# PHOTOCATALYTIC AND OPTICAL PROPERTIES OF ZINC OXIDE STRUCTURES PREPARED AT DIFFERENT UREA CONCENTRATIONS

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In this study, ZnO samples were synthesized using zinc acetate and urea with a method containing sonication, sol-gel transition and calcination steps. Urea to zinc acetate mole ratio values were changed as 0, 0.5, 1, and 2 and corresponding calcined samples were denoted as UZ-0, UZ-0.5, UZ-1, and UZ-2, respectively. Scanning electron microscopy (SEM) images indicated globular and rod-like structures. Aspect ratios of the nanorods increased as urea to zinc acetate ratio increased from 0 to 1 whereas nanoparticles with sizes of  $70 \pm 20$  nm were observed for UZ-2 sample. Brunauer, Emmett and Teller (BET) surface area values of the samples varied between 9 and 25 m<sup>2</sup>/g and increased as initial urea amount increased. Band gap energies of the samples ranged between 3.24 and 3.29 eV. Four major peaks at about 400, 420, 480 and 530 nm with different intensities were observed in the photoluminescence (PL) spectra of the samples. All the samples removed rhodamine B by both adsorption and photodegradation. The highest visible light induced photodegradation rate was exhibited by UZ-2 sample having the highest surface area and it is attributed to superior charge separation properties of this sample under visible light.

Keywords: ZnO, nanostructures, optical properties, photocatalyst, N-doping

### 1. Introduction

Semiconductor photocatalysts are promising materials for the degradation of the effluents pollutants [1-3]. containing organic Photodegradation mechanism is based on the photogeneration of electrons and holes which mediate the reduction and oxidation degradation reactions of pollutants, respectively. The reaction takes place on the surface of semiconductor photocatalysts exposed to photons having energy equal to or greater than band gap energy of the semiconductors. Once the charge separation occurs, these electrons and holes can react with adsorbed oxygen molecules, surface hydroxyl groups or adsorbed water to form reactive oxygen species, which, then, mineralize the organic pollutants [4-6].

ZnO is one of the semiconductor catalysts that have been commonly investigated due to its low cost, environmentally friendly nature and superior photocatalytic activities [1, 7]. However, because of its wide band gap energy (3.37 eV), visible light photocatalytic activities of ZnO are limited but can be achieved via special methods such as doping, tuning its defect structure, and sensitizing with visible light active dyes or other semiconductors materials [8-10]. More specifically, doping of ZnO with metals such as copper, cobalt, nickel, iron, cadmium and manganese and nonmetals including nitrogen, carbon and sulfur was genuinely shown to promote its visible light induced catalytic activities [10-15]. Among the non-metal dopants, nitrogen was considered to be ideal due to its lower electronegativity, ionic radius similar to that of oxygen, high solubility and low formation

In this study, we employed a modified method comprising of sonication, sol-gel transition and calcination steps to prepare N-doped ZnO using urea as a nitrogen source. Different from the related studies, effect of the initial urea concentration on the morphology, textural, optical and photocatalytic activity properties of the resultant ZnO structures was investigated systematically. N-doping of the sample prepared at the highest urea concentration was detected using XPS spectroscopy and all the samples were shown to have visible light induced photodegradation activities even though no considerable difference in the band gap energies of these ZnO samples was observed.

## 2. Experimental

### 2.1. Materials

Zinc acetate dihydrate (ACS grade, Merck) and urea (ACS-grade, Sigma-Aldrich) were used in the synthesis of ZnO samples. The model dye, rhodamine B (dye content  $\geq$  90%) was purchased from Merck. Fourier transformed infrared (FTIR) spectroscopy grade potassium bromide was employed to prepare pellets for FTIR experiments. All the solutions were prepared using deionized water.

energy [10, 11, 16]. Nitrogen doped (N-doped) ZnO can be prepared by applying wide variety of synthesis routes such as sol-gel, hydrothermal, solvothermal, mechanochemical, chemical vapor deposition, spray pyrolysis and magnetron sputtering techniques, resulted in ZnO structures with diverse chemical and physical properties [2, 17].

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### 2.2. Synthesis of ZnO Samples

Zinc oxide samples were prepared using urea as an additive by following three steps: sonication, sol-gel transition and calcination. First, urea and zinc acetate dihydrate at molar ratios of 0.5, 1 and 2 were dissolved in 10 ml deionized water. In all experiments, 20 mmol zinc acetate dihydrate was used and amount of urea was changed. Clear solutions obtained were sonicated at 50°C for 1 h and gelation was induced upon keeping the solutions in an oven at 120°C for 4 h. Finally, the gels were calcined in a furnace at 550°C for 3 h. Control sample (UZ-0) was prepared without urea by following the same procedure but no sol-gel transition was observed in the second step. ZnO samples prepared at different urea concentrations were denoted as UZ-X where X is the urea to zinc acetate molar ratio.

## 2.3. Characterization of ZnO Samples

Crystal structures of the samples were identified by X-ray diffraction (XRD) on a Philips Xpert-Pro (Panalytical, Almelo, Netherlands) diffractometer with an incident CuK<sub>a</sub> radiation at 1.54 Å. FTIR spectra were taken by using an FTIR-8400S (Shimadzu, Kyoto, Japan) spectrophotometer with 2 cm<sup>-1</sup> resolution. FEI Quanta 250 FEG (FEI Company, Hillsboro, OR) model instrument was used to observe scanning electron microscopy (SEM) images of the samples. Brunauer, Emmett and Teller (BET) surface area values, pore sizes and pore volumes of the samples were determined by taking nitrogen physisorption measurements on an ASAP 2010 (Micromeritics, Norcross, GA) model static volumetric adsorption equipment. Band gap

energies of the samples were calculated based on the diffuse reflectance spectrum data by employing the procedure described elsewhere [18]. The diffuse reflectance spectra of the samples were taken on a UV-2600 (Shimadzu, Kyoto, Japan) model UV-Vis spectrophotometer equipped with an integrating sphere accessory and using BaSO<sub>4</sub> powder as reference material. а (PL) Photoluminescence measurements were conducted on an LS-55 model fluorescence spectrophotometer (Perkin Elmer, Waltham, MA) equipped with a front surface accessory. For all the ZnO samples, excitation wavelength was used as 325 nm. X-ray photoelectron spectroscopy (XPS) of the samples was carried out using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer.

## 2.4. Photocatalytic Activity Measurements

Photocatalytic degradation tests were performed under both UV and visible light by using rhodamine B (RhB) as a model dye. In all experiments, 50 ml dye stock solutions with a concentration of 1x10<sup>-5</sup> M were used and each solution was contacted with 50 mg sample in the dark for 1.5 h to ensure the adsorption equilibrium between the dye molecules and the sample. Next, the solutions were exposed to a visible light source (Osram Eke halogen lamp, 150W) equipped with a 400 nm filter or a UV light source (Osram dulux S blue UVA, 2x9W) for 2 h. 0.5 ml aliquots were taken at certain time intervals and centrifuged at 8000 rpm for 3 min. Absorbance values of the supernatants were measured at 554 nm using a Shimadzu UV-2450 model UV-Vis spectrophotometer.



Fig. 1 - (a) XRD patterns and (b) FTIR spectra of the samples.

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Fig. 2 - XPS (a) survey and (b) high resolution N 1s core spectra of UZ-2.

#### 3. Results and Discussion

Primary structural analyses of the samples were performed using XRD and FTIR spectroscopy techniques. The resultant XRD curves and FTIR spectra of the calcined samples are given in Fig. 1a and Fig. 1b, respectively. In the powder X-ray diffraction patterns of all samples, sharp diffraction peaks at around 31.6, 34.2, 36.1, 47.5, 56.4, 62.6, 67.7 and 69.0 degrees corresponding to wurtzite type ZnO crystal structure with a PDF card number of 80-0074 were observed. Results of the XRD analyses showed that the syntheses of ZnO samples were performed successfully and the addition of urea to zinc source did not change the formation of ZnO crystals. Likewise, calcination of the precursors obtained in urea assisted syntheses based on wet chemistry [16], sol-gel [19] and grinding [20] methods at temperatures above 400°C were also reported to yield ZnO structures.

FTIR spectra of the samples indicated a strong band at about 400-430 cm<sup>-1</sup> and a broad band centered at 3400-3450 cm<sup>-1</sup> in consistent with the FTIR spectra of the ZnO samples reported previously [21, 22]. The former band corresponds to lattice Zn-O vibrations whereas the latter one can be attributed to the vibrations of hydroxyl groups most probably due to the presence of the physically adsorbed water [22-24]. The other weak bands (1635 cm<sup>-1</sup> and 1122 cm<sup>-1</sup>) obtained in the spectra of UZ-0 and UZ-2 indicated small impurity contents of these samples.

The surface atoms and N-doping of the sample prepared at the highest urea concentration, UZ-2, were determined using XPS spectroscopy. XPS survey and high-resolution N 1s core spectra of this sample are given in Fig. 2a and 2b, respectively. In the XPS survey scan, typical Zn 2s, Zn 2p, Zn 3s, Zn 3p, Zn 3d, Zn LMM, O 1s, and O KLL peaks were observed confirming high purity of the sample [25]. N 1s core level spectrum exhibited a small peak at about 399.4 eV indicating the presence of small but detectable number of

nitrogen atoms in ZnO [26, 27]. Considering the reported binding energy of N in zinc nitride ( $\sim$ 396-397 eV), higher binding energy obtained in this study suggested the formation of N-Zn-O bond [27].

SEM images and summary of the morphological of properties the samples are given in Fig. 3 and Table 1, respectively. Globular nanoparticles and nanorods with sizes dictated by urea to zinc ratio were observed clearly indicating the morphogenic effect of urea. Different synthesis procedures performed in the presence of urea were resulted in various morphologies including spongelike structures. distorted hexagons [16], agglomerated nanoparticles [2, 16] and nanorods [19]. Barrett-Joyner-Halenda (BJH) pore volume and BJH average pore size values based on the desorption data of the samples along with BET surface areas are given in Table 1. The surface area values increased as urea concentration increased and correlated with the BJH pore volumes of the samples. Thus, in addition to its morphology directing ability, urea also acted as a porogen, in consistent with the results of the other studies [2, 19].

Diffuse reflectance spectra and Tauc plots of the samples are given in Fig. 4a and 4b, respectively and calculated band gap energy values are given in Table 2. Band gap energies of the samples were found to range between 3.29 eV and 3.24 eV suggesting insignificant effect of nitrogen doping on the band gap of the ZnO structures obtained, similarly to the previously reported results [28, 29]. However, there also exist some studies indicating the reduction in the band gap energy of ZnO upon nitrogen doping [2, 16, 19].

PL spectra of the samples were taken to identify crystal defects of the samples and are given in Fig. 5. All the samples indicated four major peaks at about 400, 420, 480 and 530 nm. The first peak at ~400 nm (3.1 eV) is comparable to the estimated band gap energies of the samples



Fig. 3 - SEM images of (a) UZ-0, (b) UZ-0.5, (c) UZ-1 and (d) UZ-2. Scale bars: (a), (b) and (c) = 1 µm, (d) = 3 µm.

Sample	Major morphology	Average size (nm)	BET surface area (m <sup>2</sup> /g)	BJH pore volume (cm <sup>3</sup> /g)	BJH avg. pore size (Å)
UZ-0	globular & shortrod	70 ± 20 nm diameter 170 ± 50 nm length	9	0.0086	38
UZ-0.5	rod	70 ± 20 nm diameter 300 ± 100 nm length	10	0.0091	39
UZ-1	long rod	50 ± 15 nm diameter 400 ± 100 nm length	13	0.0127	37
UZ-2	globular	70 ± 15 nm diameter	25	0.0349	48

and it is resulted from the recombination of the excitonic band. Considering the experimentally determined energy level of zinc interstitials (Zn<sub>i</sub>), which is 0.22 eV below conduction band (CB), the violet/blue emission peak around 420 nm (2.95 eV) can be assigned to the Zn<sub>i</sub> to valence band (VB) transitions. The positions of extended Zni state and zinc vacancies (Vzn) were suggested to be slightly below Zn<sub>i</sub> state and 0.30 eV above VB, respectively. Therefore, the blue emission peak at ~480 nm (2.58 eV) was proposed to be due to extended Zni state to V<sub>Zn</sub> transitions [30, 31]. The nature of the transitions that manifest as a green emission observed at about 530 nm (2.34 eV) is highly controversial. It was

attributed to oxygen vacancies (V<sub>o</sub>), Zn<sub>i</sub> or antisite oxygen (O<sub>Zn</sub>) defects in different reports [32-34]. However, in a recent study, the green emission was proposed to be due to surface superoxide (O2-) formation rather than crystal defects [35]. One of the most striking difference between the PL spectra of the samples was the decrease in the green emission signal as urea:Zn ratio increased. Additionally, the blue emission at ~420 nm enhanced for the sample obtained at the highest urea concentration, UZ-2.

Table 1

Photocatalytic activities of the samples irradiated by both UV light and visible light were determined after letting the samples to reach



Table 2

Sample	Band gap (eV)	Rate constant (min <sup>.1</sup> ) under UV light	Rate constant (min <sup>-1</sup> ) under visible light
UZ-0	3.27	$\textbf{0.128} \pm \textbf{0.002}$	0.00625 ± 6.78 x 10 <sup>-5</sup>
UZ-0.5	3.27	$0.098\pm0.004$	0.00912 ± 2.25 x 10 <sup>-4</sup>
UZ-1	3.29	$\textbf{0.163} \pm \textbf{0.004}$	0.01056 ± 1.05 x 10 <sup>-4</sup>
UZ-2	3.24	$0.058\pm0.002$	0.01469 ± 1.75 x 10 <sup>-4</sup>



Fig. 5 - PL spectra of (a) UZ-0, (b) UZ-0.5, (c) UZ-1 and (d) UZ-2.



Fig. 6 - (a) UV and (b) visible light photodegradation of RhB in the presence of the ZnO samples subsequent to the adsorption in the dark.



Fig. 7 - First order kinetic plots for (a) UV and (b) visible light photodegradation of RhB in the presence of the ZnO samples.

adsorption equilibrium in the dark. All the samples adsorbed the dye with a similar extent. Approximately, 25 ± 5 % of the initial amount of the dye was adsorbed. Adsorption, UV light and visible light photodegradation kinetic curves are given in Fig. 6. First order kinetic plots and the first order rate constants for the photodegradation processes are presented in Fig.7 and Table 2, respectively. All the samples exhibited both UV light and visible light induced dye photodegradation activities but with different rates. The highest visible light photocatalytic activity was obtained for the sample UZ-2, whereas UZ-0 exhibited the lowest dye

degradation performance. Not surprisingly, the use of urea as an additive in the synthesis was resulted in the enhancement in visible light photocatalytic activity as observed for many N-doped ZnO samples [2, 28, 36-39]. In some of these N-doped ZnO samples, band gap energy values decreased and, hence, superior visible-light photocatalytic performances of these samples were attributed to enhanced absorption of light in visible region and high surface area of the samples [2, 37]. For the other group of N-doped ZnO samples where small shifts in band gap energy were obtained compared to undoped ZnO structures, faster visible light induced photodegradation rates were reported to be due to crystal defects and lower recombination rate of the charge carriers [36, 39]. In the current study, band gap energy values of the samples were calculated to be similar. Thus, it is likely that the defects, which formed intermediate energy levels in band gap might mediate absorption of visible light and effect recombination rate of electron-hole pairs [40]. Additionally, photosensitization effect of rhodamine B might also induce the visible light catalytic activity. In this case, injection of excited electrons of the dye to CB of ZnO can be possible under visible light. Then, these electrons can be captured by shallow traps nearby the CB of ZnO facilitating charge separation [41]. Hence, superior visible light driven photocatalytic activity of UZ-2 is likely to be due to its lower electron-hole recombination rate, in other words, better charge separation efficiency owing to its specific defect structures and dopant levels as well as its highest surface area. Interestingly, UZ-2 exhibited the slowest photodegradation of the dye under UV-light, which could be attributed to the impurities (organic residues) indicated in its FTIR spectrum and most probably effect of these impurities was not so significant under the visible light.

### 4. Conclusions

ZnO structures were synthesized using urea as an additive and effect of the initial urea concentrations on the morphology, textural, optical and photocatalytic properties of the resultant samples was investigated. Globular nanoparticles and nanorods with different aspect ratios observed in the SEM images of the samples clearly indicated morphology directing effect of urea. Increasing initial concentration of urea resulted in increase in the porosity and BET surface area of the ZnO structures. Although N-doping was indicated by a small peak observed in the high-resolution N 1s core spectrum of the sample with the highest initial urea concentration, UZ-2, band gap energy values were obtained to be similar. PL spectra of the samples indicated blue, blue/violet and green emission peaks with different contributions. The green emission peak was observed to decrease as initial urea concentration increased and the blue/violet emission signal associated with Zni enhanced for UZ-2. All the samples adsorbed the dye with a similar extent, and they all exhibited visible light induced photodegradation activities despite no appreciable narrowing in the band gap energies of these ZnO samples was observed. Of the samples, UZ-2 degraded the dye with a faster rate under visible light, which might be attributed to its higher surface area and superior charge separation efficiency.

In conclusion, it was shown that ZnO structures can exhibit visible light driven photocatalytic activity without shifting their band

gap from UV to the visible region. Additionally, it was also demonstrated that morphology, textural, optical, defect, and, hence, photocatalytic properties of ZnO structures can be tuned by changing the synthesis conditions; simply by using different initial urea concentrations.

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