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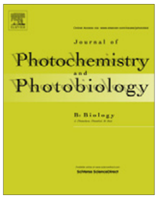

# Photocatalytic degradation of toluene using sprayed N-doped ZnO thin films in aqueous suspension

S.S. Shinde, C.H. Bhosale, K.Y. Rajpure *

*Electrochemical Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India*

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ABSTRACT

Thin films of N-doped ZnO are synthesized via spray pyrolysis technique in aqueous medium using zinc acetate and ammonium acetate as precursors. Influence of N doping onto photochemical, structural, morphological, optical and thermal properties have been investigated. Structural analysis depicts hexagonal (wurtzite) crystal structure. The effect of N doping on the photocatalytic activity of N-doped ZnO in the degradation of toluene is studied and results are compared with pure ZnO. The results show that the rate of degradation of toluene over N-doped ZnO is higher as compared to that of pure ZnO and increases with increasing N doping up to 10 at.% and then decreases. The enhancement of photocatalytic activity of N-doped ZnO thin films is mainly due to their capability for reducing the electron hole pair recombination. The photocatalytic mineralization of toluene in aqueous solution has been studied by measuring COD and TOC. Possible reaction mechanism pathways during toluene degradation over N-doped ZnO has been proposed.

## 1. Introduction

Solar energy, as an ultimate renewable energy resource, is ubiquitous on earth. The sunlight that strikes the earth in 1 h is sufficient to satisfy all human energy needs in 1 year. Thus, the design and fabrication of photocatalysts with highly efficient solar energy utilization have attracted considerable attention recently [1–3]. Various metal oxide semiconductors such as ZnO, $TiO_2$, $WO_3$ and $SnO_2$. have been studied as photocatalyst. $TiO_2$ as an oxide semiconductor has been investigated extensively since 1980s and found to be very efficient photocatalyst due to its abundant availability, cost-effectiveness and chemical stability. However, current researchers show that ZnO can also be used as a very efficient semiconductor photocatalyst when compared with $TiO_2$ [4,5]. The emitting properties of ZnO, which are developed in the system due to various kinds of intrinsic defects such as oxygen vacancies, zinc vacancies, zinc interstitials, oxygen interstitials, and antisite defect, can help to set up a catalytic system which is able to sense and shoot environmental contaminants [6,7]. Recently, much effort has been devoted to study ZnO as a very promising semiconductor for photocatalytic degradation of water pollutants. But, it has numerous shortcomings such as recombination of photogenerated electron–hole pair, low quantum yield, surface morphology of the films, which obstruct commercialization of the photocatalytic process [8,9]. Consequently, it has received enormous attention in improving the photocatalytic activity by appropriate modification of semiconductors for the degradation of wastewater. Therefore, various efforts have been developed to reduce the electron–hole recombination rate of ZnO in the photocatalytic processes. One of the interesting approaches is to dope the transition metals (Ga, Al, In), non-metals (N, F, C), alkaline and rare earth metals in order to improve charge separation between photogenerated electrons and holes [10]. Very recently, N-doped ZnO nanocrystalline thin films have attracted much attention in the photocatalytic processes owing to its high photocatalytic activity in the degradation of organic contaminants because of the large content of oxygen vacancies and strong absorption of $OH^-$ ions on the surface of the catalyst [11–13]. However, insufficient light harvesting especially in the visible-light region [14] and inefficient energy conversion [15–17], still remained two great challenges. So development of novel and efficient photocatalysts would be a major advance in photochemis try with respect to the rising concern of global energy and environmental issues. To realize such type of challenge, we prepared N-doped ZnO (NZO) photocatalyst by using spray pyrolysis technique, since spray pyrolysis is simple, cost effective technique.

Therefore, an influence of nitrogen doping concentration onto the photochemical, structural, morphological, optical, and thermal properties of sprayed NZO thin films and its photocatalytic activity has been investigated. The correlation of total organic carbon (TOC) and chemical oxygen demand (COD) measurements for extent of the degree of complete mineralization have been investigated. A possible reaction mechanism during degradation

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* Corresponding author. Tel.: +91 231 2609435; fax: +91 231 2691533.
*E-mail address:* rajpure@yahoo.com (K.Y. Rajpure).

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of toluene with N-doped ZnO photocatalyst under solar illumination is also proposed.

## 2. Experimental

Nitrogen doped zinc oxide (N:ZnO) thin films were prepared onto the corning glass substrates by using chemical spray pyrolysis technique in aqueous medium. To deposit N:ZnO thin films, zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$, AR grade, 98.8% pure) supplied by HIMEDIA and ammonium acetate ($C_2H_3O_2NH_4$, AR grade, 99% pure) supplied by THOMAS BAKER were used as initial ingredients. To attain nitrogen doping, ammonium acetate was mixed into the solution. The [N]/[Zn] ratios calculated on atomic percent used in the starting solution were 1%, 5%, 10%, 15% and 20%. It was observed that the [N]/[Zn] ratios higher than 20% resulted in degraded films probably due to a reaction of the solution with excess nitrogen. The actual [N]/[Zn] ratios in the film were relatively less than in the solution. The resulting 100 cc precursor solution was sprayed onto the preheated corning and conducting glass (spray deposited fluorine doped tin oxide on corning glass, FTO, with sheet resistance of 10–20 Ω/sq) substrates of size ($2.5 \times 7.5\ cm^2$ and $10 \times 10\ cm^2$) held at optimized substrate temperature of 450 °C through specially designed glass nozzle. The compressed air ($2.3\ kg\ cm^{-2}$) was used as carrier gas at a constant spray rate of $5\ cc\ min^{-1}$. While varying the doping concentration, other preparative parameters such as solution concentration (0.1 M), volume of solution (100 cc), nozzle-to-substrate distance (32 cm) were kept constant for all experiments. The structural properties were studied by a Philips X-ray diffractometer PW −3710 ($\lambda$, 2.2896 Å) using Cr–K$\alpha$ radiation. The morphological characterization of the films was carried out by using SEM (Model: JEOL JSM 6360), Japan. The surface topography of thin films was further analyzed from the AFM images taken by means of the atomic force microscopy (AFM, Digital Instrument, Nanoscope III) operated at room temperature. AFM images were collected in contact mode on a molecular imaging system using a silicon nitride cantilever. All values for feature heights, roots mean square (RMS) surface roughness, and surface area was calculated using digital instruments software. Optical transmission and reflectance measurements were carried out in the wavelength range 350–850 nm using Spectrophotometer Systronic Model-119 & Spectroscopic Reflectometer StellerNet Inc., USA respectively. The specific heat capacity and thermal conductivity was measured by C–T meter made by Teleph Pvt. Ltd., France.

Analytical reagent grade toluene was obtained from s.d. fine Chem. Ltd. Other chemicals such as potassium dichromate ($K_2Cr_2O_7$), sulfuric acid ($H_2SO_4$) and perchloric acid ($HClO_4$) all obtained from Loba Chemie were used with required concentrations without further purification. Solar light was used as a source of illumination. Irradiations at a location of 16°40′37″N 74°815′18″E were started around midday in April, 2009. The photodegradation reactor module consist NZO as a photoanode and stainless steel disc as a cathode at a distance of 0.1 cm. The surface area (circular) of these electrodes in contact with the electrolyte was $64\ cm^2$. The term "bias" was used for the voltage applied between the two electrodes. The NZO electrodes were illuminated from backside (through the transparent FTO substrate), employing solar light with manual inclination and azimuth tracking. The appropriate concentration of toluene was used as model pollutants in water for degradation studies under solar light illumination in the absence and in the presence of NZO photocatalyst. A fixed amount of electrolyte, the major part of which contained in an external reservoir, was recirculated through the photoelectrochemical cells with a constant flow rate of $8.4\ l\ h^{-1}$ (flow velocity $2.92\ cm\ s^{-1}$) using a Gilson MINIPLUS peristaltic pump, France with silicon tubing. Using aliquots withdrawn from the reaction mixture at some intervals, the concentrations of organic impurities in the solutions were determined by measuring the UV–Vis absorbance (extinction) using a 119 SYSTRONICS UV–vis spectrophotometer (for the measurement of full spectra) or a battery powered photometer (NANOCOLOR Model 400D, Machery-Nagel) for outdoor typical single wavelength measurements. The absorbance (extinction) was measured in 1 cm quartz cell at particular wavelength (where maximum absorption peak is observed) for various impurities. Aliquots at various intervals were diluted to record the absorption, whenever necessary (when absorption range exceeds the typical range). Total organic carbon (TOC) concentration represents the mineralization extent of organic substances in water. TOC was measured using the aliquots after acidification with phosphoric acid and purging out IC (inorganic carbon, $CO_2$) by catalytic combustion, using a Photometer model 400D. Aliquots extracted from the solutions at various intervals during the degradation reaction were also used for determining chemical oxygen demand (COD) using the standard method of oxidation with an excess of dichromate in concentrated sulfuric acid by digestion at 140 °C. The concentration of the organic solute was calculated from the dichromate extinction at various wavelengths. The schematic heterogeneous catalysis mechanism is as shown in Fig. 1.

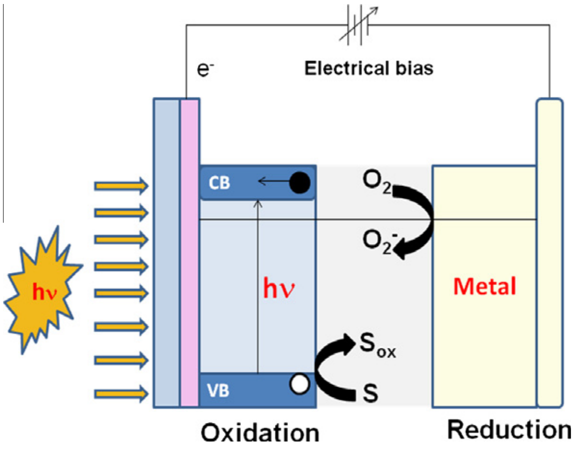

**Fig. 1.** Mechanism of heterogeneous catalysis.

## 3. Results and discussion

### 3.1. Photoelectrochemical (PEC) characterization

Fig. 2 shows the variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) of PEC cell as a function of nitrogen doping concentration. The values of $I_{sc}$ and $V_{oc}$ gradually increases with influence of N doping concentration attaining maximum response ($I_{sc} = 0.508$ mA and $V_{oc} = 0.534$ V respectively) at 10 at.% doping and then decreases for higher doping concentrations. This attributes to the change in metastable N-on-O substitution ($N_O$), which may attract another N to form a $(N_2)_O$ donor or leave the O site to diffuse in the ZnO, at the same time, generate a $V_O$ donor [18]. Generally, nitrogen can be substituted inside the ZnO in two forms: atomic nitrogen on oxygen sites ($N_O$) acting as acceptors and molecular nitrogen on oxygen sites $(N_2)_O$ acting as donors. Formation enthalpy of $(N_2)_O$ is lower than ($N_O$) which leads to n type conduction of NZO thin films. The N—N atoms have strong bonding energy compared to N—Zn bonding energy [19,20]. Upon illumination of junction, the magnitude of $V_{oc}$ increases with negative polarity towards the NZO thin films, indicating cathodic behavior of photovoltage which confirms the films are n-type in nature. The dependence of conduction type on N doping suggests that the concentration of native defects, such as oxygen vacancies ($V_O$) or zinc interstitials ($Zn_i$) is more.