Supplementary material

Construction of a novel PANI/CoAl–LDH heterojunctions with significantly enhanced visible-light-driven activity for degradation of propranolol: Degradation pathways and toxicity assessment

Zhongtian Fu[a*],Xiangyu zeng[b], Zhaonan Sun[c], Wendi Lv[b], Yuxuan Song[b]

[a.] *Key Laboratory of Ministry of Education on Safe Mining of Deep Metal Mines, Dept. of Environment Engineering, School of Resources and Civil Engineering, Northeastern University, China.*

[b.] *School of Resources and Civil Engineering, Northeastern University, Shenyang, China.*

[c.] *Liaoning Provincial Key Laboratory of Energy Storage and Utilization, Yingkou Institute of Technology, Yingkou, China.*

** Corresponding author. E-mail address: fuzhongtian@mail.neu.edu.cn*

1. Synthesis of PANI

4.0 mmol Aniline was added to 200 mL 1.0 M hydrochloric acid aqueous solution containing 4.0 mmol β-CD. After the mixture was stirred at room temperature for 5 h, 4.0 mmol ammonium persulfate was added and continuously reacted for another 10 h. The precipitate was collected by filtration and washed with water several times. The dark-green powder was finally achieved by the freeze-dried method.

2. Synthesis of PANI /CoAl-LDH

Firstly, pristine PANI was added in ethanol and sonicated for 3 h to obtain the dispersed PANI nanoparticles. Subsequently, certain amount of PANI, 1.5 mmol Co(NO3)2·6H2O, 0.5 mmol Al(NO3)3·9H2O, and 10 mmol urea were added into ethanol of 40 mL, followed by sonication for 1.5 h. Then the resulting suspension was transferred into a Teflon-lined autoclave and subjected to a hydrothermal treatment at 120 °C for 12 h. After that, the gray sample was collected, washed with deionized water/ethanol several times and dried at 60 °C overnight to obtain the heterostructure. Besides, some reference samples were synthesized by changing the mass ratio of PANI to CoAl-LDH being 4 %, 7 % and 10 %, and the as-prepared samples were denoted as 4-PCL, 7-PCL and 10-PCL, respectively. Pure CoAl-LDH without PANI was also obtained under the identical conditions.

3. Electrochemical experiment

The photocurrent and electrochemical impedance of the samples were recorded in an electrochemical workstation (CHI 660E, Shanghai, China). Indium-tin oxide (ITO)

electrodes coated with 5 mg photocatalysts served as the working electrode. In the photoelectrochemical test, the platinum sheet and the Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrolyte solution of Na2SO4 (0.1 M) were utilized in this system.

4. Photocatalytic degradation experiment

The photocatalytic performances of the photocatalysts (20 mg) were evaluated by the degradation of PRO (10 mg/L) with a 350 W Xe lamp equipped with a UV cut-off filter (λ greater than 420 nm). Before irradiation, 100 mL of the mixed solution was stirred in the dark for 30 minutes until adsorption–desorption equilibrium was attained. Subsequently, 1 mL of the degradation solution was sampled every 30 minutes, filtered through a 0.22 μm PTFE membrane, and utilized for PRO quantification.

5. Degradation pathway

The generated intermediates during the photocatalytic degradation process were detected by high-performance liquid chromatography-tandem mass spectrometry (HPLC/MS-MS, 2695-ZQ2000). Based on the density functional theory (DFT), the theoretical calculation was also conducted on the Gaussian 16 program. The geometric structure was optimized using the B3LYP/6–31 G (d, p) level and the effect of the solvent was also considered using the integral equation formalism of the polarizable continuum model (IEFPCM). The single-point energy calculation was applied at the B3LYP/6–311 G (d, p) level to determine the lowest energy of the PRO molecular structure. Besides, the electrostatic potential and natural population

analysis (NPA) charge distribution were performed by the Multiwfn package (Version 3.8). Fukui functions, including electrophilic (f^-), nucleophilic (f^+), radical attack (f^0) and condensed dual descriptor (CDD), were calculated to evaluate the potential attacked sites of PRO by Multiwfn.

6. Toxicity assessment

The generated intermediates of pollutants in the degradation process have drawn increasing attention due to their toxicity might be higher than that of the parent compound. Herein, based on the quantitative structure-activity relationship methodologies, the acute toxicity and mutagenicity were calculated by the toxicity estimation software tool (T.E.S.T.). The acute toxicities, including the LD50 (50 % lethal dose) for rats (oral ingestion), the LC50 (50 % lethal concentration) for fathead minnow (96 h), Daphnia magna (48 h) and developmental toxicity were calculated.