



Heterogeneous catalysis

CdS quantum dots modified N-doped titania plates for the photocatalytic mineralization of diclofenac in water under visible light irradiation



Jian-Wen Shi^{a,*}, Zhenyu Wang^a, Chi He^b, Hongkang Wang^a, Jian-Wei Chen^c, Ming-Lai Fu^c, Guodong Li^d, Chunming Niu^{a,*}

^a Center of Nanomaterials for Renewable Energy, State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^b Department of Environmental Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^c Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, China

^d State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

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ABSTRACT

Pharmaceutical and Personal Care Products (PPCPs) are emerging contaminants, which can affect water quality and potentially impact drinking water supplies, ecosystem and human health. Conventional wastewater treatment technologies can not efficiently remove PPCPs from water. In this study, a new photocatalyst, CdS quantum dots (QDs) modified nitrogen-doped TiO₂ plates (NTP) with dominated {001} facets, was explored to decompose diclofenac (DCF), one of PPCPs. The results show that CdS QDs were dispersed on the surface of NTP uniformly with strong interface interaction due to the special preparation procedure, where thiolactic acid was used as a linker to bind CdS QDs on NTP *in situ*. This NTP/CdS system presented much high photocatalytic activity for the mineralization of DCF under visible light irradiation, and its reaction rate constant was significantly enhanced to 1.95 times of NTP and 2.88 times of CdS, respectively. The photocatalytic activity improvement could be attributed to the enhancement of visible light absorption and the reduction of electron-hole pair recombination rate, which were resulted from N-doping, preferred crystallographic orientation and the strong interaction between NTP and highly dispersed CdS QDs.

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1. Introduction

Pharmaceutical and Personal Care Products (PPCPs) are emerging contaminants attracted increasingly concern in recent years, which are derived from extensive usage both in medical and veterinary practice [1]. Owing to their persistence against biological degradation and natural attenuation, conventional wastewater treatment technologies such as activated sludge and filtration can not efficiently remove PPCPs from water [2]. Diclofenac (DCF) is one of PPCPs, which is usually used to treat inflammatory and painful diseases of rheumatic and non-rheumatic origin [3]. DCF has been detected in a wide range of environmental samples including surface water, groundwater and drinking water, and its toxicity has been disclosed, showing adverse effects even at low concentrations

[4], like cytotoxicity to liver, kidney and gill cells, as well as renal lesions. Moreover, it has been demonstrated that the toxic effect can be considerably increased if DCF is mixed with other PPCPs [5]. Therefore, it is urgent to explore an effective approach to deal with the environmental pollution resulted from DCF.

As one of advanced oxidation processes (AOPs), TiO₂-mediated photocatalysis has been shown to be potentially advantageous for the degradation of DCF in water as it can lead to complete mineralization. Many publications have demonstrated that DCF can be decomposed due to the photocatalysis of TiO₂ [6–10]. Unfortunately, to our knowledge, only UV and near UV-Visible (366 nm) light were used to excite the photocatalytic decomposition of DCF so far [6–10], due to the restrictive light absorption of TiO₂ resulted from its wide band-gap [11]. From the viewpoint of utilizing solar light, visible light responsive TiO₂ photocatalysts with high activity for the decomposition of DCF are highly desired.

In our recent work [12], we prepared N-doped anatase TiO₂ plates (NTP) with dominated {001} facets, and showed that

* Corresponding authors. Tel.: +86 2983395372.

E-mail addresses: shijwn@163.com (J.-W. Shi), cnui@mail.xjtu.edu.cn (C. Niu).

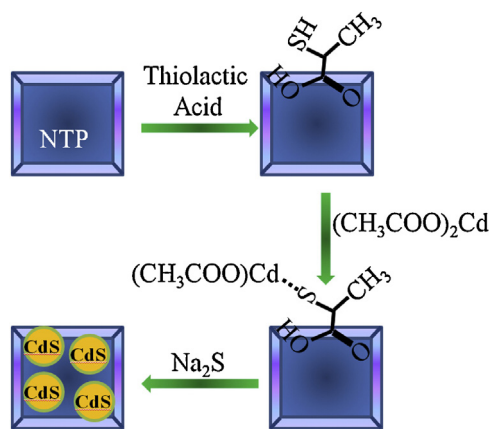


Fig. 1. Schematic diagram of the *in situ* formation of CdS QDs on NTP.

samples are visible-light photocatalytic active for methylene blue (MB) decomposition. However, its activity was low, only about 55% MB was decomposed after 120 min reaction due to the high recombination rate of the photogenerated electron-hole pairs. To improve the performance, further measures need to be taken to prevent the recombination of electron-hole pairs. The coupling TiO₂ with a narrow band gap semiconductor, such as CdS (~2.4 eV), has been proved not only could extend the response of TiO₂ to visible light, but also could reduce the recombination probability of electron-hole pairs due to the electron transfer from the conduction band of CdS to that of TiO₂ and the separation of oxidation and reduction processes to different reaction sites [13,14]. Furthermore, in order to transfer electrons effectively from CdS particles to TiO₂, it is important to have CdS QDs highly crystallised and dispersed on the surface of TiO₂ uniformly with strong interface interaction. It has been found that this can be achieved by using bi-functional organic molecules, such as 2,3-dimercaptosuccinic acid, mercaptoalkanoic acid, 4-mercaptobenzoic acid, 2-mercaptobenzoic acid, 4-mercaptophenylacetic acid, mercaptopropionic acid, as linkers [15–18]. In a previous work [19], we used a simpler and cheaper bi-functional organic molecule, thiolactic acid (TA) to prepare highly dispersed CdS QDs onto the surface of TiO₂ nanotubes *in situ*. The composite catalyst showed excellent photocatalytic activity and stability.

In present work, we attempt to explore the photocatalyst with high activity for the decomposition of DCF under visible light irradiation by coupling NTP with CdS QDs. First, we prepared NTP with dominated {001} facets by a hydrothermal process, then we attached bi-functional linker molecule, TA onto the surface of NTP *via* carboxylic group and introduced Cd²⁺ ions on the surface through ion exchange, followed by the reaction with Na₂S to *in situ* form CdS QDs and finally obtained the photocatalyst of CdS QDs modified NTP with dominated {001} facets (NTP/CdS). We found that the obtained NTP/CdS presented high visible-light photocatalytic activity for the mineralization of DCF. To our knowledge, this is the first report on the photocatalytic mineralization of DCF under visible light irradiation.

2. Experimental

2.1. The preparation of NTP

NTP was prepared by following a method reported in the previous work [20]. In a typical synthesis, 2.5 mL of HF (40%) was diluted with 27.5 mL of deionized water, then 0.9 g of TiN solid powder (particle size: 2–10 μm) was added into the solution. After stirring for 20 min, the suspension was transferred to an 80 mL Teflon-lined

autoclave and heated at 180 °C for 20 h to carry out hydrothermal reaction. Finally, the reaction product was collected by centrifugation followed by washing with deionized water for several times, and drying overnight at 80 °C to yield NTP sample.

2.2. The preparation of NTP/CdS

NTP/CdS was prepared as follows: 0.4 g of NTP particles was pretreated with a 0.3 M TA aqueous solution for 24 h, then, 25 mL of 0.2 M (CH₃COO)₂Cd solution was mixed with the pretreated NTP particles for 12 h under continuous stirring, after (CH₃COO)₂Cd treatment, the NTP particles were mixed with 25 mL of 0.5 M Na₂S aqueous solution for 12 h under continuous stirring. Finally, the product was collected by filtration and dried at 80 °C for 12 h in an oven to yield NTP/CdS. Note that the excess reagent after every step was removed by washing with deionized water repeatedly.

2.3. The preparation of CdS

For comparison, CdS was prepared as follows: 25 mL of 0.2 M (CH₃COO)₂Cd solution was mixed with 10 mL of 0.5 M Na₂S solution for 12 h under continuous stirring to form brown deposition. Then the deposition was re-dispersed, washed, and centrifuged in water and in ethanol for three cycles, respectively. Finally, product was dried at 80 °C for 12 h in an oven to yield CdS.

2.4. Characterizations

Hitachi S-4800 scanning electron microscopy (SEM) was used to obtain SEM images. The elemental composition over the selected region was analyzed by an energy dispersive X-ray spectrometer (EDX) attached to the SEM. Transmission electron microscope study was carried out by a JEM 2100 TEM (JEOL, Japan). X-ray diffraction (XRD) patterns were recorded at room temperature with an X'pert PROMPD diffractometer (PANalytical, Holland) with copper K_{α1} radiation. FTIR spectra of the samples were recorded by a Nicolet FTIR spectrometer (Magna-750) at ambient conditions. UV–vis diffuse reflectance spectroscopies (DRS) were recorded by a UV-2450 spectrophotometer (Shimadzu, Japan) equipped with an integrating sphere. The nitrogen adsorption measurements were taken at 77 K using a micromeritics (Tristar 3000, America), and specific surface areas were obtained according to the Brunauer–Emmett–Teller (BET) model.

2.5. Experimental procedures of photocatalytic decomposition

The photocatalytic experiment was carried out in a photo reaction system reported in our previous publication by using DCF as a model pollutant [21]. A 1000 W Xe lamp equipped with a 420 nm glass filter (removing the UV irradiation below 420 nm), positioned in the center of a water-cooled quartz jacket, was used to generate visible light irradiation. At the side of quartz jacket, a 50-mL cylindrical vessel was used as the reaction bottle to load reaction solution. The distance between lamp and reaction bottle was 40 mm. In the bottom of the reaction bottle, a magnetic stirrer was equipped to keep the catalyst suspended in the solution during the photocatalytic reaction. The temperature of the reaction solution was maintained at 30 ± 0.5 °C by cooling water. Photocatalyst powder (50 mg) was added into 50 mL of 50 mg/L DCF solution to form suspension. Then, the suspension was irradiated with visible light. During the irradiation, the suspension was stirred continuously. At given time interval, 3 mL of suspension was taken out and immediately centrifuged to eliminate solid particles. Total organic carbon (TOC) of filtrate was measured by using a Shimadzu TOC-VCPH analyzer.

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