Nitrogen-Implanted ZnO Nanorod Arrays for Visible Light Photocatalytic Degradation of a Pharmaceutical Drug Acetaminophen

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ABSTRACT: The present study focuses on the effects of nitrogen (N) ion implantation in vertically aligned ZnO nanorod arrays (NRAs) and the photocatalytic degradation of acetaminophen. The X-ray diffraction of these NRAs exhibit a wurtzite structure with a predominant (002) diffraction peak that shifts slightly after N-ion implantation. The field emission scanning electron microscopic images of as-prepared NRAs show a length of ~4 μm and diameter of ~150 nm. UV-visible spectroscopy reveals that the band gap of pristine ZnO NRAs decreases from 3.2 to 2.18 eV after N-ion implantation. Under visible irradiation, the N-ion-implanted ZnO catalyst exhibits significant enhancement of the photocatalytic degradation of acetaminophen from 60.0 to 98.46% for 120 min.

INTRODUCTION

Acetaminophen is one of the main active pharmaceutical components of several commercial flu and cold medicines. Acetaminophen is also used in analgesic, antipyretic, and anti-inflammatory drugs for animals and humans. It is also one of the most detectable pharmaceuticals and emerging pollutants in various aqueous environments. It was found that 58–68% of acetaminophen was extracted from the body after therapeutic use. Acetaminophen has been identified worldwide with 6 μgL⁻¹ in a European sewage water treatment effluent, 6.8 μL⁻¹ in a wastewater management plant in Korea, and more than 65 μL⁻¹ in the Tyne River in the UK. When acetaminophen is used in excess, it leads to death and liver failure. To remove acetaminophen in the wastewater environment, innovative and dominant oxidation techniques are required.

In recent years, visible light catalytic degradation is an effective method for the removal of organic pollutants to resolve the above environment problems. Semiconductor-based oxides show excellent photocatalytic activities for the degradation of pollutants in wastewater. Hence, researchers are focusing on visible-light-driven photocatalysts. Semiconductors such as TiO₂, ZnO, Fe₂O₃, WO₃, and CdS are popular photocatalysts that are used for the degradation of organic pollutants. Among these materials, ZnO has created great interest because it has a wide band gap energy (3.2 eV), high exciton binding energy of 60 meV, higher mobility, high stability, and it is environmentally friendly and nontoxic. As ZnO absorbs UV light owing to its wide band gap, efforts have been made to enhance its photocatalytic activity under visible light by doping metal, nonmetal ions, co-doping, and coupling with metal or semiconductors. ZnO has native defects because of Zn interstitials (Zni) and O vacancies resulting in n-type semiconducting behavior. Doping nonmetal ions such as N, C, and S modifies the ZnO nanostructures and shows the promising physical properties especially in the optical properties. It is observed that the band gap reduces with N-ion implantation. Such a reduction is favorable for visible photocatalytic activities. Apart from this, ion implantations are known to create defects and also anneal the oxygen defects depending upon the energy and ion fluencies. Modifications of the ZnO surface through the defect states lead to band narrowing or defect band level to absorb the visible energy. This also induces the different surface defective functionalities in controllable depth and leads to the transformation of effective surface features. Moreover, small formation energy is required for the substitution of O in ZnO and hence N-ion is the most suitable dopant.

There are different chemical and physical methods to prepare N-doped ZnO, such as chemical precipitation,
molecular beam epitaxy, atomic layer deposition, hydrothermal, magnetron sputtering, and ion implantation. Among these, ion implantation is a typical engineering process and commonly used to alter the chemical and physical properties of semiconducting materials. Compared to other doping methods, ion implantation is also a reliable method to introduce impurities into the ZnO. This study reports the synthesis of vertically aligned ZnO nanorod arrays (NRAs) by a simple aqueous solution method and the effect of low-energy N-ion implantation in ZnO. In addition, visible light photocatalytic degradation of acetaminophen in the presence of N-ion-doped ZnO NRAs has been investigated.

RESULTS AND DISCUSSION

Structural, Surface, Morphological, and Optical Studies. The N-ion doping on ZnO NRAs was performed by a low-energy ion beam implantation of 100 keV. The ion fluences implanted in ZnO NRAs are $5 \times 10^{14}$, $1 \times 10^{15}$, $5 \times 10^{15}$, and $1 \times 10^{16}$ ions/cm$^2$ and these samples are hereafter referred to as N–ZnO1, N–ZnO2, N–ZnO3, and N–ZnO4, respectively. Figure 1a displays the X-ray diffraction spectra of pristine and N-ion-implanted ZnO NRAs samples. The diffraction peak at around 34.5° is attributed to the (002) crystal plane of a wurtzite hexagonal ZnO. Absence of additional peaks in the X-ray diffraction (XRD) show that N ion implantations do not form new phases or modify the crystal structure. This implies that the N-ions are either doped in place of O ion sites or occupy the vacancies of O sites without modifying the crystal structure. This is consistent with other studies. However, N-ion implantation is expected to modify the crystallite size, surface morphology, and optical properties. Figure 1b represents a closer view of the (002) plane of all the samples and the intensity of (002) peak decreases with increasing ion fluences. Moreover, the peak position shifts slightly and this indicates doping of N-ions on the ZnO NRAs. As the atomic radii of N (0.146 nm) are higher than those of O (0.138 nm) but smaller than Zn, N ions substitute in the O sites of ZnO. The N-ion substitution increases the lattice distance, which is evident from the XRD. At higher ion fluences, N-ion concentration increases and creation of defects also increases, which result in reduction in the crystalline nature as evident in N–ZnO4. The full width at half-maximum (fwhm) also changes with N-ion implantations. As the defects density increases with ion fluences, strain is caused, which disturbs the long-range order and eventually reduces the crystalline nature manifesting as a reduction in integral peak intensity of the XRD pattern and also change in fwhm. The peak shift reflects the strain caused by ion implantation because of bond expansion or compression and modifies the spacing between the crystallographic planes. Hence, a compressional stress would result in the shift of the peak toward higher 2θ value and tensile stress toward lower 2θ values. The (002) peak shifts toward a higher diffraction angle as the ion influence increases up to N–ZnO3 and decreases for N–ZnO4. This is due to the defect creation over the different ion influences. At a low ion fluence, the implantation leads to bonding of nitrogen with Zn and reduces the lattice distance of ZnO. On increasing the ion fluence, the implantation favors the creation of the Zn intestinal states coupled with oxygen defect sites with loss of crystallinity. Because of the high structural damage in high fluences and the high interaction of N with Zn ions, the peak position blue shifts for the N–ZnO4 samples as compared with N–ZnO3. The change in defect states are confirmed through the photoluminescence (PL) measurements (discussed in the latter part). At a higher ion fluence, N ion concentration increases and the creation of defects also increases, which result in the reduction in crystalline nature. Ion implantation causes the defects and thus modifies the crystalline nature. It also relaxes or anneals the defects, depending upon ion fluences. This small shift in the XRD peak is related to the doping effect and results in defect creation. This shows that the peak position in N–ZnO4 shifts toward a lower 2θ value, which is a signature of the generation of tensile strain.

The top view field-emission scanning electron microscopy (FESEM) images (Figure 2) clearly show uniform vertically aligned ZnO NRAs for all the samples. From the cross-sectional images, the average length and diameter of the ZnO NRAs are found to be $\sim 4$ μm and 200–250 nm, respectively.

Figure 3 represents the transmission electron microscopy (TEM) (a,d) and high-resolution TEM (HRTEM) (b,e) images of pristine ZnO and N–ZnO4. The TEM image of pristine ZnO exhibits a smooth surface. However, N–ZnO4 shows change in the surface roughness produced by ion implantation. By increasing the N-ion fluences, the surface roughness increases and reduces the crystalline nature of ZnO, which is consistent with the XRD pattern reported above. A selected area electron diffraction (SAED) shows a clear ring pattern of pristine ZnO NRAs (Figure 3c), indicating the crystalline nature. In the case of N–ZnO4 (Figure 3f), the crystallinity decreases because of the ion implantation. Further, the presence of N on the ZnO NRAs lattice is evident from the PL and X-ray photoelectron spectroscopy (XPS) studies, which is discussed in the following sections.

Figure 4a represents the UV–vis spectra of pristine and N-ion-implanted ZnO NRAs. The band edge of pristine ZnO is observed at 380 nm and this optical edge shifts toward a higher wavelength, which clearly indicates that the absorption shifts
from the UV to the visible region. The band gap energy was calculated by using a K-M (kubelka-munk) plot. The band gap energy of N\textsuperscript{−}ZnO\textsubscript{1}, N\textsuperscript{−}ZnO\textsubscript{2}, N\textsuperscript{−}ZnO\textsubscript{3}, and N\textsuperscript{−}ZnO\textsubscript{4} samples are 2.57, 2.28, 2.25, and 2.14 eV, respectively. The band gap energy decreases with increasing the N-ion fluences.

The PL analysis of pristine ZnO and N-ion-implanted ZnO NRAs at room temperature are shown in Figure 4b. The spectra consist of two dominant emission peaks around 365−385 nm and 500−650 nm corresponding to electron recombination from the near band edge to the valence band (VB) and oxygen vacancies, respectively.\textsuperscript{24,25} The near band edge emission intensity was found to decrease with increasing N-ion fluences. This may be attributed to change in the unit cell upon N ion implantation as evidenced from XRD analysis (decrease in intensity and increase in fwhm (Figure 1b). On increasing the N implantation to 1 × 10\textsuperscript{16} ions/cm\textsuperscript{2} (N−ZnO\textsubscript{4}), new emission peaks emerge at 415 and 440 nm because of formation of Zn\textsubscript{n} levels below the conduction band (CB).\textsuperscript{25} The defect emission of around 500−650 nm was also found to decrease with increase in N implantation. The decrease in defect emission intensity represents substantial decrease of electron recombination in oxygen vacancies. Figure S1a−e shows the possible mechanism of charge transfer and separation in the ZnO and N-ion-implanted ZnO NRAs. When light is incident on ZnO, excited electrons transfer from VB to CB and these electrons can recombine with holes quickly, which is shown in Figure S1a. With the increasing of N-ions in ZnO NRAs, a Zn\textsubscript{n} state is formed below the CB and an N state is formed above the VB because of the incorporation of N ions in ZnO NRAs (Figure S1b−e). The defect emissions of around 500−650 nm are also found to decrease with increase in N-ion implantation. The decrease in defect emission intensity represents the substantial decrease of electron recombination in oxygen vacancies. The N-ions implanted are expected to occupy the O vacancies and also bond with the Zn ions.

The PL lifetime spectra of ZnO and N−ZnO\textsubscript{4} NRAs were measured with excitation wavelengths of 395 and 460 nm and are presented in Table S1 in Supporting Information. PL carrier lifetime spectra show that the average lifetime of ZnO and N−ZnO\textsubscript{4} NRAs are 0.98454 and 0.0827 ns, respectively. These results clearly show that the average lifetime was found to decrease for the N-ion-implanted ZnO sample.

\[ F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  

\[ \tau_{avg} = \frac{\sum_i A_i \tau_i}{\sum_i A_i} \]  

where \( A_1 \) and \( A_2 \) are the corresponding amplitudes, \( \tau_1 \) and \( \tau_2 \) are the fast and slow decay times, and \( \tau_{avg} \) is the average lifetime.

PL carrier lifetime spectra for the pristine and N−ZnO\textsubscript{4} samples were measured with excitation wavelengths of 395 and 460 nm and are presented in Table S1 in Supporting Information. PL carrier lifetime spectra show that the average lifetime of ZnO and N−ZnO\textsubscript{4} NRAs are 0.98454 and 0.0827 ns, respectively. These results clearly show that the average lifetime was found to decrease for the N-ion-implanted ZnO sample.

Figure 2. FESEM images of ZnO NRAs and N-ion-implanted ZnO NRAs with various fluences (insets show the cross-sectional images).

Figure 3. TEM, HRTEM, and SAED patterns of pristine ZnO (a−c) and N−ZnO\textsubscript{4} (d−f).
Figure 4. (a) UV−vis and (b) PL spectra of pristine ZnO and N-ion-implanted ZnO NRAs with different fluences, (c) XPS core-level spectra of Zn 2p, (d) O 1s, (e) N 1s of N−ZnO4, and (f) VB spectra of ZnO and N−ZnO4.

Figure 5. (a) Photocatalytic degradation efficiency of acetaminophen under sunlight irradiation, (b) plot of irradiation time vs ln(C0/C), (c) reusable performance of N−ZnO4, and (d) effect of scavengers on the photocatalytic degradation of acetaminophen in the presence of N−ZnO4.
XPS measurement was carried out to know the chemical state of Zn, O, and N species in N-ion-implanted samples. Figure 4c represents the individual Zn 2p XPS spectra of pristine ZnO and N–ZnO4. Zn 2p1/2 and Zn 2p1/2 binding peaks are observed at 1019.41 and 1042.41 eV, respectively.27,28 This result indicated the existence of a divalent oxidation state in both pristine and N-implanted ZnO samples. For the N–ZnO4 sample, the Zn 2p1/2 and Zn 2p1/2 peaks showed a slight chemical shift in binding energy compared to pristine ZnO because of N-ion implantation.

Figure 4d illustrates the O 1s core-level spectrum fit in three peaks.29 The peaks at 529.9 eV were mainly assigned to the oxygen coordinated with Zn atoms (Zn–O). The peak at 531.1 eV was attributed to the oxygen adsorbed on the sample surface and the peak at 532.2 eV corresponds to the water molecules on the surface.

Figure 4e shows the N 1s spectra of the N-ion-implanted ZnO sample. In the spectra, the binding energy of 404 eV was not observed, which clearly suggested that N molecules were not incorporated with ZnO crystal by the ion implantation method. In N 1s spectra, the binding energy was observed at 399.8 eV, which suggests that the N atom was partially replaced with the oxygen atom in the ZnO crystal.30 The binding energy of N in zinc nitride at (396–397 eV), the greater binding energy at 398.8 eV should be related to the formation of N–Zn–O bonds. Hence, it is reasonable that the N 1s binding energy at 399.8 eV was observed (O–Zn–N bond), which is higher than that at 396–397 eV (N–Zn–N bond).31

The VB values of pristine ZnO and N–ZnO4 are calculated as 2.89 and 2.36 eV, respectively, using the VB XPS spectra as shown in Figure 4f. After N-ion implantation, the VB value decreases to 2.36 eV extended defect states because of N implantation. The CB values have been calculated from the following equation

\[ E_{VB} = E_{CB} + E_g \]  
(3)

where \( E_{VB} \) is the value of VB, \( E_{CB} \) is the value of CB, and \( E_g \) is the band gap energy of the material.

Photocatalytic Activity. Figure 5a shows the photocatalytic degradation of acetaminophen (20 ppm) under sunlight for 120 min using pristine ZnO NRAs and N-ion-implanted ZnO NRAs with various fluences. Before photocatalytic degradation, the suspensions are placed in the dark for 20 min to ensure adsorption/desorption equilibrium. The calculated degradation efficiency of pristine ZnO NRAs is 41.53%. On the other hand, the N-ion-implanted samples such as N–ZnO1, N–ZnO2, N–ZnO3, and N–ZnO4 exhibit degradation efficiencies of 60, 90.61, 94.6, and 98.46%, respectively. The degradation efficiency increases by increasing the N-ion doping concentration in ZnO. Figure 5b shows a linear relationship between degradation rate versus irradiation time, indicating that the degradation of acetaminophen follows a pseudo-first-order kinetics. The pseudo-first-order equation can be represented as

\[ \ln(C_0/C) = kt \]  
(4)

where \( C_0 \) is the initial concentration of acetaminophen, \( C \) is the final concentration after photo-irradiation, \( t \) is the photodegradation time, and \( k \) is the first-order rate constant. The N-ion-implanted samples exhibit excellent photocatalytic activities. The calculated apparent rate constants are 0.008, 0.02, 0.024, and 0.038 min\(^{-1}\) for N–ZnO1, N–ZnO2, N–ZnO3, and N–ZnO4, respectively. Moreover, the rate constant of N–ZnO4 NRAs is 10-fold higher than that of pristine ZnO NRAs (0.0045 min\(^{-1}\)), indicating that N–ZnO4 shows a better photocatalytic activity than pristine ZnO.

Reusability is a major factor in photodegradation as it is difficult to separate a powder-like catalyst from the pollutant. Instead, using a film-like catalyst makes removal from the pollutant relatively easy. Figure 5c presents the reusability performance of N–ZnO4 NRAs. The degradation efficiency decreases from 98.46 to 97.63% after five repeated cycles. The slight decrease in the photocatalytic activity during the recycling process may be due to the small amount of residual acetaminophen present on the catalyst surface.

Effect of scavengers on acetaminophen degradation in the presence of N–ZnO4 catalyst is shown in Figure 5d. Mainly, the reactive species involved in the photodegradation process are superoxide anion radicals (O\(_2^−\)), hydroxyl radicals (OH\(^−\)), electrons (e\(^−\)), and holes (h\(^+\)). Benzoquinone (BQ, 1 mmol), ethylenediaminetetraacetic acid (EDTA, 1 mmol), and methanol (1 mmol) were used as O\(_2^−\), h\(^+\), and OH\(^−\) scavengers. Without adding a scavenger, the degradation efficiency is 98.4%. After adding scavengers such as BQ, EDTA, and methanol, the degradation efficiencies decrease to 28.52, 65.6, and 78.36%, respectively. These results clearly reveal that O\(_2^−\) played a major role in acetaminophen degradation.

Semiconducting materials such as TiO\(_2\) and ZnO have been widely studied for their photocatalytic activities. Owing to their wide band gaps, these materials are inactive in the visible region. The doping of nonmetals such as N, S, and F with ZnO shifts the light absorption from the UV region to the visible region. Figure 6 shows the schematic diagram of the mechanism of acetaminophen degradation under visible light in the presence of N-ion-implanted ZnO NRAs. The N-ion implantation in the ZnO lattice leads to the formation of a new energy state, that is, the N 1s band is observed above the O 1s of VB and shifted the band gap to the visible region, which is evident from the absorption spectra (Figure 4a).

The degradation efficiency of pristine ZnO NRAs was 41.53% and those of N-ion-implanted samples such as N–ZnO1, N–ZnO2, N–ZnO3, and N–ZnO4 were 60, 90.61, 94.6, and 98.46%, respectively. ZnO NRAs possess a higher band gap (3.17 eV) and are only active in the UV portion of the visible region. The doping of nonmetals with ZnO shifts the light absorption from the UV region to the visible region.
N-ion implantation in ZnO NRAs creates localized states closer to the VB associated with implanted N-ions (Figure S1b in the Supporting Information). These states are active under the visible region of sunlight. Thus, N-ion-implanted ZnO NRAs are active in both UV and visible regions of sunlight and relatively more numbers of electrons (compared to pristine ZnO NRAs) are excited to CB and get transferred to dye molecules, resulting in faster degradation.

On further increasing the N-ion implantation dosage (N−ZnO4), the localized donor state associated with the N-ion transferred into extended states and shifts the VB position and reduces the band gap as seen from VB spectra (Figure 4f). These defect states (N and Zn) reduce the band gap substantially down to 2.14 eV and transform the N−ZnO4 sample to highly active under the visible region (Figure S1e in Supporting Information). Further, high N-ion implantation favors formation of zinc interstitial levels formed below the CB. PL carrier lifetime measurement carried out at 390 and 460 nm revealed that both the transition from VB to CB and Znii and N-via electron transfer to the dye molecule via band edge and Zn levels (Figure 6). These results are well in correlation with reactive oxygen species (ROS) (O₂•-) production as the generated O₂•- radicals were found to increase with N-ion implantation owing to enhanced supply of electrons to the surface.

CONCLUSIONS

Vertically aligned ZnO NRAs were synthesized by a chemical bath deposition method and implanted with a low energy of 100 keV N-ions at various fluences. These N-ion-implanted ZnO NRAs exhibit significant visible light absorption owing to the presence of Zn−N bonding and defects. This enhances the photocatalytic degradation of acetaminophen, attributed to the effective separation of photoinduced electrons and holes. After five repeated cycles, there is no substantial decrease in the degradation efficiency, indicating the high stability of the catalyst. These results infer that O₂•- is the main reactive species for effective acetaminophen degradation.

EXPERIMENTAL SECTION

Materials. Zinc nitrate (Zn(NO₃)₂) and hexamethylene-tetramine (HMTA) were purchased from Sigma-Aldrich. All other reagents were of analytical grade and used as received without any further purifications.

Fabrication of Vertically Aligned ZnO NRAs. A two-step process was adopted to synthesize ZnO NRAs. In the first step, a ZnO seed layer (buffer layer, thickness 150 nm) was deposited via DC sputtering on a precleaned glass substrate. In a second step, to grow vertically aligned ZnO NRAs, aqueous solutions of Zn(NO₃)₂ (25 mM) and HMTA (25 mM) were mixed in an experimental flask. The seed layer-deposited substrate was submerged into the flask, sealed, and maintained at 95 °C for 24 h. Finally, the ZnO NRAs grown on the substrate were rinsed with distilled water and ethanol and then dried at 100 °C in the air for 60 min.

Fabrication of N-Ion-Implanted ZnO NRAs. The N-ion doping on ZnO NRAs was performed by using the low-energy ion beam facility at the Inter University Accelerator Centre, New Delhi. This experiment was carried out at room temperature with an ion energy of 100 keV and ion fluences of 5 × 10¹⁴, 1 × 10¹⁵, 5 × 10¹⁵, and 1 × 10¹⁶ ions/cm² and the samples are referred to as N−ZnO1, N−ZnO2, N−ZnO3, and N−ZnO4, respectively. These N-ion-implanted ZnO-NRAs are not subjected to the annealing step to recover the crystalline damage or anneal the defects as defects play a major role in the photocatalytic properties of the material.

Characterization. An XRD analysis was performed using an X'Pert PRO diffractometer (PANalytical) using Cu Kα radiation. FESEM pictures were obtained using an FEI-Quanta-FEG 250 microscope. A Philips Tecnai 20 transmission electron microscope was used to record the images of the samples. XPS was performed using a Thermo Scientific instrument equipped with an Al K Alpha X-ray source. The PL spectra of the ZnO NRAs were measured with an excitation wavelength of 325 nm. UV−vis spectra were obtained using a JASCO-V660 spectrophotometer.

Photocatalytic Experiment. In a typical procedure, vertically aligned ZnO NRAs (10 × 10 mm) are immersed in a 20 ppm acetaminophen solution (5 mL). The solution is kept in the dark for 30 min in order to attain adsorption/desorption equilibrium and irradiated under visible light for various time intervals. The acetaminophen degradation is determined by using UV−vis analysis. The degradation efficiency is calculated by the following equation.

% of degradation = (C₀ − Cᵣ)/C₀ × 100

where C₀ is the absorption at zero time and Cᵣ is the absorption at a given time t.¹⁴

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00557.

Possible mechanism of charge transfer of bare ZnO and N-ion-implanted ZnO NRAs with different fluences; the PL lifetime spectra of bare ZnO and N−ZnO4 NRAs at two different excitonic wavelengths of 390 and 460 nm; decay values of ZnO and N−ZnO4 ZnO NRAs; and XPS core-level spectra of O 1s (PDF)

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Notes

The authors declare no competing financial interest.

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