

# Ce<sup>3+</sup> impregnated ZnO: a highly efficient photocatalyst for sunlight mediated mineralization†

Cite this: *RSC Adv.*, 2014, 4, 16043

Received 6th January 2014  
Accepted 10th March 2014

DOI: 10.1039/c4ra00097h

www.rsc.org/advances

Iqbal M. I. Ismail,<sup>ab</sup> M. Aslam,<sup>a</sup> T. Almeelbi,<sup>ac</sup> S. Chandrasekaran<sup>a</sup> and A. Hameed<sup>\*ad</sup>

The surface of pre-synthesized hexagonal ZnO was tailored by Ce<sup>3+</sup> states. The modified catalyst inveterate enhanced spectral response in the visible region and substantially quenched the luminescence without altering the morphology of the 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<sub>2</sub> without leaving any secondary intermediates. The affluent availability of non-toxic photocatalysts such as TiO<sub>2</sub> and ZnO makes this approach more attractive for environmental remediation, especially decontamination of water.<sup>1–9</sup>

ZnO, with a bandgap of 3.2 eV, is an important substitute for TiO<sub>2</sub> and sometimes preferred due to its higher photon absorption cross section.<sup>10–12</sup> 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.<sup>2,13,14</sup> 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 wide-spread commercial use of this technology, it is highly desirable 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.<sup>2</sup> 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<sup>3+</sup> and Ce<sup>4+</sup> ions. However, these approaches are either based on composite formation or on inserting (doping) the Ce<sup>3+</sup> or Ce<sup>4+</sup> ions (Ce<sub>x</sub>Zn<sub>1-x</sub>O) in the lattice of ZnO.<sup>15</sup>

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

The comparison of the solid-state absorption spectra of bare and 10% Ce<sup>3+</sup> 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 and the additional edge at ~2.4 eV, predicts that Ce<sup>3+</sup> entities deposit layer-by-layer at the surface of ZnO to form surface bound Ce<sub>2</sub>O<sub>3</sub>. As presented in Fig. 1(c), the presence of surface Ce<sup>3+</sup> entities significantly suppresses the luminescence of pure ZnO, which indicates the enhanced lifetime of excited states. The intensity of the characteristic bands of ZnO at 382 nm, 429 nm and 505 nm<sup>16</sup> is decreased by ~68%, ~100% and ~50%, respectively, which specifies that the presence of Ce<sup>3+</sup> significantly affects the bandgap, Zn interstices and surface oxygen (Zn-O<sup>-</sup>) vacancies. The depletion of surface oxygen (the band at 505 nm) for Ce<sup>3+</sup> impregnated ZnO, as evidenced by PL spectra, supports the sharing of surface oxygen by the impregnating Ce<sup>3+</sup> with Zn<sup>2+</sup>.

<sup>a</sup>Centre of Excellence in Environmental Studies (CEES), King Abdulaziz University, Jeddah 21589, Saudi Arabia. E-mail: afmuhammad@kau.edu.sa

<sup>b</sup>Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

<sup>c</sup>Department of Environmental Sciences, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

<sup>d</sup>National Centre for Physics, Quaid-e-Azam University, Islamabad 44000, Pakistan

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra00097h

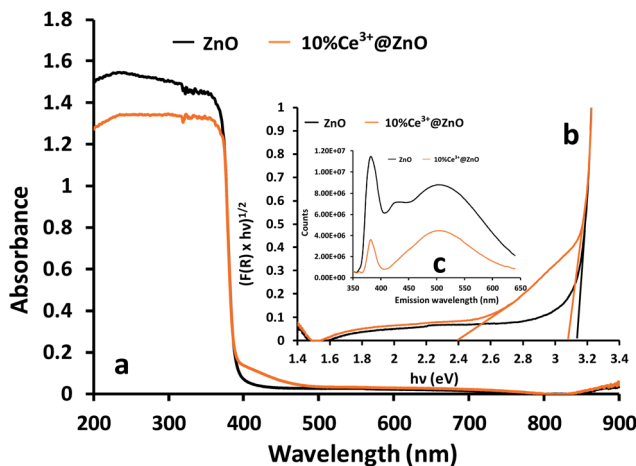


Fig. 1 Comparison of (a) solid state absorption spectra, (b) graphical evaluation of bandgaps, (c) PL spectra of bare and  $\text{Ce}^{3+}$  impregnated hexagonal ZnO.

The SEM analysis (Fig. S1, ESI<sup>†</sup>) revealed that the surface deposition of  $\text{Ce}^{3+}$  does not alter the morphology of the hexagonal ZnO support and the incoming  $\text{Ce}^{3+}$  ions are evenly distributed on the ZnO surface. Noticeably, the diminishing of sharp edges of the hexagonal ZnO particles in  $\text{Ce}^{3+}$  impregnated powder further verifies the homogeneous distribution of  $\text{Ce}^{3+}$  entities. The XRD pattern of  $\text{Ce}^{3+}$  impregnated ZnO is presented in Fig. S2 (ESI<sup>†</sup>). The major reflections at  $2\theta$  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  $2\theta = 28.85^\circ$  represented the hexagonal  $\text{Ce}_2\text{O}_3$  (002) phase (JCPDS-23-1048). The shifting of the observed reflection at  $2\theta = 28.85^\circ$  by 0.6 degrees compared to  $2\theta = 29.45^\circ$  (JCPDS-23-1048) confirms the existence of  $\text{Ce}_2\text{O}_3$  as a surface bonded entity. The other reflections due to surface  $\text{Ce}_2\text{O}_3$  are entrapped in high intensity ZnO peaks. The calculated crystallite size of the surface  $\text{Ce}_2\text{O}_3$ , as evaluated by the extrapolation of reflections at  $2\theta = 28.85^\circ$ , was  $\sim 6.6$  nm. The change in the oxidation state of  $\text{Ce}^{3+}$  was not evidenced.

The photocatalytic activity of the synthesized  $\text{Ce}^{3+}$  impregnated ZnO, in comparison to that of bare ZnO, was evaluated for the degradation and mineralization of 2-chlorophenol (2-CP). The optimized amount (100 mg) was suspended in 100  $\text{cm}^3$  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 total organic carbon (TOC) for degradation (loss of aromaticity) and mineralization (conversion to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) progress respectively, at regular intervals of time. Along with monitoring of the 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  $\text{Ce}^{3+}$  impregnated ZnO is presented in Fig. S3 (ESI<sup>†</sup>). The  $\text{Ce}^{3+}$  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 a 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  $\sim 40\%$  2-CP degradation for bare ZnO,  $\sim 86\%$  of 2-CP substrate was removed in the presence of  $\text{Ce}^{3+}$  loaded ZnO. The impregnated catalyst completely ( $\geq 99.5\%$ ) degraded 2-CP substrate in 90 minutes of exposure while for bare ZnO  $\sim 95\%$  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  $\sim 98\%$  TOC removal for  $\text{Ce}^{3+}$  loaded catalyst in 150 minutes of exposure, 49% organic carbon removal was observed for bare ZnO, which was even lower than that observed for  $\text{Ce}^{3+}$  impregnated catalyst in 20 minutes of exposure.

The comparison of degradation and TOC removal profiles of 2-CP (Fig. 2(a) and (b)) clearly elaborates that although ZnO is capable of degrading 2-CP in natural sunlight, it fails to carry out efficient mineralization (TOC removal). On the other hand,  $\text{Ce}^{3+}$  impregnated catalyst showed an 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, and 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 exists between ZnO and impregnated  $\text{Ce}^{3+}$  states.

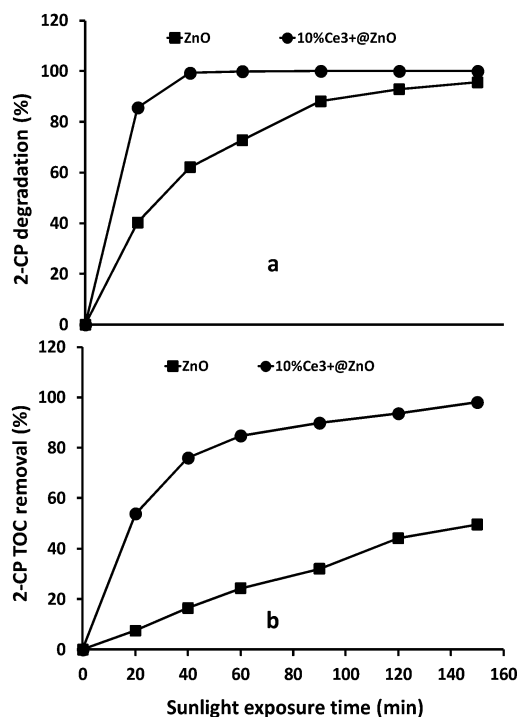
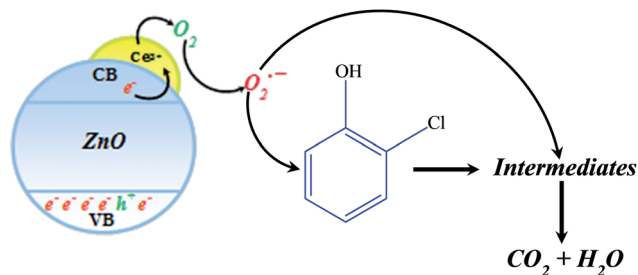


Fig. 2 Comparison of (a) HPLC based percentage degradation (b) TOC removal of 2-CP over bare and  $\text{Ce}^{3+}$  impregnated hexagonal ZnO.



Scheme 1 The possible mechanism of 2-CP mineralization.

The rapid degradation and mineralization of 2-CP substrates suggest the involvement of superoxide anion radicals, both in the degradation and in the mineralization process; however, further investigation is needed in this regard. These 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 Scheme 1.

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

## Conclusions

The surface presence of  $\text{Ce}^{3+}$  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 to the existing collection of photocatalysts.

## Synthesis and characterization of $\text{Ce}^{3+}$ impregnated ZnO photocatalyst

The  $\text{Ce}^{3+}$  modified ZnO catalyst was synthesized by impregnating the pre-synthesized hexagonal ZnO. In a representative synthesis, a precisely weighed amount of ZnO was added to a  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution containing 10%  $\text{Ce}^{3+}$  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  $\text{Ce}^{3+}$  impregnated ZnO catalysts were recorded by a Perkin Elmer UV-visible diffuse reflectance spectrophotometer in the 190–900 nm range. DRS were further manipulated to evaluate the absorption edges by plotting  $(F(R) \times hv)^{1/2}$  versus  $hv$  (photon energy, eV). HORIBA Scientific (Jobin Yvon Fluoro Log 3), France, macro PL system was used to record the photoluminescence spectra of bare and  $\text{Ce}^{3+}$  modified ZnO powders at 325 nm excitation wavelength. The emissions were

recorded from 350 to 650 nm. The powder XRD patterns of bare and  $\text{Ce}^{3+}$  impregnated powders were recorded by an Xpert X-ray powder diffractometer (Philips PW1398) with a Cu  $K\alpha$  radiation source from 20° to 80° ( $2\theta$ ) with a step time of 3 seconds and step size of 0.05°. Scherer's equation was applied on the main reflections to evaluate the crystallite size of various phases. The changes in the morphology of the ZnO base and the surface presence of  $\text{Ce}^{3+}$  species were examined by a field emission scanning electron microscope (JEOL JSM 6490-A).

## Photocatalytic studies

The photocatalytic activity of bare and  $\text{Ce}^{3+}$  impregnated ZnO in sunlight irradiation was measured by exposing 100  $\text{cm}^{-3}$  of a 30 ppm 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  $\text{cm}^{-3}$ ) 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 100 mg/100  $\text{cm}^3$  catalyst loading; therefore, the experiments were performed with 100 mg catalyst loading. All the experiments were performed in a sunlight illumination of  $1000 \pm 100 \times 10^{-2}$  LUX and for a fixed period of daylight. The progress of the 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 hours. The catalyst was removed by using a 0.20  $\mu\text{m}$  Millipore filter. The collected samples were analyzed by high performance liquid chromatography (HPLC) (SPD-20A, Shimadzu Corporation, Japan) using 60:40 methanol-water mixture as the solvent and a C18 column. Based on peak response, 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 the photocatalytic process. A TOC-VCPH total carbon analyzer supplied by Shimadzu Corporation, Japan, measured the TOC of the samples.

## Acknowledgements

The authors are thankful to CEES, King Abdulaziz University and Ministry of Higher Education, Kingdom of Saudi Arabia, for support.

## Notes and references

- M. H. Hernández-Alonso, F. Fresno, S. Suárez and J. M. Coronado, *Energy Environ. Sci.*, 2009, 2, 1231–1257.
- S. Rehman, R. Ullah, A. M. Butt and N. D. Gohar, *J. Hazard. Mater.*, 2009, 170, 560–5699.
- A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol., C*, 2000, 1, 1–21.
- D. S. Bhatkhande, V. G. Pangarkar and A. A. C. M. Beenackers, *J. Chem. Technol. Biotechnol.*, 2002, 77, 102–116.
- C. Lettmann, H. Hinrichs and W. F. Maier, *Angew. Chem., Int. Ed.*, 2001, 40, 3160–3164.

- 6 M. A. Lazar, S. Varghese and S. S. Nair, *Catalysts*, 2012, **2**, 572–601.
- 7 A. Mills, R. H. Davies and D. Worsley, *Chem. Soc. Rev.*, 1993, **22**, 417–425.
- 8 M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, *Water Res.*, 2010, **44**(10), 2997–3027.
- 9 P. Pichat, *Photocatalysis and Water Purification: From Fundamentals to Recent Applications*, Wiley-VCH Verlag GmbH, Germany, 1st edn, 2013.
- 10 Y. Y. Wu, H. Yan and P. Yang, *Top. Catal.*, 2002, **19**, 197–202.
- 11 M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nat. Mater.*, 2005, **4**, 455–459.
- 12 M. Law, L. E. Greene, A. Radenovic, T. Kuykendall, J. Liphardt and P. Yang, *J. Phys. Chem. B*, 2006, **110**, 22652–22663.
- 13 A. Hameed, T. Montini, V. Gombac and P. Fornasiero, *Photochem. Photobiol. Sci.*, 2009, **8**, 677–682.
- 14 A. Hameed, V. Gombac, T. Montini, L. Felisari and P. Fornasiero, *Chem. Phys. Lett.*, 2009, **483**, 254–261.
- 15 (a) C. Karunakaran, P. Gomathisankar and G. Manikandan, *Mater. Chem. Phys.*, 2010, **123**, 585–594; (b) V. Vuppala, M. G. Motappa, S. S. Venkata and P. H. Sadashivaiah, *Eur. J. Chem.*, 2012, **3**, 191–195; (c) R. Saravanan, N. Karthikeyan, S. Govindan, V. Narayanan and A. Stephen, *Adv. Mater. Res.*, 2012, **584**, 381–385.
- 16 M. Willander, O. Nur, J. R. Sadaf, M. I. Qadir, S. Zaman, A. Zainelabdin, N. Bano and I. Hussain, *Materials*, 2010, **3**, 2643–2667.