

# Photocatalytic degradation of pentabromophenol by N-doped ZnO

*A high activity photocatalysts N-ZnO has been synthesized by hydrothermal method. The characterization of the prepared N-ZnO nanocomposite 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 pentabromophenol. The results of the trapping agent experiments show that the rate determining step in the degradation reaction of PBP with N-ZnO is the rate of electron accumulation in the conductive band. The N-ZnO nanocomposite exhibits excellent photostability after four run experiments. The possible photoreductive mechanism has been proposed. This study provides an efficient method to removal of pentabromophenol.*

*Keywords: Photocatalytic, N-doped ZnO, degradation, pentabromophenol, containment*

## 1. Introduction

Persistent organic pollutants (POPs) such as halogen organic pollutants have aroused significant concerns because of global distribution and bioaccumulation in the environment<sup>[1,2]</sup>. Photocatalysis is one of the most effective technologies for the remediation of POPs<sup>[3-5]</sup>. TiO<sub>2</sub> and ZnO have widely used for the degradation of POPs due to their excellent photocatalytic capability, high chemical stability, and environmental friendliness<sup>[6-8]</sup>. Especially, ZnO have attracted much attention in this field because ZnO is more active than TiO<sub>2</sub> after modifying by optimized conditions<sup>[9-12]</sup>. ZnO has wide band gap 3.3 eV and excellent photocatalytic activity<sup>[9]</sup>. Many efforts have been performed to modify ZnO in order to enhance its photocatalytic activity<sup>[12,13]</sup>.

N-doped ZnO is a feasible way to enhance the quantum efficiency of photocatalyst and improve the photocatalytic activity<sup>[14,15]</sup>. 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<sup>[14]</sup>. Thus, the N-doped ZnO exhibits better photocatalytic due to the lower electron-hole recombination rate<sup>[16]</sup>. However, compared to the extensive researches on photocatalytic oxidation ability of N-doped ZnO<sup>[10,13]</sup>, the photocatalytic reduction performance of N-doped ZnO, especially on degradation of the halogen organic pollutants is quite rare, which may reveal another important application for N-doped ZnO. The main objective of this study is to investigate the photocatalytic reduction activity of N-ZnO by photoreduction of the typical halogen organic pollutants – pentabromophenol (PBP). To the best of our knowledge, it is the first time to research the photocatalytic degradation of PBP with N-ZnO. This finding will unveil an efficient method for the degradation of PBP.

## 2. Experimental section

### 2.1 MATERIALS

PBP was purchased from Sigma-Aldrich (USA). Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O and 1,3-propanediol were purchased from Chemical Co., Shanghai. 2-propanol (i-PrOH), DMSO, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>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 Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O was added to 78ml of ethanol solution by ultrasonic treatment at 5h. A certain amount of ethylenediamine was then slowly added to Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>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 $\alpha$  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<sub>2</sub> adsorption-desorption isotherms were obtained by a Quantachrome Autosorb-IQ instrument

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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

PBP stock solution ( $1 \times 10^{-3}$  mol/l) in methanol was diluted with methanol ( $1 \times 10^{-4}$  mol/l). 10mg N-ZnO was added to 10ml PBP 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 ( $> 360$ nm) was placed to eliminate the direct photolysis of PBP. The degradation kinetics of PBP with N-ZnO was assumed to fit with pseudo-first order. To investigate the effect of hole scavenger on the reaction kinetics, PBP stock solution ( $1 \times 10^{-3}$  mol/l) in methanol was diluted with  $CH_3OH$  and  $C_2H_5OH$ , respectively.

PBP 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 ( $250 \times 4.6$ mm,  $5\mu m$  film thickness). The mobile phase  $CH_3OH$ /ammonium acetate (1%) 9:1 (v/v) with 1ml/min and the detector wavelength was at 305nm. The quantification of PBP was obtained by a calibration curve with PBP 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 slice like structure with irregular edges (Fig. 1a). As seen from Fig. 1a, N-ZnO samples exhibits small particles with sizes about  $10\mu m$ . The TEM images of N-ZnO show the thin slice planar structure (Fig. 1b).

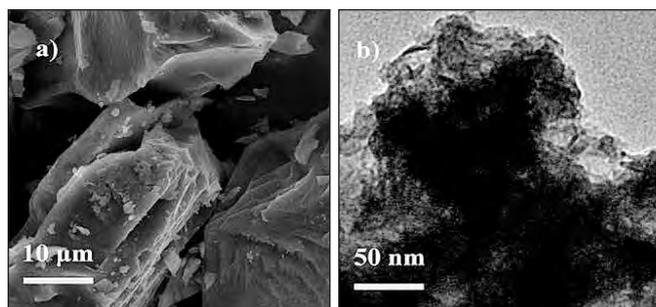


Fig. 1. (a) SEM images of N-ZnO; (b) TEM images of N-ZnO synthesis of N-ZnO

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 260-700nm. N-ZnO exhibits the two obvious absorbances at 291nm in UV region and 420nm in visible light region. It implies that N-ZnO may have good photocatalytic activity.

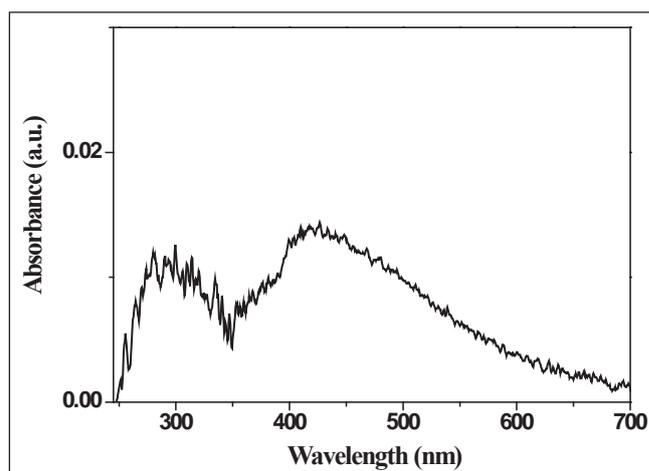


Fig. 2. UV-Vis absorption spectra of N-ZnO

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), (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.

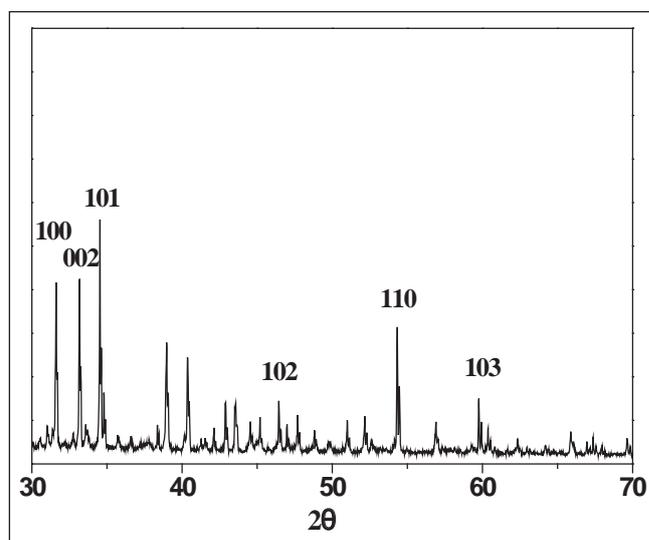


Fig. 3. XRD patterns of N-ZnO

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 18.35 w% zinc, 26.71 w% oxygen, 28.93 w% nitrogen, 19.63 w% carbons and 6.55% 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 21.50 m<sup>2</sup>/g, showing the better adsorption ability.

TABLE 1. ELEMENTAL COMPOSITION AND S<sub>BET</sub> (m<sup>2</sup>/g) FOR N-ZnO

Zn (%)	O (%)	N (%)	C (%)	H (%)	S <sub>BET</sub> (m <sup>2</sup> /g)
18.35	26.71	28.93	19.63	6.55	21.50

### 3.2 DEGRADATION KINETICS

As seen from Fig. 4, the reduction of PBP scarcely occurs without N-ZnO under UV irradiation (> 360nm). PBP also shows slight degradation when the reaction is performed with N-ZnO under heat or dark. Interestingly, rapid degradation of PBP is observed with N-ZnO under UV irradiation (> 360nm), and about 50% of PBP disappeared after irradiation of 1h. The decay is fitted by pseudo-first-order kinetics. The obtained rate constant of degradation is 0.92 ± 0.03 h<sup>-1</sup>. It indicates that PBP could be efficient photochemical degradation with N-ZnO.

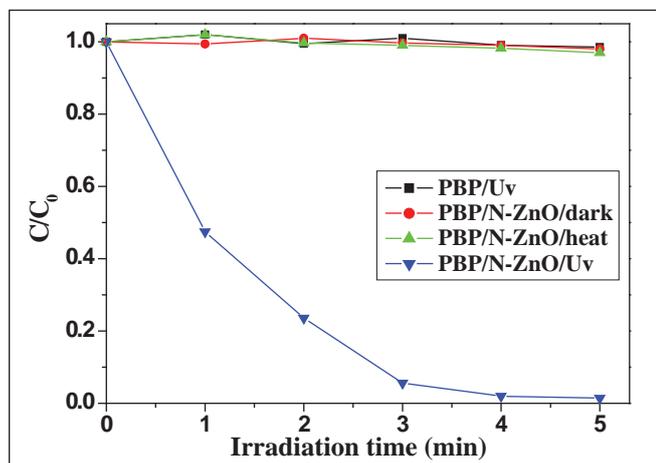


Fig. 4. Temporal curves of the degradation of PBP under different conditions. PBP: 1.0 × 10<sup>-4</sup> mol/l, N-ZnO: 1mg/ml, solvent: CH<sub>3</sub>OH, wavelength > 360nm, anoxic condition

### 3.3 THE EFFECT OF THE TRAPPING AGENTS

The holes scavenger experiments have been performed to further declare the rate determining step of the reaction. As seen from Fig. 5, in the presence of C<sub>2</sub>H<sub>5</sub>OH, the reaction rate decreases sharply compared to the reaction rate in CH<sub>3</sub>OH. The experimental results show that the reaction rates are in the order of CH<sub>3</sub>OH > C<sub>2</sub>H<sub>5</sub>OH corresponding to the oxidation ability of alcohols with holes on the valence band (VB) via dehydrogenation. In the process of the photocatalytic reaction, when the VB holes are trapped by holes scavenger, the electrons will accumulate on conduction band (CB). The oxidation ability of the holes scavenger will directly influence the accumulation of the electrons on CB. It indicates the rate of electrons accumulation on CB largely influences the photoreductive degradation of PBP with N-ZnO. On the other hand, when the experiment performs at air condition, the debromination reaction greatly decreases. When the experiment performs at O<sub>2</sub> condition, the debromination

reaction is almost inhibited. The oxygen control experiment also shows that O<sub>2</sub> inhibits the degradation of BDE209 due to reacting with the electron on CB. These above results prove that it is the electrons on CB that leads to PBP reductive debromination and the rate of accumulation of the electrons on CB is the rate-determining step.

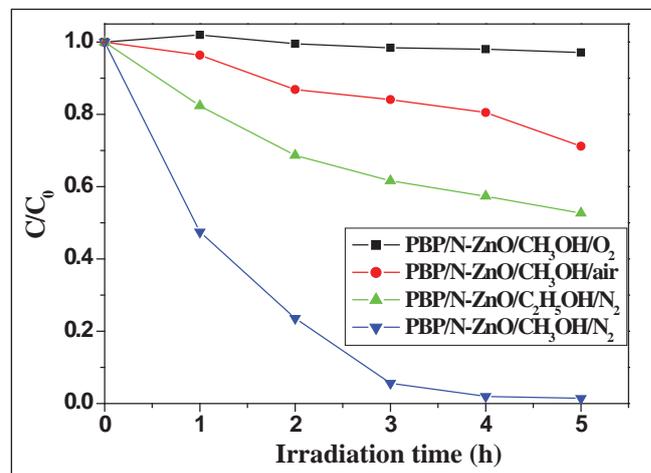


Fig. 5. Temporal curves of the degradation of PBP with N-ZnO in different solvents under irradiation. PBP: 1.0 × 10<sup>-4</sup> mol/l, N-ZnO: 1mg/ml, wavelength > 360nm, solvent: hexane, toluene, acetone, CH<sub>3</sub>CN, DMSO, CH<sub>3</sub>OH, respectively; isopropyl alcohol, 0.33 mol/l (as hole 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 PBP after four cycles. The degradation rate of PBP exhibits no obvious decrease. It proves that N-ZnO has good photostability.

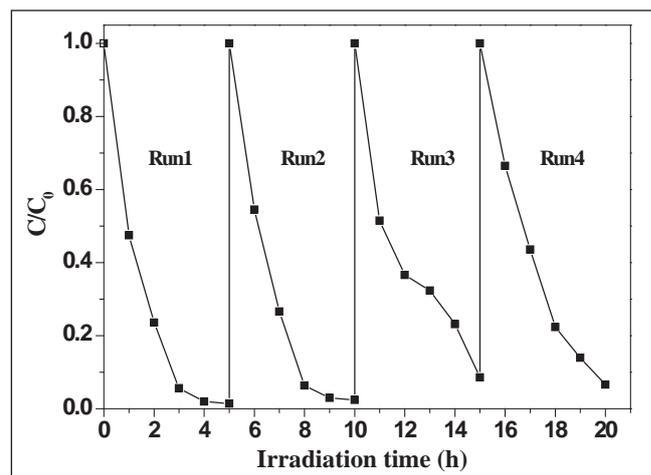


Fig. 6. Cycling runs in the degradation of PBP with N-ZnO under irradiation. PBP: 1.0 × 10<sup>-4</sup> mol/l, N-ZnO: 1mg/ml, solvent: CH<sub>3</sub>OH, wavelength > 360nm, anoxic condition

### 3.5 PHOTOREDUCTIVE MECHANISM

N-doped the photocatalysts could absorb the photon energy during electron excitation<sup>[18]</sup>. The intra-band gap formed

by N related defects play an important role acting as the electron transfer intermediate. The existence of N related defect states greatly shorten the bandgap between VB and CB, and electron is excited from N related defect state to CB, which results the lower electron-hole recombination rate. Thus, the N-doped ZnO shows enhanced photocatalytic activity. Based on the above discussion, a possible reaction mechanism has been proposed with the degradation of PBP in CH<sub>3</sub>OH solution by N-ZnO. Under UV irradiation (> 360nm), the excited N-ZnO produces of VB hole and CB. The electron excited from N<sub>0</sub><sup>-</sup> to CB<sup>[18]</sup>. When the VB holes are scavenged by trapping agents (CH<sub>3</sub>OH), the electrons accumulate on CB because PBP receives the electrons on CB of N-ZnO and then abstract hydrogen atom from CH<sub>3</sub>OH and yields degradation products. This study indicates 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 PBP under irradiation (> 360nm). In addition, the results of the trapping agent experiments show that the rate of electron accumulation in the conductive band rate is the determining step in the degradation reaction of PBP with N-ZnO. Meanwhile, N-ZnO shows good photostability for degradation of PBP after four runs experiments. This result shows that N-ZnO can be an excellent candidate for dealing with halogen organic pollutants.

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