

Photoreductive degradation of polybrominated diphenyl ethers by N-doped ZnO

A high activity photocatalysts N-ZnO has been synthesized by hydrothermal method. The characterization of the prepared N-ZnO nano-composite has been examined by SEM, TEM, ultraviolet-visible diffuse reflectance spectroscopy, X-ray diffraction, elemental analysis, Brunauer-Emmer Teller surface area. Under irradiation (>360 nm), N-ZnO shows high photocatalytic activity for the debromination of polybromo diphenyl ethers (PBDEs). The photocatalytic degradation kinetics of PBDEs has been investigated under different reaction conditions. The N-ZnO nano-composite exhibits excellent photostability after four run experiments. The possible photoreductive mechanism has been proposed. This study provides an efficient method to removal of halogen organic pollutants.

Keywords: N-doped ZnO, photoreduction, degradation; polybrominated diphenyl ether, pollutants.

1. Introduction

Persistent organic pollutants (POPs) have aroused significant concerns because of global distribution and bio-accumulation in the environment^[1,2]. As the typical persistent pollutants, polybrominated diphenyl ethers (PBDEs) have attracted particular attention in this field due to extensive use as flame retardants and toxicity transmitting along the food chain^[3,4]. Owing to increasing usage, high hydrophobicity and persistence, PBDEs have been detected in sediments, marine organisms, food samples, and human mother's milk^[5-7]. PBDEs are strongly resistant to oxidative degradation. Many studies have been focused on the environmental transformation of PBDEs^[8-10]. For example, PBDEs undergo photolytic debromination on the surface of clay minerals, metal oxides and sediment^[9] and in toluene solution^[10]. However, the development of potential methods for PBDE removal in contaminated environmental systems is totally ignored^[11, 12]. Therefore, it is urgent to explore efficient methods for the removal of PBDEs.

In recent years, ZnO has received wide attention in catalytic applications due to its wide band gap 3.3 eV and

excellent photocatalytic activity^[13]. Nevertheless, the low quantum efficiency of ZnO needs to be improved in practical application. N-doped ZnO is a feasible way to enhance the quantum efficiency of photocatalyst and improve the photocatalytic activity^[14,15]. Because the N-doped ZnO show a P-type semiconductor property and the intra-band gap N related defects play a role of electron transfer intermediate^[14]. Thus, the N-doped ZnO exhibits better photocatalytic due to the lower electron-hole recombination rate^[16]. The main objective of this study is to test the possibility of N-ZnO for effective photoreduction of PBDEs. BDE209 (Fig. 1) as the major product of PBDEs, was selected as a target PBDEs. To the best of our knowledge, it is the first time to research the photocatalytic degradation of PBDEs with N-ZnO. This finding will unveil an efficient method for the degradation of PBDEs

2. Experimental section

2.1 MATERIALS

BDE209 was purchased from Sigma-Aldrich (USA). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ethylenediamine were purchased from Chemical Co., Shanghai. 2-propanol (i-PrOH), DMSO, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, hexane, toluene, acetone were analytical reagents (Chemical Co., Shanghai). They were used without further purification. Deionized and doubly distilled water was used throughout the study.

2.2 SYNTHESIS OF N-ZNO

N-ZnO was prepared as follows: 1.515 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 78 mL of ethanol solution by ultrasonic treatment 5h. A certain amount of ethylenediamine was then slowly added to $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution and continued stirring at 0.5h. The mixture was put in a hydrothermal reactor and heated at 180°C for 12h.

2.3 CHARACTERIZATION OF N-ZNO

The morphologies of N-ZnO were examined by SEM (Hitachi S4300) and TEM (Philips CM200 FEG TEM at 200 kV). The XRD patterns were measured on a Regaku D/Max-2500 diffractometer with the Cu K α radiation (1.5406 Å). UV-vis absorption spectra were obtained with 10×10 mm quartz cuvettes by a Hitachi U-3010 spectrophotometer (Hitachi Co. Japan). N_2 adsorption-desorption isotherms

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were obtained by a Quantachrome Autosorb-IQ instrument at 77K. The specific surface areas were detected by BET method. Elemental analysis data were performed by EuroEA elemental analyser.

2.4 BATCH PHOTOCATALYTIC DEGRADATION EXPERIMENTS

BDE209 stock solution (1×10^{-3} mol/L) in tetrahydrofuran was diluted with methanol (1×10^{-5} mol/L). 10mg N-ZnO was added to 10 mL BDE209 solution in a Pyrex vessel. Reaction solution was magnetically stirred during the irradiation. The Pyrex vessel was purged with N_2 for 15 min to remove O_2 and protected under N_2 atmosphere during the irradiation. A PLS-SXE300 Xe lamp (Beijing Trusttech Co. Ltd.) was used as the light source. A cutoff filter ($\lambda > 360$ nm) was placed to eliminate the direct photolysis of BDE209. The degradation kinetics of BDE209 with N-ZnO was assumed to fit with pseudo-first order. To investigate the effect of organic solvents on the reaction kinetics, BDE209 stock solution (1×10^{-3} mol/L) in tetrahydrofuran was diluted with different six organic solvent, respectively and isopropyl alcohol (0.33 mol/L) was added as hole scavenger.

BDE209 was quantified by HPLC, which has a SHIMADZU HPLC system (LC-20AT pump and UV/VIS SPD-20A detector) with a DIKMA Platisil ODS C-18 column (250 $\times$ 4.6mm, 5 μ m film thickness). The mobile phase was 2% H_2O in acetonitrile with 1mL/min and the detector wavelength was at 240nm. The quantification of BDE209 was obtained by a calibration curve with a BDE-209 standard solution.

3. Results and discussion

3.1 CATALYST CHARACTERIZATION

As shown in Fig. 1, the morphology and microstructure of N-ZnO is characterized by SEM and TEM. The SEM image of N-ZnO shows layer like structure, which has the slightly irregular edges (Fig. 1a). As seen from Fig. 1a, N-ZnO samples exhibit small particles with sizes range of 1-10 μ m. The TEM images of N-ZnO show the thin layered planar structure (Fig. 1b).

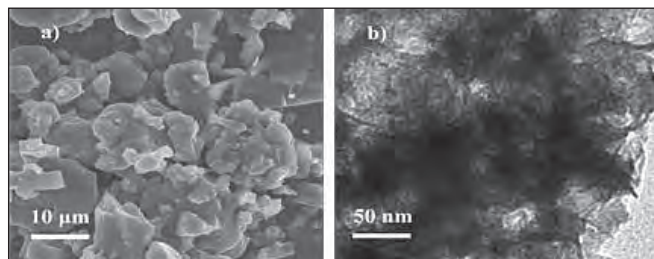


Fig. 1: (a) SEM images of N-ZnO; (b) TEM images of N-ZnO Synthesis of N-ZnO

The optical property of N-ZnO sample is investigated by UV-vis diffuse reflectance spectra. As shown in Fig. 2, N-ZnO shows broad strong absorption in the region of 250-700 nm. N-ZnO exhibits the two obvious absorbances at

277 nm in UV region and 417 nm in visible light region. It implies that N-ZnO may have good photocatalytic activity.

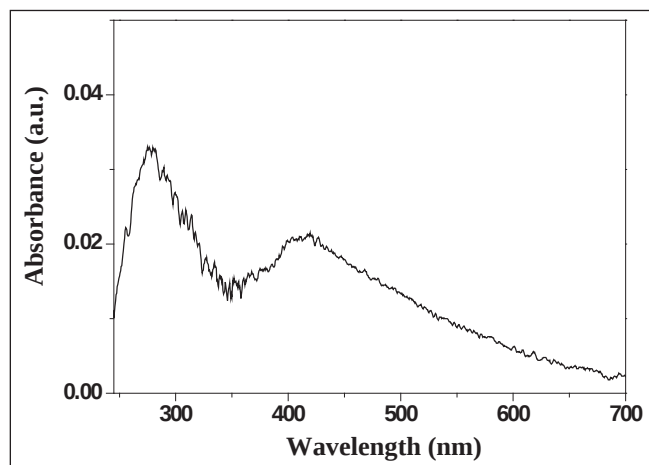


Fig. 2: UV-Vis absorption spectra of N-ZnO

Fig. 3 shows the X-ray diffraction patterns of N-ZnO. The pattern of the N-ZnO sample has the peaks (100), (002), (101) at lower angles and the peaks (102), (110), (103) at higher angles corresponding to the powder diffraction standards data (JCPDS no. 076-0704) for ZnO [17]. In addition, the pattern of the N-ZnO sample exhibits some other diffraction peaks, which shows that N ions doped into the ZnO are changed the crystal lattice of ZnO. Therefore, it proves that N ions are successful doped into the ZnO lattice.

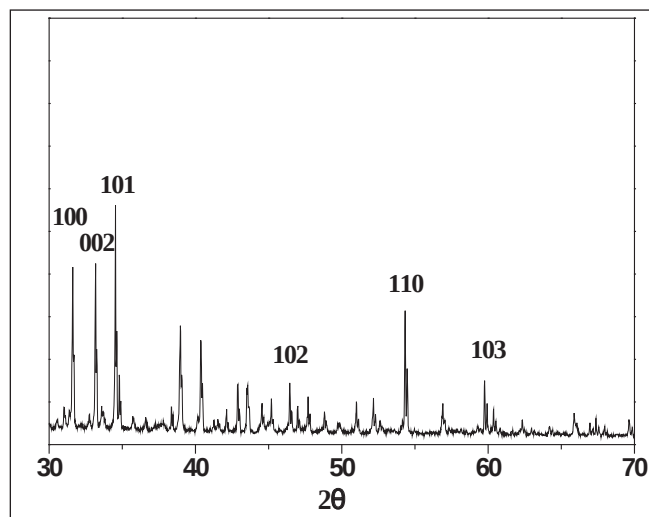


Fig. 3: XRD patterns of N-ZnO

Chemical composition analysis of N-ZnO has been performed to reveal the elemental composition of N-ZnO. As seen from Table 1, it shows that N-ZnO is composed of 17.94 w% zinc, 26.03 w% oxygen, 28.25 w% nitrogen, 19.28 % carbon and 6.12% hydrogen. It further proves that N is successfully doped in the ZnO. In the heterogeneous catalytic reaction, the photocatalytic reaction occurs primarily on the surface of the catalyst, so the catalyst's surface area may have a large effect on the reaction rate. The specific surface area

has been detected by BET method. The specific surface area of the N-ZnO is 23.50 m²/g, suggesting the better adsorption ability on the surface of N-ZnO.

TABLE 1. ELEMENTAL COMPOSITION AND S_{BET} (m²/g) FOR N-ZnO

Zn (%)	O (%)	N (%)	C (%)	H (%)	S_{BET} (m ² /g)
17.94	26.03	28.25	19.28	6.12	23.50

3.2 DEGRADATION KINETICS

As seen from Fig. 4, the reduction of BDE209 scarcely occurs without N-ZnO under UV irradiation (>360nm). BDE209 also shows slight degradation when the reaction is performed with N-ZnO under heat or dark. Interestingly, rapid degradation of BDE209 is observed with N-ZnO under UV irradiation (>360nm), and about 75% of BDE209 disappeared after irradiation of 15 min. The decay is fitted by pseudo-first-order kinetics. The obtained rate constant of degradation is $0.36 \pm 0.02 \text{ min}^{-1}$. It indicates that BDE209 could be efficient photochemical degradation with N-ZnO.

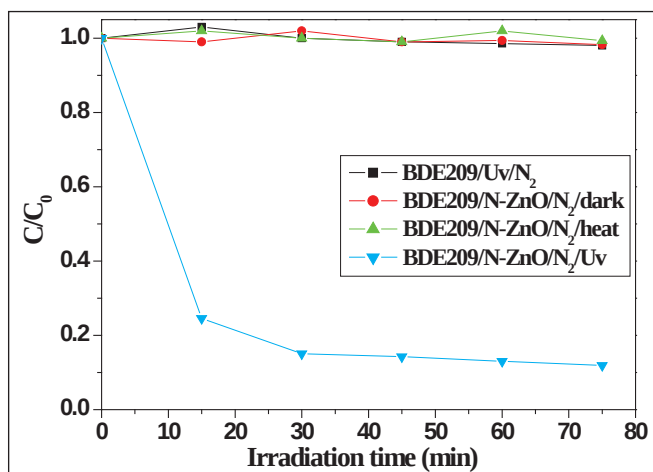


Fig. 4: Temporal curves of the degradation of BDE209 under different conditions. BDE209: $1.0 \times 10^{-5} \text{ mol/L}$, N-ZnO: 1mg/mL, solvent: CH₃OH, wavelength >360 nm, anoxic condition.

3.3 THE EFFECT OF ORGANIC SOLVENTS

The debromination of BDE209 has been further carried out in six organic solvents, respectively (Fig. 5). The degradation of BDE209 with N-ZnO is not observed in hexane, toluene and acetone solution, where the polarity of organic solvent is weak. BDE209 is effectively degraded in the presence of N-ZnO in the strong polarity solvents, such as CH₃CN, dimethyl sulfoxide (DMSO) and CH₃OH on the same experiment conditions, which the order of reaction rate was CH₃OH > DMSO > CH₃CN. Nevertheless, the polarity is not the only factor that controls the photocatalytic degradation of BDE209 with N-ZnO. The DMSO shows the strongest polarity among all the six organic solvents, but the debromination in the CH₃OH exhibits highest the reaction rate.

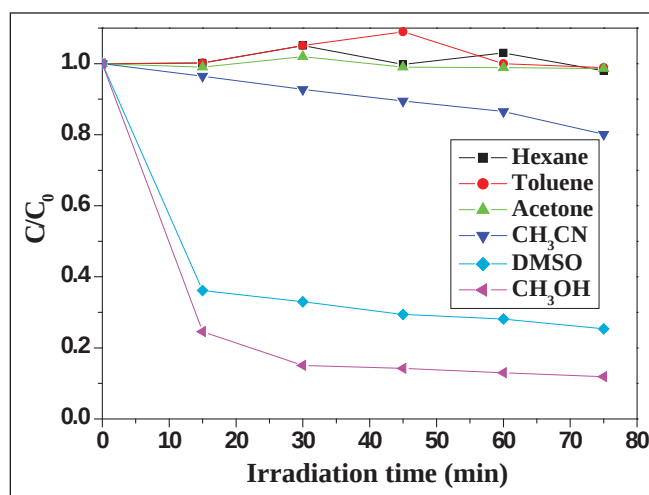


Fig. 5: Temporal curves of the degradation of BDE209 with N-ZnO in different solvents under irradiation. BDE209: $1.0 \times 10^{-5} \text{ mol/L}$, N-ZnO: 1mg/mL, wavelength >360nm, solvent: hexane, toluene, acetone, CH₃CN, DMSO, CH₃OH, respectively; isopropyl alcohol, 0.33 mol/L (as hole scavenger); anoxic condition.

3.4 PHOTOSTABILITY OF N-ZnO

The recycling experiments have been performed to test the photostability of N-ZnO. As shown in Fig. 6, the photocatalyst N-ZnO still shows strong photoreductive activity for degradation of BDE209 after four cycles. The degradation rate of BDE209 exhibits no obviously decrease. It proves that N-ZnO has good photostability.

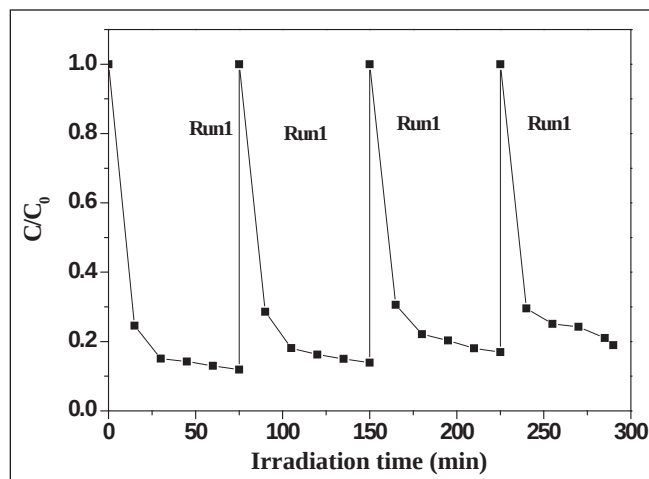


Fig. 6: Cycling runs in the degradation of BDE209 with N-ZnO under irradiation. BDE209: $1.0 \times 10^{-5} \text{ mol/L}$, N-ZnO: 1mg/mL, solvent: CH₃OH, wavelength >360nm, anoxic condition.

3.5 PHOTOREDUCTIVE MECHANISM

It is well known that N-doped the photocatalysts could absorb the photon energy for moving electrons from VB to CB during electron excitation^[18]. The existence of N-related defect states largely shorten the bandgap between VB and CB, and electron can be excited from N-related defect state to CB. The intra-band gap N-related defects play a role of electron transfer intermediate. Thus, the

N-doped ZnO shows better photocatalytic activity due to the lower electron-hole recombination rate. Based on the above discussion, a possible reaction mechanism has been proposed with the degradation of PBDEs in CH₃OH solution by N-ZnO. Under irradiation (> 360 nm), the excited N-ZnO produces of VB hole and CB. The electron excited from N₀ - to CB^[18]. The electrons accumulate on CB because the VB holes are scavenged by trapping agents (CH₃OH). PBDEs receive the electrons on CB of N-ZnO and sequentially abstract hydrogen atom from methanol (holes trapping agent) and yields debrominated products. This study shows that N-ZnO can be an excellent candidate for dealing with halogen organic pollutants.

4. Conclusions

The photocatalyst of N-ZnO has been synthesized by hydrothermal method and shows highly photoreductive activity for degradation of BDE209 under irradiation (> 360 nm). In addition, N-ZnO shows good photostability for degradation of BDE209 after four runs experiments. This result shows that N-ZnO can be an excellent candidate for dealing with halogen organic pollutants.

Acknowledgements

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