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COMMUNICATION

Ce^{3+} impregnated ZnO: A highly efficient photocatalyst for sunlight mediated mineralization

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The surface of pre-synthesized hexagonal ZnO was tailored by Ce^{3+} states. The modified catalyst inveterate enhanced spectral response in the visible region and substantially quenched the luminescence without altering the morphology of ZnO support. Compared to bare ZnO, the synthesized catalyst exhibited significant high activity both for degradation and mineralization of 2-chlorophenol (2-CP) in sunlight exposure.

Heterogeneous photocatalysis is a versatile approach as it is associated with the complete conversion of organic carbon to CO_2 without leaving any secondary intermediates. The affluent availability of nontoxic photocatalysts such as TiO_2 and ZnO makes this approach more attractive for environmental remediation especially decontamination of water.[1-9]

ZnO, with the bandgap of 3.2 eV, is an important substitute of TiO_2 and sometimes preferred due to its higher photon absorption cross section.[10-12] However, ZnO suffers the problems of fast recombination rate and low stability under illumination. It is well established that the photocatalytic activity and the stability of ZnO can be enhanced by modifying its surface.[2, 13, 14] Being renewable, the use of sunlight as an excitation source, for the generation of highly energetic reactive radicals, is a conspicuous option and can expand the scope of this technology. However, the non-availability of sunlight active photocatalysts limits the use of this cheap natural photon source in photocatalysis. Therefore, for the future and widespread commercial use of this technology, it is highly desired to develop either new sunlight responsive active photocatalysts or modify the existing active photocatalysts for better sunlight response and activity. Various strategies are reported in the literature to make ZnO, responsive in the visible region.[2] These strategies include metal ion doping, composite formation, surface modification by metal impregnation and insertion of non-metals such as S and N. Several reports are available in the literature to enhance the spectral response and photocatalytic activity of ZnO by using Ce^{3+} and Ce^{4+} ions however, these approaches are either based on the composite

formation or inserting (doping) the Ce^{3+} or Ce^{4+} ions (Ce$_x$Zn$_{1-x}$O) in the lattice of ZnO.[15]

In this communication, considering photocatalysis as surface phenomenon, we adopted an innovative approach for suppressing the undesired $e^-\square$ h^+ pair recombination, improved absorption of photons in the visible region and enhanced photocatalytic activity without disturbing the lattice of ZnO. The impregnated Ce^{3+} ions instead of being inserted into the lattice reside at the surface of ZnO by sharing the singly charged surface oxygen to form Zn^{2+}-O-Ce^{3+} type structures.

The comparison of the solid state absorption spectra of bare and 10% Ce^{3+} impregnated ZnO powders is presented in Fig. 1(a), where compared to pure ZnO, an increased absorption in the visible region (400-510 nm) can be observed. The appearance of two absorption edges in the graphical evaluation of bandgap (Fig. 1(b)), the major absorption edge at ~3.1 eV that represents the ZnO support while the additional edge at ~2.4 eV predict that Ce^{3+} entities deposit layer-by-layer at the surface of ZnO to form surface bound Ce$_2$O$_3$. As presented in Fig. 1(c), the presence of surface Ce^{3+} entities significantly suppresses the luminescence of pure ZnO, which indicate the enhanced lifetime of excited states. The intensity of the characteristic bands of ZnO at 382 nm, 429 nm and 505 nm[16] is decreased by ~68%, ~100% and ~50% respectively, which specifies that the presence of Ce^{3+} significantly affects the bandgap, Zn interstices and surface oxygen (Zn-O$^-$) vacancies. The depletion of surface oxygen (the band at 505 nm), for Ce^{3+} impregnated ZnO, as evidenced by PL spectra, supports the sharing of surface oxygen by the impregnating Ce^{3+} with Zn^{2+}.

The SEM analysis Figure S1 (supplementary details) revealed that the surface deposition of Ce^{3+} do not alter the morphology of hexagonal ZnO support and the incoming Ce^{3+} ions are evenly distributed on ZnO surface. Noticeably, the diminishing of sharp edges of the hexagonal ZnO particles in Ce^{3+} impregnated powder further verifies the homogeneous distribution of Ce^{3+} entities. The XRD pattern of Ce^{3+} impregnated ZnO is presented in Figure S2

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(supplementary details). The major reflections at 2θ values of 31.957, 34.603, 36.437, 47.711, 56.758, 63.012, 68.098, 69.236, 72.714, and 77.102 were matched with hexagonal ZnO (JCPDS-36-1451). The appearance of reflection at 2θ = 28.85°, represented the hexagonal Ce_2O_3 (002) phase (JCPDS-23-1048). The shifting of the observed reflection at 2θ = 28.85° by 0.6 degrees compared to 2θ = 29.45° (JCPDS-23-1048) confirms the existence of Ce_2O_3 as surface bonded entity. The other reflections due to surface Ce_2O_3 are entrapped in high intensity ZnO peaks. The calculated crystallite size of the surface Ce_2O_3, as evaluated by the extrapolation of reflections at 2θ = 28.85°, was ~6.6 nm. The change in the oxidation state of Ce^{3+} was not evidenced.
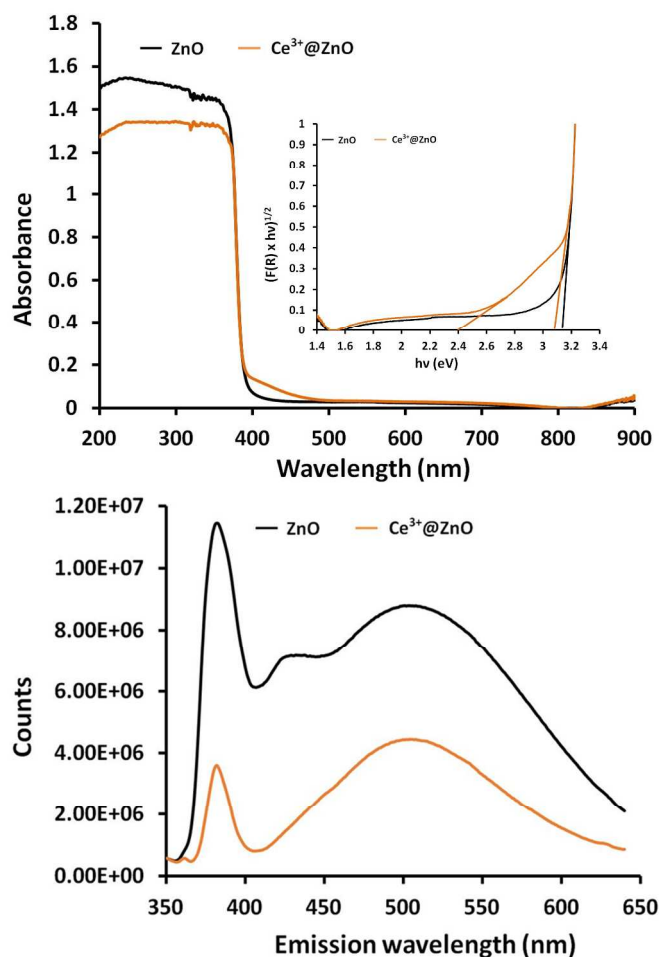

Fig. 1. Comparison of (a) solid state absorption spectra (b) graphical evaluation of bandgaps (c) PL spectra of bare and Ce^{3+} impregnated hexagonal ZnO.

The photocatalytic activity of the synthesized Ce^{3+} impregnated ZnO, in comparison to bare ZnO, was evaluated for the degradation and mineralization of 2-chlorophenol (2-CP). The optimized amount (100 mg) was suspended in 100 cm^3 of 30 ppm solution. The catalyst/2-CP suspension was exposed to sunlight in a glass reactor and the progress of the reaction was monitored by analyzing the samples by HPLC and TOC for the degradation (loss of aromaticity)

and mineralization (conversion to CO_2 and H_2O) progress respectively, at regular interval of time. Along with the monitoring of decrease in 2-CP concentration, HPLC analysis was also used for the estimation of intermediates formed during the degradation process. The comparison of HPLC degradation profiles of 2-CP in the sunlight exposure over bare and Ce^{3+} impregnated ZnO is presented in Figure S3 (supplementary details). The Ce^{3+} loaded catalyst showed higher activity for the degradation of 2-CP compared to bare ZnO. For bare ZnO, 2-CP is degraded with the formation of high concentration of intermediates compared to impregnated catalyst where the simultaneous degradation of 2-CP substrate as well as intermediates was observed.

The percentage degradation of 2-CP as a function of sunlight exposure time is presented in Fig. 2 (a). In the initial 20 minutes of sunlight exposure, compared to ~40% 2-CP degradation for bare ZnO, ~86% of 2-CP substrate was removed in the presence of Ce^{3+} loaded ZnO. The impregnated catalyst completely (≥ 99.5%) degraded 2-CP substrate in 90 minutes of exposure while for bare ZnO ~95% of 2-CP was removed in 150 minutes. Compared to impregnated catalysts, a low TOC removal, as presented in Fig. 2 (b), was observed for bare ZnO. Compared to ~ 98% TOC removal for Ce^{3+} loaded catalyst in 150 minutes of exposure, 49% organic carbon removal was observed for bare ZnO, which was even lower than that observed for Ce^{3+} impregnated catalyst in 20 minutes of exposure.
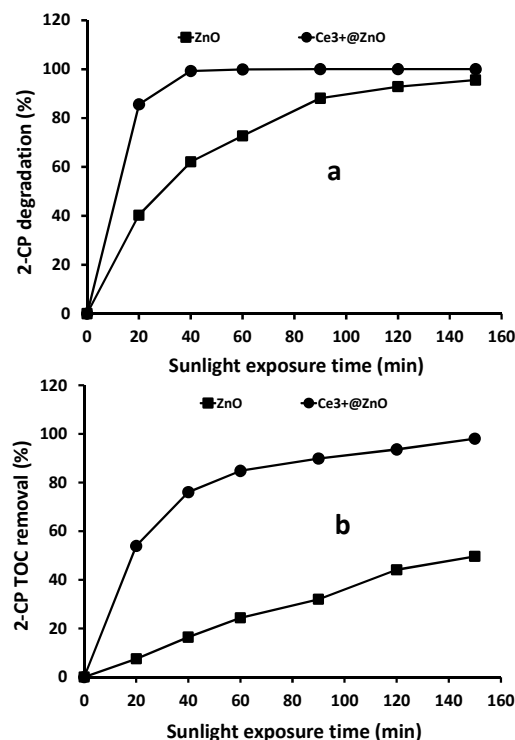

Fig. 2. Comparison of (a) HPLC based percentage degradation (b) TOC removal of 2-NP over bare and Ce^{3+} impregnated hexagonal ZnO.

The comparison of degradation and TOC removal profiles of 2-CP (Fig. 2 (a), (b)) clearly elaborates that although ZnO is capable

of degrading 2-CP in the natural sunlight however, it fails to carry out efficient mineralization (total organic carbon removal). On the other hand, Ce^{3+} impregnated catalyst showed excellent ability of simultaneous degradation and mineralization of 2-CP substrate. ZnO is a wide bandgap (3.1 eV) photocatalyst and can harvest only 3-5% of total incident photons (UV region) of the sunlight. Another negative aspect associated with ZnO is the high recombination of charge carriers. Therefore, it fails to deliver the photo-excited electrons to reductants thus a significant number of photons are lost in the recombination process. The significantly high simultaneous removal of 2-CP substrate and intermediates led to the conclusion that a "trap" and "transfer" synergy exist between ZnO and impregnated Ce^{3+} states.

The rapid degradation and mineralization of 2-CP substrate suggest the involvement of superoxide anion radicals both in the degradation and mineralization process however, further investigation is needed in this regard. The investigations are underway in our laboratories and the results will be reported in detail. The anticipated plausible mechanism of 2-CP mineralization is presented in the *scheme 1*.
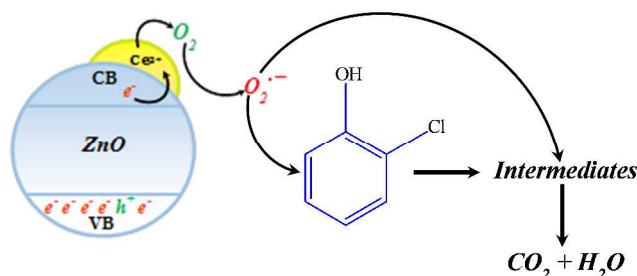
Scheme 1. The possible mechanism of 2-CP mineralization

The photocatalytic activity of the synthesized catalyst was also evaluated in the visible portion of the sunlight by using Pyrex glass as UV filter. A sustained activity of the catalyst was observed for Ce^{3+} impregnated catalyst compared to ZnO where a substantial decrease in the degradation of 2-CP was observed.

Conclusions

The surface presence of Ce^{3+} ions not only suppresses the unwanted e^--h^+ recombination in ZnO but also improves the delivery of captured electrons to reductants that enhances the photocatalytic degradation of 2-CP substantially in sunlight exposure. It is hoped that after detailed investigation, the current catalyst will be a significant addition in the existing collection of photocatalysts.

Notes and References

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Synthesis and characterization of Ce^{3+} impregnated ZnO photocatalyst

Ce^{3+} modified ZnO catalyst was synthesized by impregnating the pre-synthesized hexagonal ZnO. In a representative synthesis, the precisely weighed amount of ZnO was added to the $Ce(NO_3)_3.6H_2O$ solution containing 10% Ce^{3+} ions with respect to the amount of ZnO. After drying the suspension at 120°C, the nitrates were decomposed at 200°C. As per our observation, elevated temperature beyond 200°C significantly affect the uniformity of the synthesis procedure. The dried powder was calcined at 500°C for use in photocatalytic studies.

The solid-state absorption and diffuse reflectance spectra (DRS) of bare and Ce^{3+} impregnated ZnO catalysts were recorded by Perkin Elmer UV-visible diffuse reflectance spectrophotometer in 190-900 nm range. DR spectra were further manipulated to evaluate the absorption edges by plotting $(F(R) \times h\upsilon)^{1/2}$ versus $h\upsilon$ (photon energy, eV). *HORIBA Scientific (*Jobin Yvon *Fluoro Log 3),* France, *macro PL system* was used to record the photoluminescence spectra of bare and Ce^{3+} modified ZnO powders at 325 nm excitation wavelength. The emissions were recorded from 350-650 nm. The powder XRD patterns of bare and Ce^{3+} impregnated powders were recorded by Xpert x-ray powder diffractometer (Philips PW1398) with Cu $K\alpha$ radiation source from 20º to 80º (2θ) with a step time of 3 seconds and step size of 0.05º. Scherer's equation was applied on main reflections to evaluate the crystallite size of various phases. The changes in the morphology of ZnO base and the surface presence Ce^{3+} species were examined by Field Emission Scanning Electron Microscope (JEOL JSM 6490-A).

Photocatalytic studies

The photocatalytic activity of bare and Ce^{3+} impregnated ZnO in sunlight irradiation was performed by exposing 100 cm^{-3} of 30 ppm of 2-CP solution containing the optimized amount (100 mg) of catalyst. The optimization of catalyst loading was performed by exposing the catalyst-2-CP suspensions (100 cm^{-3}) having different catalyst loadings ranging from 10 to 500 mg for a fixed period of 30 minutes. The degradation curve lost linearity without significant change in the degradation beyond 100mg/100 cm^{-3} catalyst loading therefore; the experiments were performed with 100 mg catalyst loading. . All the experiments were performed in the sunlight illumination of $1000\pm100 \times 10^{-2}$ LUX and fixed period of the daylight. The progress of degradation process was monitored by drawing the samples after every 20 minutes in the first hour and after 30 minutes in the next 1.5 hr. The catalyst was removed by using 0.20μm Millipore filter. The collected samples were analyzed by high performance liquid chromatography (HPLC) HPLC, (SPD-20A, Shimadzu Corporation, Japan) using 60:40 Methanol-water mixture as solvent and c18 column. Based on peak response, a 254 nm was selected for analysis. Thermo scientific, USA, ion chromatograph, Dionex (ICS-5000 + EG Eluent Generator), was used to measure the released ions during photocatalytic process. TOC-VCPH total carbon analyzer

supplied by Shimadzu Corporation, Japan, measured total Organic Carbon (TOC) of the samples.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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