

Microwave assisted citrate gel combustion synthesis of ZnO Part-II: assessment of functional properties

S. Ananthakumar^{a,*}, S. Anas^a, J. Ambily^a and R.V. Mangalaraja^b

^aMaterials and Minerals Division, National Institute for Interdisciplinary Science and Technology (CSIR), Thiruvananthapuram-695019, Kerala, India

^bDepartment of Materials Engineering, University of Concepcion, Chile

In this study, the functional properties of nanocrystalline ZnO derived through a microwave assisted citrate gel decomposition technique were examined by UV-Vis and PL spectroscopy. The prepared ZnO and ZnO containing Al^{3+} , Ag^+ and a mixture of ($\text{Al}^{3+} + \text{Ag}^+$) dopants were subjected to photocatalytic degradation of methylene blue dye under UV irradiation and photoluminescence analysis. The band gap reduction and photo-oxidation reaction kinetics were assessed. The functional property studies revealed that ZnO nano clusters showed a UV absorption edge at 393 nm with band gap energy of 3.159 eV. A significant band gap reduction is found in mixed ions doping [$\text{Al}^{3+} + \text{Ag}^+$] compared to single Ag^+ and Al^{3+} dopants. The photo-oxidation reaction follows pseudo- first-order reaction kinetics and a k_{obs} constant of 0.273 was determined with mixed dopants. An enhanced photoactivity was confirmed by the ultrasonication of a ZnO-dye suspension. The PL measurements showed blue and red emission in Ag^+ and Al^{3+} doped ZnO, respectively. The mixed ions [$\text{Al}^{3+} + \text{Ag}^+$] resulted in a pronounced intense orange-red emission in the visible region. In addition to this, the photoactivity of microwave-derived ZnO clusters was confirmed in a kaolin clay matrix. The kaolin modified with 2 wt% ZnO was found to be photoactive and it degraded the methylene blue dye within 3 h under UV irradiation.

Key words : Photocatalysis, Photoluminescence, Functional ZnO.

Introduction

Research is underway to make ZnO-based window materials for solar cells, visible-light photocatalysts and white-light emitting phosphors, since ZnO is transparent to most of the solar spectrum. It shows visible light absorption in the range 500 -700 nm [1]. Nano particulate ZnO dispersions, containing a narrow particle size below 10 nm, show UV-shielding property in the whole region of the UV spectrum [UV-A and UV-B]. Due to the excellent photo reactivity, non toxicity, long-term stability and low price of ZnO, commercial interest is rather high to make photoactive ZnO nano composite coated ceramic tiles, photoactive cements, ZnO/polymer organic-inorganic hybrids, and ZnO/Ag metal oxide- metal semi-conductors [2, 3]. However for effective use, the ZnO band gap has to be minimized from 3.38 eV to below 2.0 eV, since it is the recommended band gap value for achieving a visible-light active photocatalyst. This is important because of the fact that the solar spectrum has only < 7% UV energy and more than 50% visible energy. But the phase pure ZnO acts as an efficient photocatalyst only under UV irradiation.

One of the strategies adopted for tuning the band gap is to employ suitable dopants by which the electronic structure of ZnO can be altered. The dopant ions such as Al, Co, Ag, Pb and Mn have incorporated in ZnO and their effect has already been studied and reported [4-6]. The dopants increase the bulk surface area and surface defects which generate more active sites for the reaction at an energy level lower than the conduction band of pure ZnO and thus absorbs visible light via these defect sites causing enhancement in the optical absorption of ZnO. Doping of non metal impurities [N, S, and C] was recently reported and it is seen that the impurity dopants favorably alter the chemical states under certain calcination conditions (temperature and atmosphere) thereby producing visible light active ZnO photocatalyst [7, 8].

Usually chemical methods result in nano to sub micrometre sized ZnO powders with varying crystalline quality, particle size and shape, bulk surface area, dispersion stability and surface texturing [9, 10]. These characteristics are correlated with the photoactivity under UV and visible light. However, to date ZnO having 100% photoactivity remains a challenge for researchers. Photocatalytic decolorization of Rhodamine-B by hierarchically nano porous ZnO hollow spheres synthesized through hydrothermal route has recently been published by Yu *et al.* [11]. The photocatalytic degradation efficiency of hexagonal cone-shaped ZnO nanoparticles has also been demonstrated by Ren *et al.* [12]. Sol gel derived ZnO-Fe₂O₃ mixed oxide photocatalyst

*Corresponding author:
Tel : +91-471-2515289
Fax: +91-471-2491712.
E-mail: ananthakumar70@gmail.com

has been developed and in such coupled semiconductors reduction of ZnO band gap from 3.35 eV to 3.0 eV is seen. The authors have reported that ZnO-Fe₂O₃ material showed increased photo degradation of potassium cyanide [13].

In this study we synthesized ZnO nano clusters and ZnO with Ag⁺ and Al³⁺ dopants through a microwave-assisted citrate gel decomposition technique. When we compare this technique with other chemical methods, it involves rapid heating without any control over the rate and therefore tailored particle size and morphology were difficult. The only advantage is that we can obtain ZnO in a very short processing time. We were curious to know the effect of such a rapid processing on the formation and functional properties of ZnO. The powder processing and particle characteristics were reported in the first part of the investigation. Here we report the functional properties, mainly photocatalytic and photoluminescence characteristics. In addition to that, the ZnO powders were dispersed in a kaolin clay matrix and assessment of its functional characteristics under UV irradiation was also studied.

Experimental

The detailed experimental procedure for the synthesis of Ag and Al-doped ZnO through microwave-assisted citrate gel decomposition is presented in Part-1 of this study.

Characterizations

Diffuse reflectance spectroscopy (DRS) was used to determine the threshold wavelength and photo-absorbance of the ZnO. A UV-Vis spectrophotometer (Shimadzu, Japan, UV-2401 PC) equipped with an integrated sphere assembly was used for the analysis. Room temperature UV-visible spectra were recorded in the wavelength region 200 to 800 nm⁻¹ using BaSO₄ as the standard. The optical gap (E_g) of the doped and single phase ZnO was determined from the diffused reflectance spectra measurement.

The well known Kubelka-Munk function $[F(R)]$ given in equation (1) was used for the band gap calculation [14];

$F(R) = (1-R)^2/2R$ (1) where R is the reflectance and $F(R)$ is equivalent to the absorption coefficient. Photoluminescence spectra were recorded on Fluoro Log-4 (Horiba Jobin Yvon, USA) at room-temperature using a Xe lamp.

Photocatalytic study by dye degradation test under UV irradiation

The photocatalytic activities were studied by methylene blue (MB) degradation under a UV irradiation test as per the standard procedure reported by Baiju *et al.* [15]. During the experiment, samples were collected every 10 minutes and UV-Vis spectra were recorded. The degradation profiles were drawn by plotting the maximum absorbance of the main intensity peak (663 nm) of methylene blue with respect to the time. A blank dye solution was also irradiated for about 1 h to confirm that the dye was not photo bleached by the UV irradiation.

Kaolin-ZnO composite preparation

Kaolin source was obtained from English Indian Clays Ltd, India [25 μ m, 97% purity] and surface activated by washing with dilute HNO₃. A clay suspension containing 2 wt% ZnO clusters prepared in the present study was milled for 2 h. The pH of the suspension was maintained at pH = 6. After milling, the clay + ZnO composite particles were separated by centrifugal filtration and dried under humid conditions. The methylene blue dye degradation test was conducted to evaluate the photo degradation efficiency of ZnO-modified kaolin using the procedure described above.

Results and Discussions

The UV- absorbance spectra for the single phase and doped ZnO powders processed in this study are shown in Fig. 1. The undoped ZnO has shown a near visible absorption edge in the wavelength range of 394 nm and in doped ZnO it was seen at 395 nm, 397 nm and 398 nm for the Ag⁺, Al³⁺ and mixture of Ag⁺+Al³⁺ dopants, respectively. Upon doping a marginal increase in the absorbance is noticed. Also, a maximum decrease in the absorption edge is observed in ZnO having the Ag⁺ dopant ion. The doping with Al³⁺ has shifted the adsorption position of the ZnO to the near visible region. However, when a mixture of Al³⁺ and Ag⁺ ions is doped, the absorbance is increased. The shifting of the absorption limit to a higher wavelength by silver and Al³⁺+Ag⁺ mixed dopants indicate a modification of the electronic band structure of the doped ZnO. This can be understood from the Tau plot presented in Fig. 2. This clearly shows a linear Tau region above the optical absorption edge. Extrapolation of the linear, straight line region to the photon energy axis yields the ZnO band gap and the values determined for the ZnO powders prepared in this study are presented in Table. 1.

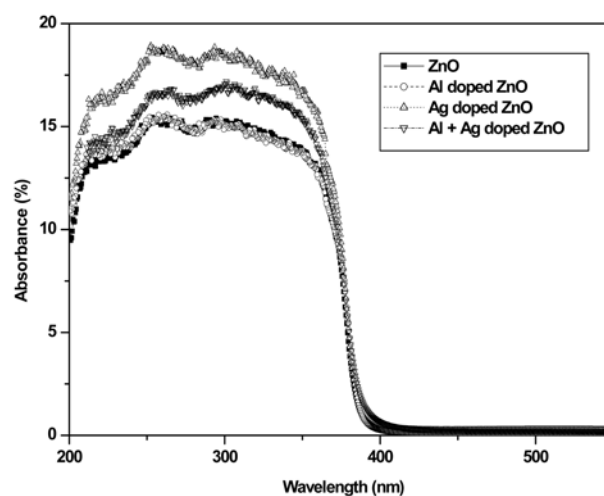


Fig. 1. UV-absorbance (in term of Kubelka-Munk equivalent absorbance units) of ZnO powders processed by microwave-assisted citrate gel decomposition.

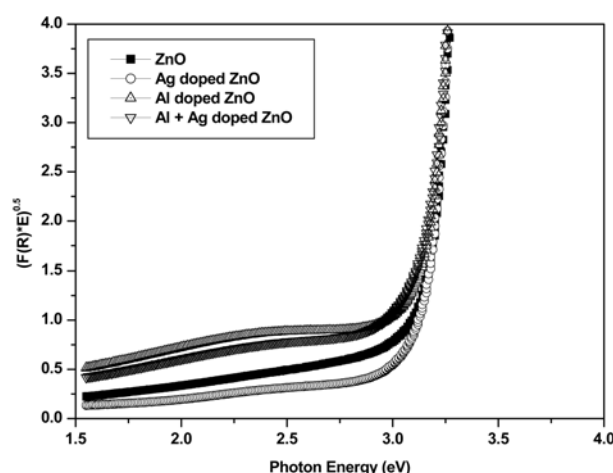


Fig. 2. Optical band gaps of the ZnO with respect to dopants.

Table 1. Variation of band gap energies and absorption edges with doping.

Sample details	Band gap energy (eV)	Absorption edge (nm)
ZnO	3.159	394
ZnO + Ag ⁺	3.140	395
ZnO + Al ³⁺	3.135	397
ZnO + [Ag ⁺ + Al ³⁺]	3.121	398

It is observed that the theoretical ZnO band gap value of ~ 3.38 eV is slightly reduced for the ZnO prepared using microwave-assisted citrate gel decomposition. Other than the factor of a small particle size, the morphology can also cause a band gap reduction in a ZnO photocatalyst [15]. However, a large band gap reduction is achieved only when ZnO is doped with transition metals. Typical dopants such as Sn, Ag, Ti, Al are already reported to reduce the band gap energy [5, 16, 17]. In this study, we introduced Ag and Al doping ions and it is noticed that the difference in the band gap values between the single Ag⁺ and Al³⁺ dopants, is only negligible. However, when both dopants are combined this shows significant reduction in the band gap. Also one can mention that the extent of the band gap reduction by the single Ag⁺ and Al³⁺ doping is very much lower than expected. However, here the amount of doping is also less and as with the earlier studies a large band gap reduction is possible only when the dopants are added excessively, may be > 5 wt%. Although the band gap reduction is low, the photocatalytic studies confirm the efficiency of the doped ZnO prepared in this study. The results on the MB dye degradation test conducted for our ZnO samples are shown in Fig. 3. The intensity decrease in the characteristic absorption peak at 664 nm of the methylene blue clearly shows the efficiency of the photocatalytic property. From the figure we can see that as the irradiation time increases there is a gradual reduction in the peak intensity and the dye is completely decomposed within 110 minutes exposure.

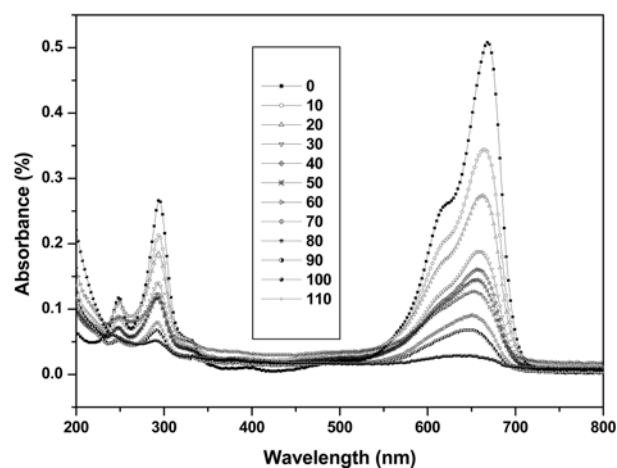


Fig. 3. Methylene blue dye degradation plots of Al and Ag doped ZnO with various irradiation times (minutes).

The experiment is also carried out for single phase ZnO and the results are very close to the performance of the doped ZnO. In fact, agglomerated ZnO powder with hexagonal crystallites only is obtained in both cases with a marginal difference in the crystallite size. The ZnO showed 30 nm in size which gets reduced to 24 nm upon doping which has no noticeable effect on the photocatalytic nature. The photocatalytic property of ZnO is studied earlier in powders derived through sol gel, hydrothermal, precipitation and sputtering [18–20]. In most of the cases, it was concluded that, irrespective of the addition of dopants, the photocatalytic characteristic of ZnO was mainly attributed by the primary factors of oxygen vacancies, crystal defects and surface-associated hydroxyl groups. The crystallite size and morphology are only the secondary factors influencing the photo-physical mechanism. Other than these common factors, in our case, we have also seen the presence of carbon in combustion derived ZnO. Carbon is another active semiconductor dopant that can contribute to the photoactivity. Recently, it was proposed that the hydrogen from a moist atmosphere can easily get into the interstitial ZnO lattice sites as well as on the surface as an impurity and can act as either a donor (H⁺) or an acceptor (H⁻) to make ZnO more conductive [21]. Therefore, in our study, we estimated the presence of hydrogen species on the microwave-calcined ZnO powders after exposing them humid air by solid state ¹H MAS NMR and the spectrum is given in Fig. 4. This showed well-resolved multiple hydrogen resonance peaks between 0–4 ppm. In general ¹H NMR spectra for solids show broad line-widths that are largely attributed to ¹H–¹H dipolar interactions, chemical shift anisotropies and overlapping signals due to the narrow distribution of ¹H chemical shifts in solids. We observed a sharp ¹H NMR resonance at 4.119 confirming that our ZnO powder also has active hydrogen species. These observations indicate that although the microwave-assisted combustion resulted in large agglomerated ZnO particles; its photocatalytic nature is

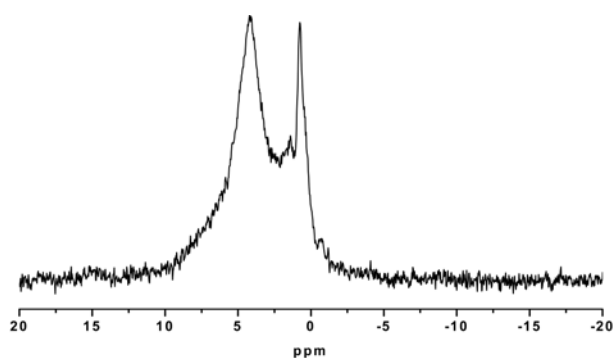


Fig. 4. Solid State ^1H MAS NMR spectrum for as-synthesized ZnO nanoparticles.

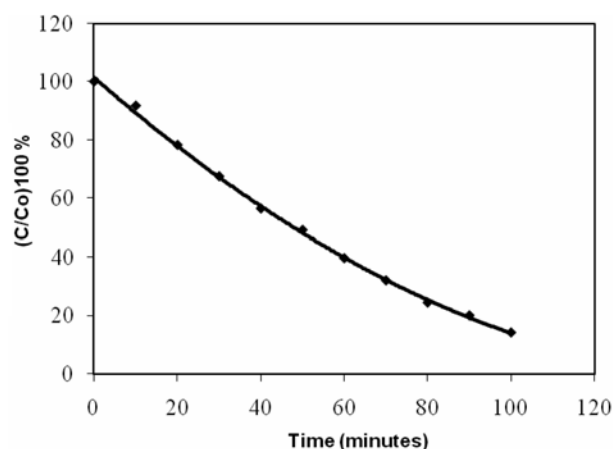


Fig. 5. Photocatalytic degradation of methylene blue by doped ZnO under UV light.

very similar to the powders derived through controlled wet-chemical methods.

Fig. 5 is the MB dye degradation as a function of time. It shows that the dye gets decomposed completely within 2 h justifying the efficiency of the microwave-assisted citrate gel derived ZnO as a photocatalyst. In fact there are studies on the dye degradation behavior of ZnO having either silver or aluminium dopant ions. But their combined photocatalytic activity is not well explored. Hsiao *et al.* have pointed out that aluminium doped zinc oxide has a higher photocatalytic activity than undoped zinc oxide at the same precursor concentrations and the catalytic effect is found to increased with increasing precursor concentrations [22]. Lu *et al.* reported that the silver ion doping had a negative effect on the photocatalytic performance when the dopant level exceeded 1.65 at.% [23]. The combined performance has not been earlier studied and our investigation shows that the addition of Ag+Al dopants below 2 wt% gives a better photocatalytic effect when compared to the individual dopants.

The photo-oxidation kinetics of the dye decomposition reaction is also established from the Langmuir-Hinshelwood model [24]. This model assumes that the sorption of both oxidant and reductant is a rapid equilibrium process and therefore the rate-determining step of the reaction involves

both species present in the monolayer at the solid-liquid interface. Also, the photocatalytic degradation reaction of methylene blue by a photocatalyst under UV radiation exhibits pseudo-first-order kinetics. According to the model the dye degradation for a given time is expressed as $-d[\text{MB}]/dt = k_{\text{obs}} [\text{MB}]$, on integration it gives $\ln([\text{MB}]_0/[\text{MB}]) = k_{\text{obs}} t$ for the condition $[\text{MB}] = [\text{MB}]_0$ at $t = 0$. Here, k_{obs} is the pseudo-first-order rate constant and $[\text{MB}]$ is the concentration of methylene blue dye. The reaction kinetics plot derived between $\ln([\text{MB}]_0/[\text{MB}])$ versus time is shown in Fig. 6. From the slope, the value of k_{obs} is calculated. The photo-oxidation reaction kinetics for all the doped ZnO powders and their rate constants are shown in Table. 2.

The kinetic results revealed that a mixture of ion dopants ($\text{Al}^{3+} + \text{Ag}^+$) is comparatively better. In ZnO photocatalysts, the photons cause the excitation and generation of electron/hole pairs at a wavelength of 394 nm, that act as driving force for the photocatalytic degradation of dyes. The electrons are excited from the valence band of ZnO, formed by the 2p orbital of oxygen, to the conduction band formed by the 4s orbital of zinc. With single Al^+ dopant, due to the lower conduction band of aluminium than that of ZnO, it can act as a sink for the photo generated electrons. The holes move in the opposite direction from the electrons, photo generated holes get trapped within the ZnO, making charge separation more efficient. As a result of this, the photocatalytic activity is comparatively stronger in aluminium doped ZnO. In Ag^+ doping we have seen the kinetic rate constant is low. This indicates that the Ag^+ is not completely in the ZnO structure because of the nature of the microwave-assisted decomposition reaction. Due to rapid interactions of microwaves and a vigorous exothermic

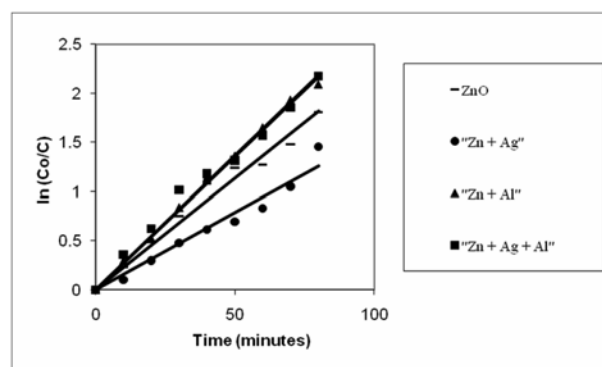


Fig. 6. Plot of $\ln([\text{C}]_0/[\text{C}])$ Vs Time (minutes). The slope of the curve gives the pseudo-first-order kinetic rate constant, k_{obs} .

Table 2. Variation of kinetic rate constants with doping.

Sample	Kinetic rate constants (minutes ⁻¹)
ZnO	0.0227
ZnO+ AgNO ₃	0.0157
ZnO + Al(NO ₃) ₃	0.0271
ZnO+ AgNO ₃ + Al(NO ₃) ₃	0.0273

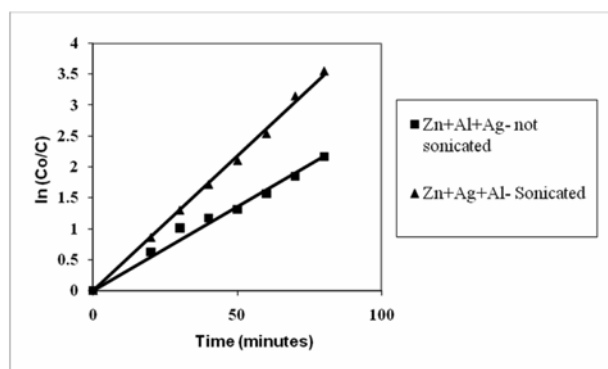


Fig. 7. Effect of ultrasonication on the kinetic rate constant of aluminium and silver doped ZnO.

reaction, the silver dopant has a chance to either oxidize or evaporate from the system, especially when the amount is low. Also, the $4d^{10}$ configuration in Ag_2O does not show any ability to capture the conduction band electrons. It deactivates the surface and reduces the photocatalytic degradation efficiency. However, in the mixture of silver and aluminium dopants, the recombination of the photo-generated electron/hole pairs is suppressed and therefore the mixture showed higher photo catalytic activity.

Since the homogeneous dispersion of the photocatalyst in the dye medium can still improve the efficiency of dye degradation, we have applied ultrasonication to the ZnO-dye suspension and the effect is shown in Fig. 7. Interestingly the ultrasonication for even 15 minutes increased the rate constant value, k_{obs} , by two fold and it was determined as $0.0436 \text{ minutes}^{-1}$. A rate constant of $0.0273 \text{ minutes}^{-1}$ was obtained for the sample which was not sonicated. The ultrasonication obviously breaks the metal oxide clusters and increased the presence of individual ZnO nano crystals in the medium. It ultimately resulted in more active sites on the catalyst surfaces and therefore increased the reaction kinetics.

The photocatalytic efficiency of mixed ion doped ZnO prepared in the present study is also confirmed by mixing the dye +ZnO slurry in the kaolin clay matrix. The clay +ZnO + dye mixture was placed as spots on glass slides and then subjected to UV-light for methylene blue dye degradation. It was found that after 3 h of UV exposure, there is a visible change in the color of methylene blue on the composite samples. In fact the amount of ZnO present in the clay was only 2 wt%. However, this result is encouraging and indicates that even with a small quantity of the mixed ion doped ZnO, the kaolin clay can act as a smart material for functional applications. Whereas the kaolin clay + dye mixture has not shown any difference in the color even after exposure to UV light for many hours.

Luminescent property of citrate gel derived ZnO

The PL spectra recorded for all the ZnO samples prepared in this study are shown in Fig. 8. Usually two emission

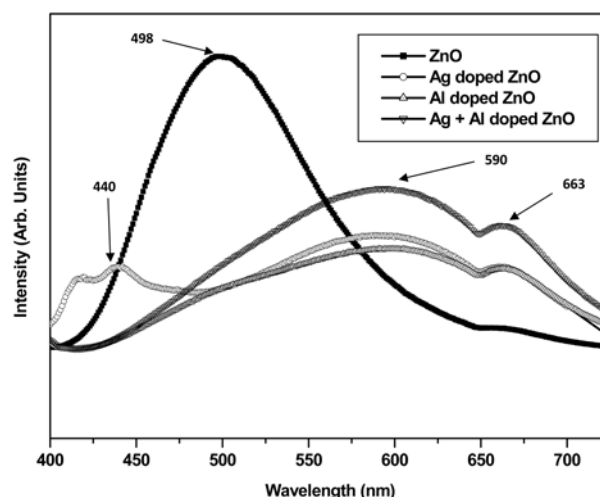


Fig. 8. PL spectra of single phase ZnO and doped ZnO containing Ag and Al.

peaks, one in the UV region and another in the visible region are shown for ZnO nanomaterials. In our studies, the PL spectrum taken on single phase ZnO showed only a broad green emission band in the visible region (498 nm). The green emission is mainly due to the presence of oxygen vacancies and the defect structure of ZnO [25]. The large numbers of defect sites were the effect of rapid microwave heating. Whereas the PL spectrum corresponding to the ZnO containing a mixture of Ag^+ + Al^{3+} dopants shows a broad band PL emission in the range 450 nm to 650 nm, centered at about 593 nm (yellow-orange emission). Another deep level transition can also be observed at 663 nm (red emission). This can be explained in a way that in mixed oxide dopants, due to an increased oxygen deficiency concentration; the emission band was shifted to the orange-red visible region. This indicates that the microwave-derived ZnO clusters can exhibit good visible luminescence even though they have physical dimensions much larger than that of other ZnO derived by controlled wet chemical methods.

The visible luminescence intensity of the mixed ion doped ZnO were comparably higher than the visible emission of the ZnO prepared with individual Ag^+ and Al^{3+} dopants. The silver doped ZnO exhibits an emission peak centered at around 440 nm. This is an indication of the violet-blue luminescence of the sample and is probably due to the radiative defects Zn_i (zinc interstitial) and V_{Zn} (zinc vacancy) [26]. But the visible broad band at around 590 nm is also observed in a less intense manner when compared to ZnO containing both dopants. In the case of aluminium doped ZnO, a broad deep-level (DL) emission from 400 to 700 nm with the peak at around 590 nm is noticed. When Al^{3+} is introduced into ZnO, oxygen defects in the structure are increased and a corresponding red shift occurs to the deep levels [27]. Irrespective of the single dopants, the mixed ion doped systems showed significantly higher emission intensity in the deep levels and it can further be tuned if the dopant

concentration is altered suitably for the microwave-assisted synthesis of ZnO.

Conclusions

Functional properties of ZnO processed through a microwave-assisted citrate gel decomposition are assessed. The single phase ZnO exhibits a UV absorption edge at 393 nm. A band gap reduction from 3.38 eV to 3.12 eV is achieved by mixed ion $[Al^{3+}+Ag^{+}]$ doping. The methylene blue dye decomposition test confirms that the microwave-derived ZnO can be efficient photocatalysts even though they processed by rapid microwave heating. The ZnO prepared in the present study showed complete removal of the dye color in <120 minutes under UV irradiation. Ultrasonication was found to be effective for accelerating the photo-oxidation reaction kinetics of a ZnO dispersion. The kinetics of the photocatalytic reaction obey the Langmuir-Hinshelwood model. The doped ZnO was further incorporated into a kaolin matrix and its photocatalytic property was assessed. It was shown that kaolin having only 2 wt% ZnO is able to decompose the dye molecule under UV irradiation in < 3 h indicating that the kaolin can be modified suitably by multifunctional pigments and additives. The PL analysis of single-phase ZnO exhibited a broad visible green emission in the range of 498 nm. But the doped ZnO shows blue and red emissions for the silver and aluminium ion dopants respectively. The mixed ion doping resulted in intense and deep level transitions in the orange-red regions.

References

1. C. Hariharan, Appl. Catal., A: General 304 (2006) 55-61.
2. C.A.K. Gouvea, F. Wypych, S.G. Moraes, N. Duran and P. Peralta-Zamora, Chemosphere 40 (2000) 427-432.
3. D.C. Olson, J. Piris, R.T. Collins, S.E. Shaheen and D.S. Ginley, Thin Solid Films 496 (2006) 26-29.
4. H.-M. Zhou, D.-Q. Yi, Z.-M. Yu, L.-R. Xiao and Jian Li, Thin Solid Films 515 (2007) 6909-6914.
5. S. Ekambara, Y. Iikubo and A. Kudo, J. Alloys Compd. 433 (2007) 237-240.
6. T.-H. Ko, H. Chub and Y.-J. Liou, J. Hazard. Mater. 147 (2007) 334-341.
7. L.-C. Chen, Y.-J. Tu, Y.-S. Wang, R.-S. Kan and C.-M. Huang, J. Photochem. Photobiol., A 199 (2008) 170-178.
8. J. Lu, Q. Zhang, J. Wang, F. Saito and M. Uchida, Powder Technol. 162 (2006) 33-37.
9. U. Pal, J.G. Serrano, P. Santiago, G. Xiong, K.B. Ucer and R.T. Williams, Opt. Mater. 29 (2006) 65-69.
10. Y.J. Jang, C. Simer and T. Ohm, Mater. Res. Bull. 41 (2006) 67-77.
11. J. Yu, C. Li and S. Liu, J. Colloid Interface Sci. 326 (2008) 433-438.
12. X. Ren, D. Han, D. Chen and F. Tang, Mater. Res. Bull. 42 (2007) 807-813.
13. A. Hernandez, L. Maya, E. Sanchez-Mora and E.M. Sanchez, J. Sol-Gel Sci. Technol. 42 (2007) 71-78.
14. H. Lin, C.P. Huang, W. Li, C. Ni, S.I. Shah and Y-H Tseng, Appl. Catal. B 68 (2006) 1-11.
15. A. Zachariah, K.V. Baiju, S. Shukla, K.S. Deepa, J. James and K.G.K. Warrier, J. Phys. Chem. C 112 (2008) 11345-11356.
16. Y.J. Jang, C. Simer and T. Ohm, Mater. Res. Bull. 41 (2006) 67-77.
17. Y. Zheng, C. Chen, Y. Zhan, X. Lin, Q. Zheng, K. Wei and J. Zhu, J. Phys. Chem. C 112 (2008) 10773-10777.
18. V.K. Ivanov, A.S. Shaporev, F.Y. Sharikov and A.Y. Baranchikov, Superlattices Microstruct. 42 (2007) 421-424.
19. C.-C. Hsu and N.L. Wu, J. Photochem. Photobiol., A 172 (2005) 269-274.
20. N. Sobana and M. Swaminathan, Sep. Purif. Technol. 56 (2007) 101-107.
21. A. Janotti and C.G. Van De Walle, Nat. Mater. 6[1] (2007) 44-47.
22. K.-C. Hsiao, S.-C. Liao and Y.-J. Chenb, Mater. Sci. Eng. A 447 (2007) 71-76.
23. W. Lu, S. Gao and J. Wang, J. Phys. Chem. C 112 (2008) 16792-16800.
24. E. Evgenidou, I. Konstantinou, K. Fytianos, I. Poullos and T. Albanis, Catal. Today 124 (2007) 156-162.
25. J. Zhou, F. Zhao, Y. Wang, Y. Zhang and L. Yang, J. Lumin. 122-123 (2007) 195-197.
26. S. Zhao, Y. Zhou, K. Zhao, Z. Liu, P. Han, S. Wang, W. Xiang, Z. Chen, H. Lu, B. Cheng and G. Yang, Physica B 373 (2006) 154-156.
27. F.K. Shan, B.C. Shin, S.C. Kim and Y.S. Yu, J. Korean Phys. Soc. 42 (2003) 1374-1377.