



Design of visible light responsive photocatalysts for selective reduction of chlorinated organic compounds in water



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ABSTRACT

Periodic density functional theory (DFT) calculations were performed for β - Bi_2O_3 photocatalyst that was modified with 32 elements. Our focus was to design visible light responsive photocatalysts for selective reduction of chlorinated organic compounds (COCs) in water. The wanted photocatalysts should have (1) a moderate adsorption potential for COCs; (2) a wide adsorption spectrum for harvesting visible light; and (3) a reduction potential enough to destroy COCs. Based on these assumptions, a combined grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulation study was used to investigate the adsorption and diffusion behaviors of COCs in 32 modified β - Bi_2O_3 ; a Becke-three-parameter-Lee-Yang-Parr (B3LYP) DFT method was used to calculate the energy band structures and redox potentials of different modified β - Bi_2O_3 . Sequentially, these modified β - Bi_2O_3 were synthesized by solvothermal method, and the photo-reactivity of them were quantified in terms of the conduction band (CB) electron reduction using pentachlorophenol (PCP), trichloroethylene (TCE), and γ -hexachlorocyclohexane (HCH) as model COCs. The results demonstrated that the adsorption, photoabsorption, and photo-reactivity of modified β - Bi_2O_3 appear to be a complex function of the periodicity of 32 doped elements, which can be explained by the structural changes on the crystalline form and energy band structure. Based on this principle, a series of competent photocatalysts were believed to be efficient on the reduction of COCs. We designed and synthesized: (1) Ti- β - Bi_2O_3 photocatalyst that performed best on reduction of PCP ($37.2 \mu\text{mol L}^{-1}$) with apparent quantum yield (Φ_{PCP}) of 1.20%; (2) Sr- β - Bi_2O_3 photocatalyst for TCE ($76.2 \mu\text{mol L}^{-1}$) reduction (Φ_{TCE} 1.03%); and, (3) Zr- β - Bi_2O_3 photocatalyst for HCH ($27.5 \mu\text{mol L}^{-1}$) reduction (Φ_{HCH} 0.67%).

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1. Introduction

Photocatalytic degradation of chlorinated organic compounds (COCs) is an important application of photocatalysis in the field of environmental remediation [1,2]. COCs comprise a large group of synthetic organic chemicals. Many of them are known or potential threats to ecosystem and human health [3–5]. Well-known organic pollutants, such as chlorophenols (CPs) [6], chloroethenes (CEs) [7], and organic chlorinated pesticides (OCPs) [8], are among the most prevalent COCs and occurred worldwide in the environment.

Photocatalysis is a promising alternative method for degradation of COCs because this process can use solar light [9,10].

However, the degradation efficiency of COCs by conventional photocatalysis in actual wastewater is relatively low [11]. The main drawbacks include the following aspects: (1) the photocatalytic activity of conventional photocatalysts need further strengthened; (2) the visible light absorption of conventional photocatalysts is insufficient to harness the full advantage of clean sunlight energy [12]; (3) both pollutants and harmless compounds are reduced/oxidized by photocatalysis, thereby wasting photo-generated carriers and decreasing the photocatalytic destruction of the target compounds [13,14].

The photocatalytic degradation of COCs can be improved by reinforcing the photo-reactivity of photocatalyst [15,16]. However, determining the optimum photocatalytic activity, photoabsorbability, and selectivity of a photocatalyst is quite challenging. This is determined by the internal process of photocatalysis. For example, let us consider the impact of the energy band structure of photocatalyst on reducing power of electron (e^-) in conduction band (CB) or

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oxidizing power of the hole (h^+) in valence band (VB), and the wavelength of light that is absorbed that creates an exciton. Higher CB edge potential of a photocatalyst might provide more active reductive electrons and lower potential at VB edge might yield holes with greater oxidizing power. Inevitably, this means extending of the band gap. While narrowing the band gap will enhance its photoabsorptivity in the region of visible light [17]. The “narrowing” (for harvesting more visible light), on one hand, constituted a contradiction with the “extending” (for greater redox power). On the other hand, the narrowed band gap make extra energy of photons (with more energy than the band gap) is lost through collisions in a process known as “relaxation” [18,19]. Therefore, a photocatalyst with suitable energy band structure is desired to be designed precisely. Unfortunately, the photocatalysts and its impact on the band gap, quantum yield, conduction band reduction power and valence band hole oxidizing power are not yet fully understood. The experimental screening of the optimal photocatalyst is expensive and laborious. Therefore, the customized development of photocatalyst for selective removal of specific COCs is still a tough problem.

In the present study, we tried to design one or more visible light responsive photocatalysts, using computational simulation to selectively reduce COCs in water. More importantly, we intended to verify the relationships between the simulations and experimental principles based on the theoretical calculation, characterization and experimental verification. Herein, β - Bi_2O_3 was selected as the template for theoretical analysis because β - Bi_2O_3 , as a semiconductor with photocatalytic activity, which is easy to make and can be easily doped to create a wide variety of photocatalytic properties [20,21]. Computational simulations was employed to design and screen new photocatalysts theoretically. The photocatalytic experiments were then conducted to calibrate the results of the computational prediction using pentachlorophenol (PCP), tetrachloroethylene (TCE), and γ -hexachlorocyclohexane (HCH) as model COCs.

2. Experimental

2.1. Preparation and characterization

Modified β - Bi_2O_3 were prepared by a solvothermal method, as described in our previous work [20]. The present method is different from the reported method that the tetrabutyl titanate was replaced by various nitrates or chloride of specific element. Exceptionally, the preparations of Tc-, Ru-, and Rh- β - Bi_2O_3 were failed (see Supplementary data). We tried to keep consistent in each synthesizing process because the following calculations were based on the assumption that the crystal forms and morphologies of different modified β - Bi_2O_3 were unchanged after modification. To verify the assumption, the morphology of modified β - Bi_2O_3 was observed with a Hitachi S-4800 (Japan) field emission scanning electron microscope (FESEM). Powder X-ray diffraction (XRD) patterns of the samples were recorded using an X'Pert PRO MPD diffractometer (PANalytical, Netherlands) with a source of Cu-K α radiation ($\lambda = 0.15418$ nm). Area and Pore Analyzer (Micromeritics, USA) at liquid nitrogen temperature (-196°C). The surface areas were obtained using the Brunauer–Emmett–Teller method. The XRD patterns of 29 elements modified and pure β - Bi_2O_3 are shown in Fig. S1. The results indicate that nearly all of the samples retained their crystal form of β -phase (except Ag- β - Bi_2O_3). All samples were constructed by the nanoparticles with sizes tens to hundreds nanometer (Fig. S2). As listed in Table S1, the surface areas of these modified β - Bi_2O_3 were within the region of 54.4–65.1 $\text{m}^2 \text{g}^{-1}$ and the pore sizes were distributed within 16.2–22.6 nm (except Ag- and Mo- β - Bi_2O_3). The similar morphologies and porous structure

promised that the comparisons of photo-reactivity of different photocatalysts were made on the similar foundation.

Further characterizations aim at the verification of calculation results: UV–vis diffuse reflection spectra (DRS) were collected using a Specord 200 UV–vis spectrophotometer (Analytik Jena, Germany). Binding energies were measured by X-ray photoelectron spectroscopy (XPS) with a PHI 5600 XPS instrument (Netherlands) employing pressed powder pellets contacted by silver lacquer with an aluminum foil. All XPS spectra were referenced to the C1s peak of adventitious hydrocarbon contamination located at 284.8 eV.

2.2. Adsorption: molecular simulation

Molecular dynamics (MD) simulation based on Universal force field was used to monitor the diffusion-adsorption behaviors of COCs in the 32 modified β - Bi_2O_3 by using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) codes. The total energy and the non-bond interactions were monitored and the snapshots were collected at the interval of 2500 steps frame by frame. The adsorption of COCs on modified β - Bi_2O_3 was generated one trajectory for each frame. All the properties were calculated based on the sampling trajectory after the equilibrium in each simulation. Each property was calculated for every snapshot in a trajectory, and the final result was represented by the mean values of the whole trajectory.

The grand canonical monte carlo (GCMC) simulation was conducted to calculate the adsorption binding energy of COCs on modified β - Bi_2O_3 . The simulation super-cells contained 18 ($3 \times 3 \times 2$) unit cells with periodic boundary conditions applied in all three dimensions. For each state point, GCMC simulation consisted of 1.0×10^7 equilibration steps and followed by 1.0×10^7 steps to obtain the thermodynamics properties. Universal force field (UFF) was adopted to describe all interaction force throughout the simulation. The overall adsorption energy may consist of five components: [22].

$$E_T = E_{OS} - E_{WS} + E_{OO} - E_{WW} - E_{WO} \quad (1)$$

where E_T is the overall adsorption energy, E_{OS} is the interaction energy between COCs and adsorbent, E_{WS} is the interaction energy between water and adsorbent, E_{OO} is the interaction energy between COC molecules, E_{WO} is the interaction energy between COC and water molecules, and E_{WW} is the interaction energy between water molecules. Herein, the E_{OS} and E_{WS} can be calculated by the GCMC and MD simulations. The terms E_{OO} , E_{WW} , and E_{WO} can be related to the solubility of the COCs and the octanol–water partition coefficient [23].

2.3. Adsorption: batch experiments

The COCs adsorption experiments were carried out in different Erlenmeyer glass flasks of 100 mL. Prior to each experiment, a predetermined amount of modified β - Bi_2O_3 and COCs were added to each flask with stirring (120 rpm). The samples were collected at various time intervals. We used an UltiMate3000 High Performance Liquid Chromatography (HPLC, Dionex, USA) equipped with a Betasil C18 column (100 mm \times 2.1 mm \times 4.6 μm) to measure the COCs concentration in water. The flow rate was maintained at 0.5 mL min^{-1} with a mobile phase of methanol and 2.0 mmol L^{-1} acetic acid in water (v/v: 85/15), and the VWD-3100 single wavelength detector was operated at 280 nm, 275 nm, and 258 nm for PCP, TCE, and HCH, respectively.

The experimental data was analyzed by fitting the linear form of Langmuir isotherms given by Eq. (2) [24]:

$$Q_e = Q_L K_L C_e / (1 + K_L C_e) \quad (2)$$

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