DFT) using Gaussian 09. The optimized geometries and vibration frequencies were obtained using the B3LYP function, along with the 6-311++G(d,p) basis set. The band structure calculations of photocatalysts were conducted with the Cambridge Serial Total Energy Package (CASTEP) code within Materials Studio Package based on the density functional theory. The crystal data (ICSD #24610, #412590, and #94498 for BiOI, $Bi_4O_5I_2$, and $Bi_4O_5Br_2$, respectively, as shown in Fig. S1, Supporting information) were utilized as the original crystal models. The generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation functional. Ultrasoft pseudopotentials were used for all chemical elements. The 2s and 2p states were considered for O with six electrons, ns and np (n = 4 and 5 for Br and I, respectively) states were used for Br or I with seven electrons, and 6s and 6p states were taken into account with five electrons of Bi. The kinetic energy cutoffs of 380 eV for the smooth part of the electronic wave functions to achieve a total-energy difference below 5.0×10^{-7} eV atom^{-1}, and 12 empty orbitals were implemented. The Brillouin zone was sampled with a Monkhorst-Pack k-point grid of $6 \times 6 \times 3$ to achieve a k-point separation about 0.04 Å^{-1}. The energies and electronic structures were calculated based on the optimized geometries.

2.4. Characterization

The crystalline structures of the samples were determined using powder X-ray diffraction (XRD) with a Bruker D8 Advance (Bruker AXS, Germany) X-ray diffractometer with Cu Kα radiation. The morphology was observed using a field-emission scanning electron microscope (FE-SEM, Zeiss Ultra 55, Germany). The specific surface areas were measured using nitrogen adsorption-desorption isotherms at 77 K according to the Brunauer-Emmett-Teller analysis (BET, Quadrasorb SI, Quantachrome Instruments, USA). A desorption isotherm was used to determine the pore size distribution using the Barrett-Joyner-Halenda (BJH) method. The UV–vis diffuse reflection spectra (DRS) were recorded on a UV–vis spectrophotometer (UV-3010, Hitachi, Japan) using $BaSO_4$ as a reference and were converted from reflection to absorbance by the Kubelka-Munk method. Electron paramagnetic resonance (EPR, JES FA-200, JEOL, Japan) in combination with spin-trapping techniques was utilized to detect free radicals, and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a spin trap.

Cyclic voltammetry (CV) was carried out on a CHI 910B (Shanghai Chenhua Apparatus Corporation, China) electrochemistry workstation with a scan rate of 50 mV s^{-1} in 0.1 mol L^{-1} HAc–NaAc buffer solution. A glassy carbon electrode (GCE), a platinum plate, and a saturated calomel electrode (SCE) were served as the working, counter, and reference electrodes, respectively. The redox potentials of target pollutants, including BPA and phenol, with different concentrations were evaluated from the results of voltammogram analyses. The CV measurement of