Fabrication of Au:ZnO thin films by a solution-assisted route for application in photo-electrocatalytic degradation of methylene blue (MB)

Bhishma Karki[1*], Jeevan Jyoti Nakarmi[1], Rhiddi Bir singh[2], Manish Banerjee[3]

[1]*Department of Physics, Tribhuvan University, Kirtipur 44618, Kathmandu, Nepal*
[2]*Department of Chemistry, Tribhuvan University, Kirtipur 44618, Kathmandu, Nepal*
[3]*Department of Chemistry, National Institute of Technology, Patna, Patna 800005, Bihar, India*

[*]Corresponding author: Email: magnum.photon@gmail.com

Received: 07 November 2016, Revised: 17 December 2016 and Accepted: 26 May 2017

DOI: 10.5185/amp.2017/984
www.vbripress.com/amp

Abstract

The influence of Au doping in ZnO thin films was studied with respect to photoelectrocatalytic degradation of methylene blue (MB). Influence of Au doping concentration onto PEC structural morphological, optical and luminescence properties of the ZnO thin films were thoroughly investigated. The maximum value of Isc and Voc for 3 at. % Au:ZnO thin films confirms the optimization of doping percentage. XRD and SEM were used to study the structure and morphology of the films. Films were nanocrystalline and exhibit a hexagonal crystal structure with no additional phases of gold compounds. For degradation of MB, Au:ZnO films were used as photoelectrode, it was observed that due to Au:ZnO 80% degradation of MB occurs in 150 min. Moreover, large area (100 cm^2) Au doped ZnO thin films have been prepared on FTO coated glasses (10–15 Ω). Photocorrosion of ZnO electrode was examined by atomic absorption spectroscopy and no zinc was observed in AAS measurement.

Keywords: Thin film, spray-pyrolysis, optical, degradation, photocatalysis.

Introduction

ZnO has been thoroughly investigated as a potential material in semiconductor photocatalyst for water purification. However, a major bottleneck is to achieve high photocatalytic efficiency in such systems is the fast recombination of photoinduced charge carriers [**1, 2**]. In order to overcome this, it is required to dope noble metals, such as gold [**3, 4**], platinum [**5, 6**] and silver [**7, 8**] in the ZnO semiconductors. Moreover, both Au and Au^+ show strong antibacterial properties [**9-12**].

ZnO is an inorganic antibacterial agent, and therefore it is anticipated that ZnO will be an attractive supporting material for Au atoms. Additionally, these Au:ZnO may inhibit the growth of bacteria synergistically owing to the potent interaction between the two components. Considering these facts, it is worth to dope gold in ZnO matrix, which not only inhibit photocorrosion of ZnO electrode but also enhance the degradation of methylene blue (MB) and inactivation rate of the bacteria.

Gold doping in ZnO films have been previously investigated by several groups using different deposition techniques. These studies involved synthesis of Au:ZnO composite materials using either complicated procedure or non-expandable approach which limits the application of these materials on industrial/commercial scale. The properties of doped ZnO films are affected by various parameters, such as the solution concentration, annealing temperature and the substrates. While substrates change according to the demand of the application, other factors need to be optimized to obtain a uniform film. Therefore solution-based route which allows varying all these properties without any difficulties evolved as a recent potential deposition technique.

The present work deals with the synthesis and characterization of Au doped ZnO thin films on large area substrates. Influence of doping concentration onto PEC structural, morphological, and optical properties is studied. Finally, these films have been used to study photoelectrocatalytic degradation of MB and their efficiency compared with the pure ZnO films.

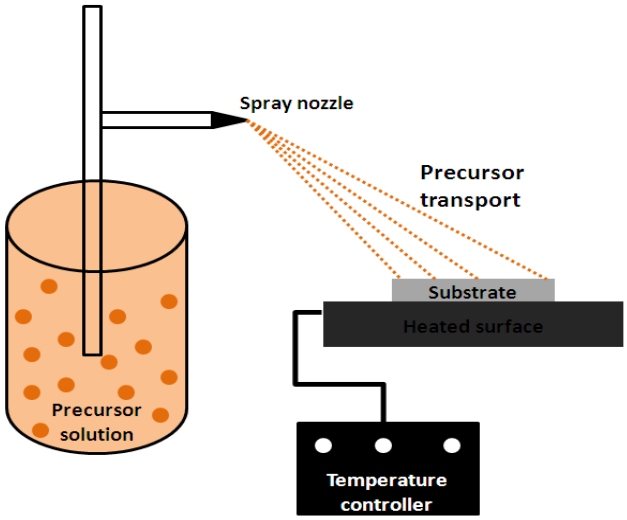
Experimental

The spray pyrolysis technique employed for fabrication of Au:ZnO thin films used corning glasses and conducting FTO as the substrates. The quality of the film largely depends on factors such as roughness, porosity,

uniformity and adherence of the thin film. Therefore, the cleaning process depends on the nature of contaminants, type of substrate and extent of cleanliness required as per the application of the material. Some common contaminants are oil, dust particles, grease and other unwanted chemicals. The corning glasses of dimensions 0.125cm x 7.5cm x 2.2cm and 0.125cm x 10cm x 10cm have been used as substrates.

A detergent solution 'Labolene' was first used to wash the surface of the substrate, followed by rinsing with water. Thereafter, the substrates were boiled in 0.1 (M) chromic acid for about 5 minutes. After cleaning with distilled water, the acidic contaminants were removed by keeping it in NaOH solution. The substrates were again washed with water and cleaned ultrasonically. At the end, the substrates were dried in methanol vapors.

Thereafter, fluorine doped tin oxide (FTO) conducting coatings were fabricated on the corning glass substrates. The chemicals used to produce the thin films i.e. (i) Ammonium fluoride (99%), (ii) Pentahydrated stannic chloride (purity 99 %) (iii) Oxalic acid (99 %) and (iv) Isopropanol (99 %) were procured from SD Fine Chemicals Ltd., Mumbai.



Scheme1. Schematic diagram of the spray pyrolysis method.

50 ml solution of 2M stannic chloride (35.7 gm) was prepared in doubled distilled water and to it was dissolved 7.14 gm of ammonium fluoride. The precipitate residue was cleared off by addition of a small amount of oxalic acid. 20 ml spraying solution was prepared by mixing 10 ml isopropanol with 10 ml of the above solution.

The resultant mixture was sprayed onto corning glass substrates of 2.5 cm × 7 cm dimension through a specially designed glass nozzle. Compressed air (2.5 kg cm-^{2}) was used as carrier gas and a constant spray rate of 4.5 ml min^{-1} was maintained. The substrate was kept at a temperature of 475 ^{O}C. The sheet resistance and transparency of the conducting films thus prepared were 5-15 Ω and 90-95 % respectively. After this, FTO films were deposited on large area corning glass substrates of size 0.125 cm × 10 cm × 10 cm using the as-prepared solution. The films were uniform with resistance of 5-15 Ω at the centre and around 20-30 Ω at the periphery.

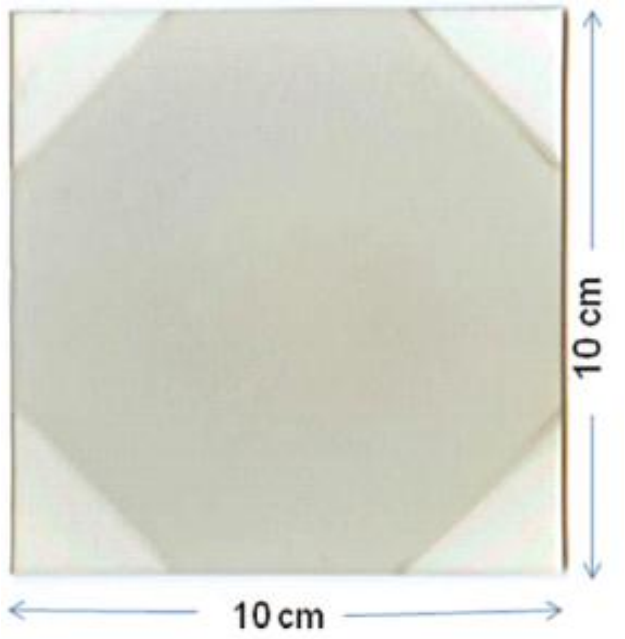


Fig. 1. ZnO thin film on FTO coated glass.

The FTO substrates were initially etched in HCl and rinsed with acetone before using them in Au:ZnO deposition. Au:ZnO thin films were deposited onto corning glass substrates and FTO using spray pyrolysis technique. Initial ingredients used to fabricate Au:ZnO thin films viz. (i) Zinc Acetate dihydrate (AR grade, 99.9% pure), (ii) Methanol (99.9%), (iii) Acetic Acid (99 %), and (iv) Chloroauric acid (99 %), were procured from Thomas Baker Chem. Mumbai.

Both pure ZnO and Au:ZnO composite thin film were fabricated onto the ultrasonically cleaned glass substrates using zinc acetate precursor by spray pyrolysis method (**Scheme1**). While zinc acetate solution was used to prepare pure ZnO films, Au:ZnO composite films were prepared by mixture of Chloroauric acid and zinc acetate as precursor. An appropriate quantity of $HAuCl_4$ (0.2 M) solution was added to the zinc acetate solution to accomplish different doping concentrations (i.e. 1, 2, 3 and 4 at. %) and thus the initial and deposited samples are denoted by ZnO pure, $ZnOAu_1$, $ZnOAu_2$, $ZnOAu_3$, $ZnOAu_4$ respectively. The solutions were thereafter sprayed over pre-heated substrates with the specially designed glass nozzle. A sequence of processes takes place like vaporization, solute condensation and thermal degradation finally resulting in the deposition of ZnO thin films.

During the deposition, different process parameters like solution quantity (100 ml), solution spray rate (5 ml/min), carrier gas flow rate (2.5 kg cm^{-1}), nozzle to substrate distance (30 cm), etc. were kept at their optimized values. An optimum constant deposition temperature of 400 ^{O}C was maintained for all samples.

Results and discussion

Structural analysis

The structural variations and identification of phases were investigated by XRD technique. The diffraction angle (2Θ) was varied between 20 to 80^{O}. **Fig. 2** shows XRD pattern of the Au:ZnO thin film for various Au doping concentrations. The XRD patterns reveal that all the films were polycrystalline in nature. The diffraction peaks are good agreement with JCPDS data card No. 80-0074. Upon increasing Au concentration, (002) plane of ZnO begins to improve up to 3 at. % Au concentration and then decreases. The excess Au doping atoms can be thermodynamically plausible to unite into metallic gold cluster and therefore show c–axis preferred orientation of ZnO film [**16-17**].

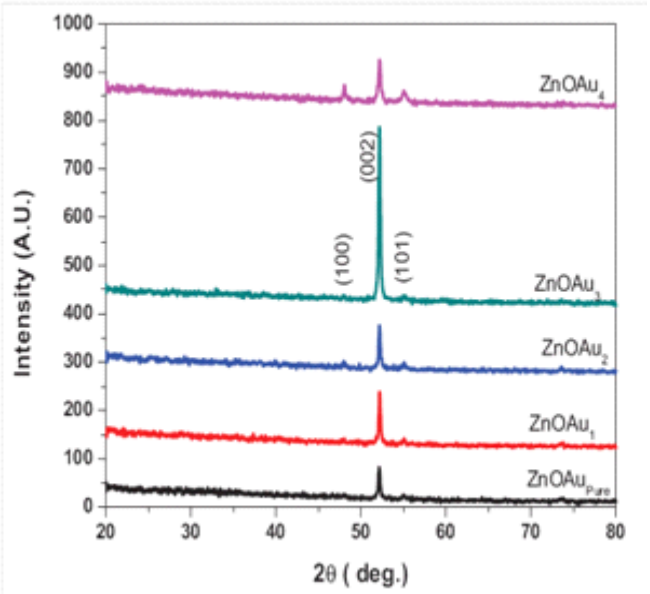


Fig. 2. XRD pattern of the Au:ZnO thin film for various Au doping concentrations prepared by spray pyrolysis technique onto glass substrates for different gold doping concentrations.

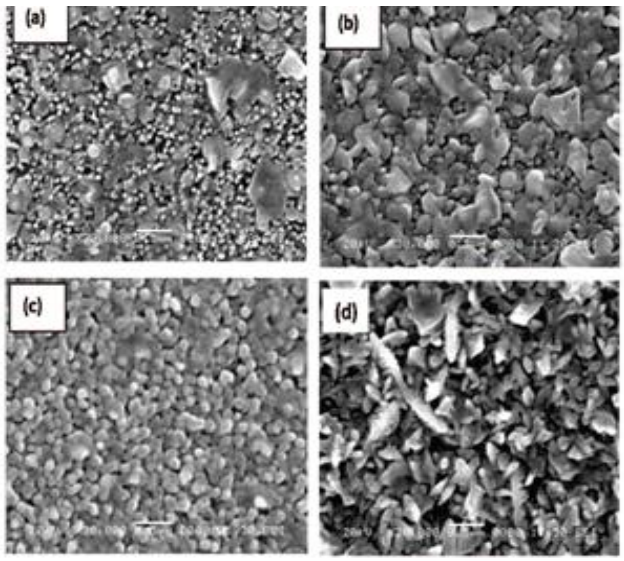


Fig. 3. (a) ZnOAu1, (b) $ZnOAu_2$, (c) $ZnOAu_3$, (d) $ZnOAu_4$, shows the SEM micrographs at different doping concentrations of gold.

Morphological properties

Fig. 3. (**a-d**) shows the SEM micrographs at different doping concentrations of gold. With the increase in Au doping amount in ZnO matrix, grain size increases. At 3 at. % Au doping grains are spherical, uniform and compact and beyond 3 at. % like fish scales. The compositional analysis of typical 3 at. % Au doped film is carried out by EDAX technique (**Fig. 4**). It is observed that oxygen rich films were formed by spray pyrolysis method. The oxygen content is more due to presence of environmental air. The elements and their mass % and atomic wt % are listed in **Table 1** obtained from EDAX (**Fig. 4**).

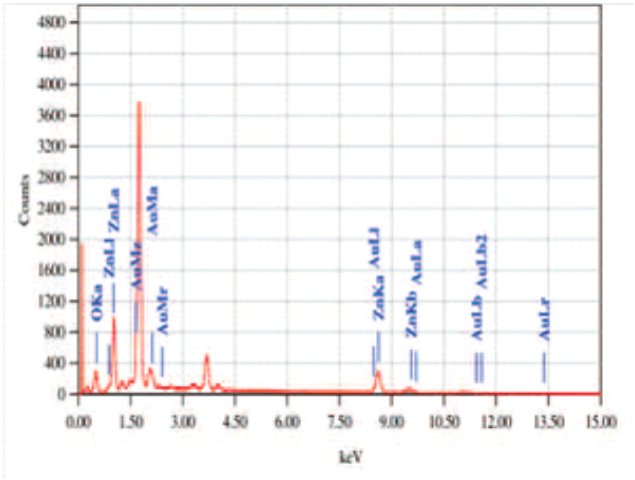


Fig. 4. EDAX pattern of typical 3 at. % Au-doped ZnO thin film.

Table 1. EDAX data typical 3 at. % Au doped thin films.

Element	(Mass %)	At %
OK	24.47	57.83
Zn K	74.58	41.79
Au L	0.95	0.38
Total	100	100

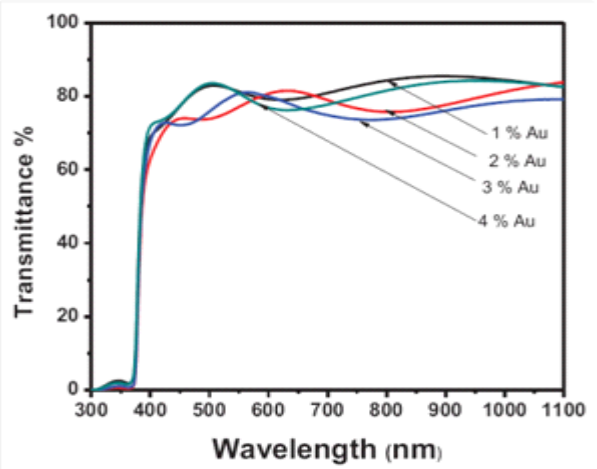


Fig. 5. Optical transmittance spectra of composite Au:ZnO thin films deposited at different gold doping concentrations.

Optical properties

Fig. 5 shows the transmittance spectra for composite Au:Zno thin films. The sinusoidal nature of transmittance spectra is attributed to the interference phenomenon between the film and glass substrate [**18**]. The average transmittance is about 80 % in the visible region. The reduction in transmittance may be due to strong scattering and absorption processes. The strong scattering observed is due to the presence of grain boundaries, the point defects and disorders in ZnO films. Optical absorption spectra of Au:ZnO samples are shown in Fig. 6 and inset shows Tauc plot of $(\alpha h\nu)^2$ vs $h\nu$ of typical film doped with 3 at. % Au doping. The absorption edge is observed at 389 nm. The band gap energy for typical film is 3.26 eV. There is slight decrease in band gap energy with increase in Au concentration, which corroborates the sequential improvement of the formational quality of ZnO framework [**19**].

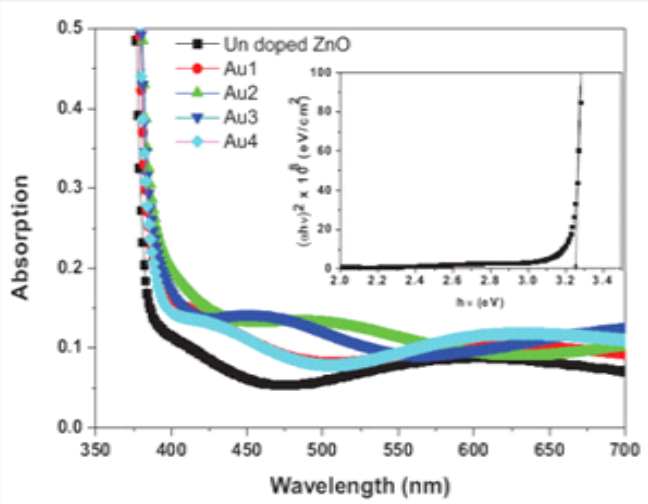


Fig. 6. Optical absorption spectra of Au:ZnO thin films deposited at various gold doping concentrations.

Photoluminescence properties

The photoluminescence (PL) measurements were done at ambient temperature under the excitation wavelength 290 nm. **Fig. 7**. (**a**) show PL spectra of the pure ZnO and 3 at. % Au doped ZnO thin films and (**b**) shows deconvolution of undoped ZnO, (**c**) shows deconvolution of 3 at. % Au:ZnO film. The. PL spectra of pure ZnO show UV peak at 334 nm (weak), 360 nm (strong) and relatively weak visible peaks at 400, 420 and 440 nm. However, for 3 at. % Au doped ZnO film, UV emission at wavelength 337 (weak) and 360 nm (strong) and visible emission at wavelength 420 nm, were observed. The UV intensity of the Au doped ZnO film is enhanced by a factor of about 4.5 and visible emission intensity is increased by factor 2 when compared with undoped ZnO film. Chen et al. showed that the UV and visible emission intensities could be engineered by Au nanoparticles [**20**]. The major changes in photoluminescence behavior of Au:ZnO composite nanoparticles were also observed by Lee *et al.* and Mishra *et al.* [**21-22**]. It was observed that the energy density of excitation source was increased in the presence of gold particles which improved the excitation process and decay rate significantly [**23-24**]. The visible emission at wavelength 440 nm and 400 nm are completely suppressed, while visible emission at wavelength 420 nm increases remarkably. Similar observations are also reported by Li *et al.* [**25**] and Sing *et al.* [**26**].

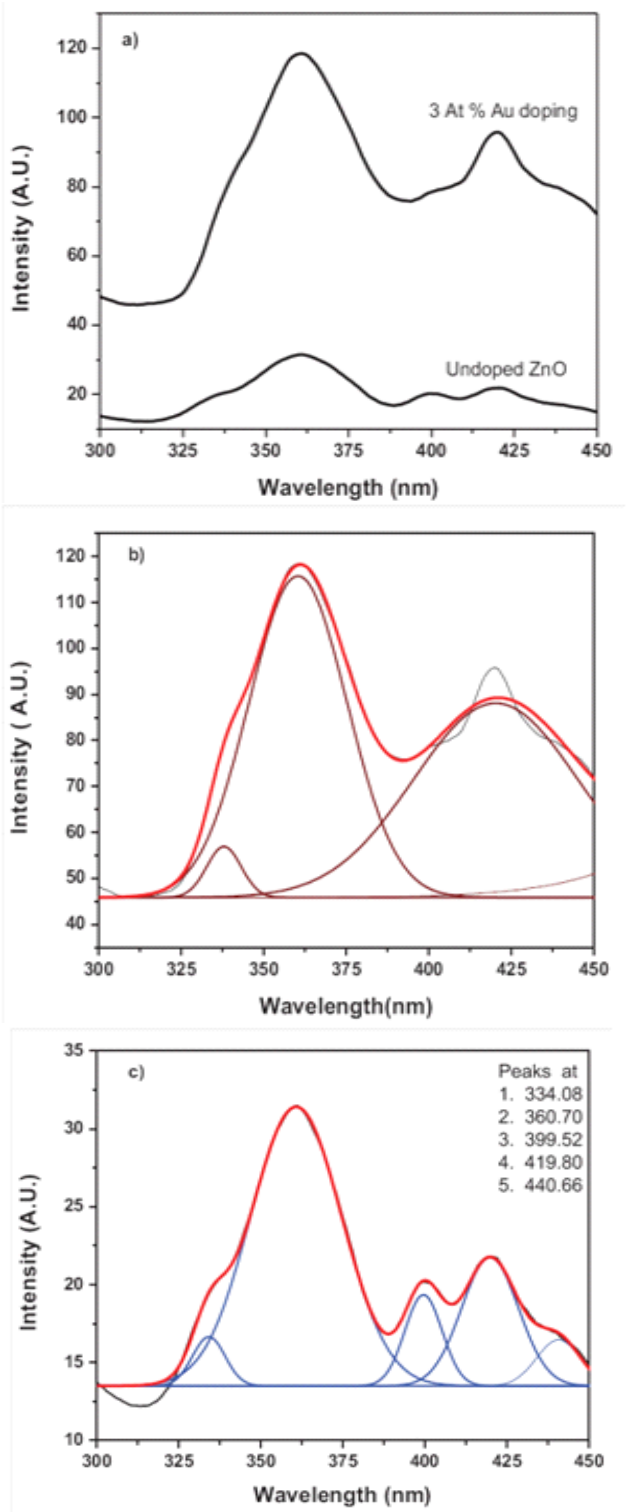


Fig. 7. (a) Show Photoluminescence spectra of the pure ZnO and 3 at. % Au doped ZnO thin films and (b) shows deconvolatoion of undoped ZnO, (c) shows deconvoation of 3 at. % Au:ZnO film.

Characterization of Au:ZnO thin films

Photoelectrochemical (PEC) characterization

From I-V measurement it is seen that the I_{sc} and V_{oc} values increase as the Au Percentage increases. This increase in the current values is related to the surface plasmons resonance (SPR) of Au nanoparticles. The variation in I_{sc} and V_{oc} values with concentration of Au is shown in **Fig. 8**. The high density free electrons oscillate under the influence of light (surface plasmon resonance). When an incident light of wavelength greater than particle size is used to irradiate the noble metal nanoparticle, the high-density electrons form a cloud and oscillate. When Au particles combine with ZnO, the electrons accumulate at the interface between gold and zinc oxide resulting in transfer of electrons from gold particle to ZnO [**13**]. This is due to the strong interaction coupling between Au and ZnO leading to transfer of electron from Au to ZnO as the Au-ZnO nanoparticles are formed [**14-15**].

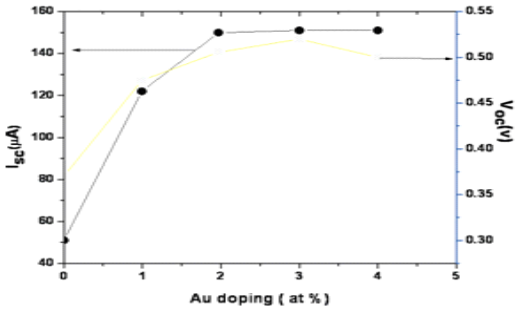


Fig. 8. Variation of Isc and Voc for the PEC cell formed with Au:ZnO thin films versus Au doping concentration.

Photoelectrocatalytic degradation of methylene blue (MB)

It discharges from certain industries like textile and other finishing units shows alarming level of environmental impurities, undissolved solids, organic surfactants, and certain heavy metals which can be very toxic. The colored materials can be treated by three methods, namely: (1) physical methods such as adsorption, reverse osmosis and precipitation, (2) chemical processes of oxidation (by oxidizings agents like HNO_3, $H2O_2$, etc.) and reduction (by reducing agents like thio, sulphites, etc.) and (3) biochemical methods by application of aerobic and anaerobic treatments [**27**]. The demerit of precipitation methods is that it is associated with sludge formation while that of the adsorption process is that the adsorbents is required to be occasionally regenerated. This will incur additional costs and sometimes may undergo very lengthy process. Biological treatment is an inefficient process when complicated aromatic molecules are present. Advanced oxidation processes guarantees a potential treatment option for textile wastewater compared to other treatment processes [**28-30**]. The usefulness of R:ZnO/UVA (R=Ag, Au) photoelectrocatalytic processes is that it avoids sludge formation during the treatment process. They can be performed at ambient conditions with the possibility of complete conversion of organic compound to CO_2 [31].

In this study we have evaluated the effectiveness of the R:ZnO/UVA (R=Au) in the decolorization of dye by photoelectrocatalytic process. Methylene blue (MB) was adopted as a model dye to observe photocatalytic degradation using R:ZnO (R= Au) electrodes.

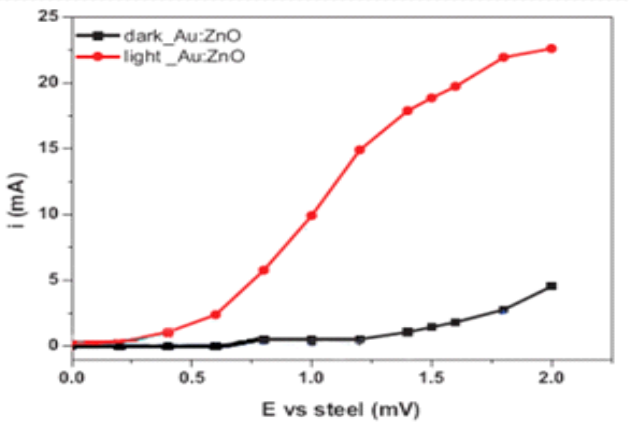


Fig. 9. Dark and light current for Au:ZnO electrodes (64 cm^2) under UVA illumination for 0.1 M NaOH against applied voltage w.r.t. steel counter with a flow rate of 12.2 lh^{-1}.

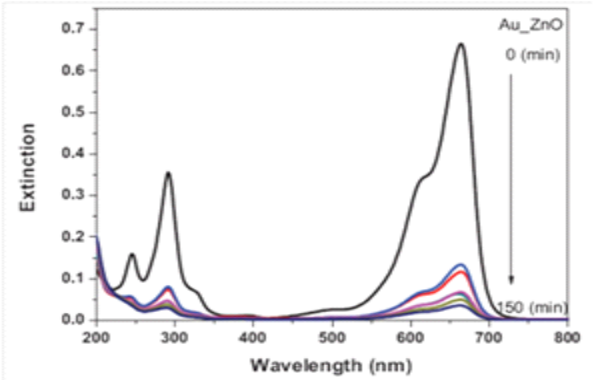


Fig. 10. Extinction spectra of MB with Au:ZnO under UVA light illumination.

The testing of degradation of MB during photoelectrocatalytic process using Au:ZnO photocatalyst has been carried out measuring current i by varying potential E across the Au:ZnO thin films 64 cm^2, 1 mm apart, under the illumination of UVA. Steel electrodes are used in the experiment. The i-E curve is shown in **Fig. 9**. The current reached its saturation value of about 18.7 mA at bias voltage of 1.5 V across Au:ZnO. The average photocurrent during degradation of MB experiment is 18 mA for Au:ZnO. In last part of experiment there is slight decrease in photocurrent probably due to intermediate byproducts formed during photocatalytic reaction. **Fig. 10** shows extinction of MB with reaction time for Au:ZnO electrode. It is observed that initial degradation rate is very fast in case of Au:ZnO electrodes. The percentage of decolorization is calculated using formula.

$$Decolorization\ (\%) = \frac{A-A_0}{A_0} \times 100$$

where A_0 is absorbance at t= 0 and A is absorbance at time t.

Conclusion

Pure and noble metal (Au) doped zinc oxide thin films were successfully fabricated by a solution-based route under controlled procedure on large area substrates. These films have been thoroughly investigated for their PEC, structural, morphological, compositional and optical characteristics. The maximum value of Isc and Voc for 3 at. % Au:ZnO thin films confirms the optimization of doping percentage. The nanocrystalline films with hexagonal crystal structure showed promising capacity for degradation of methylene blue. Au:ZnO films were used as photoelectrode, it was observed that 80% degradation of MB occured in 150 min. No significant photocorrosion of ZnO electrode was noticed as observed by atomic absorption spectroscopy. The percentage of COD reduction was less than the percentage of decolorization which can be attributed to the formation of intermediate smaller organic compound. Therefore, it required more time to achieve complete mineralization of MB. From the kinetic parameters and degradation efficiency, it can be concluded that Au:ZnO photocatalyst synthesized by the solution-based route exhibit potential application in the degradation of MB.

Acknowledgments

The author would like to acknowledge Prof. Dr. Narayan Prasad Adhikari and Prof. Dr. Binil Aryal for research guidance and support.

References

1. Stavale, F.; Pascua, L.; Nilius, N.; Freund, H.-J. Morphology and Luminescence of ZnO Films Grown on a Au (111) Support. J. Phys. Chem. C 2013, 117, 10552−10557.
2. K. L. Foo, U. Hashim, C. H. Voon, Mohammad Kashif, and Md. Eaqub Ali, "Au decorated ZnO thin film: application to DNA sensing," Microsystem Technologies-Micro-And Nanosystems-Information Storage And Processing Systems, 2016, 22, 903–910.
3. N. Hongsith, C. Viriyaworasakul, P. Mangkorntong, N. Mangkorntong, S. Choopun, Ethanol sensor based on ZnO and Au-doped ZnO nanowires, Ceramics Int. 2008, 34, 823-826.
4. Fermin, D. J., Tiwari, D., Harniman, R., Griffiths, I., Cherns, D., Koehler, T.,Klenk, R.Cu2ZnSnS4 Thin Films Generated from a Single Solution Based Precursor: The Effect of Na and Sb Doping Chem. Mater., 2016, 28 (14), 4991–4997
5. Shined D. V. et al. Revisiting metal sulfide semiconductors: a solution-based general protocol for thin film formation, Hall effect measurement, and application prospects, Adv. Funct. Mater. 2015, 25, 5739–5747.
6. C.O. Chey, X. Liu, H. Alnoor, O. Nur, M. Willander, Fast piezoresistive sensor and UV photodetector based on Mn-doped ZnO nanorods, Phys. Status Solidi RRL 2015, 9, 87–91.
7. H. Khallaf, G. Chai, O. Lupan, H. Heinrich, S. Park, A. Schulte, L. Chow, Investigation of chemical bath deposition of ZnO thin films using six different complexing agents, J. Phys. D: Appl. Phys. 2009, 42,135304.
8. W. Li, C. Kong, H. Ruan, G. Qin, G. Huang, T. Yang, W. Liang, Y. Zhao, X. Meng, P. Yu, Electrical properties and Raman scattering investigation of Ag doped ZnO thin films, Solid State Commun. 2012, 152,147–150.
9. O. Lupan, L. Chow, G. Chai, A single ZnO tetrapod-based sensor, Sens. Actuators B 2009, 141 ,511–517.
10. S. W. Lam, K . Chiang, T. M. Lim, R. Amal, G. K. C. Low, Appl. Catal. B: Environ., 2007,72, 363.
11. G. Cheng, X. Wu, B. Liu, B. Li, X. Zhang, Z. Du, ZnO nanowire Schottky barrier ultraviolet photodetector with high sensitivity and fast recovery speed, Appl. Phys. Lett. 2011, 99, 203105.
12. G. Chai, O. Lupan, E. Rusu, G. Stratan, V. Ursaki, V. S¸ ontea, H. Khallaf, L. Chow, Functionalized individual ZnO microwire for natural gas detection, Sens. Actuators A 2012, 176,64–71.
13. O. Lupan, L. Chow, G. Chai, A single ZnO tetrapod-based sensor, Sens. Actuators B 141 2009, 141,511–517.
14. O.Lupan,V.Cretu,M.Deng,D.Gedamu,I.Paulowicz,S.Kaps,Y.K.Mishra,O. Polonskyi, C. Zamponi, L.Kienle, Versatile growth of freestanding orthorhombic α-molybdenum trioxide nano-and microstructures by rapid thermal processing for gas nanosensors, J.Phys.Chem.C 2014, 118, 15068–15078.
15. A. Mendoza-Galvan, C. Trejo-Cruz, J. Lee, D. Bhattacharyya, J. Metson, P. Evans, U. Pal, Effect of metal-ion doping on the optical properties of nanocrystalline ZnO thin films, J. Appl. Phys. 2006, 99, 014306.
16. Li, X. Zhao, W. Fan, Structural, electronic, and optical properties of Ag-doped ZnO nanowires: first principles study, J. Phys. Chem. C 2011,115, 3552–3557.
17. L. Chow, O. Lupan, G. Chai, H. Khallaf, L. Ono, B. Roldan Cuenya, I. Tiginyanu, V. Ursaki, V. Sontea, A. Schulte, Synthesis and characterization of Cu-doped ZnO one-dimensional structures for miniaturized sensor applications with faster response, Sens. Actuators A 2013,189,399–408.
18. D. Liu, Y. Lv, M. Zhang, Y. Liu, Y. Zhu, R. Zong, Y. Zhu, Defect-related photoluminescence and photocatalytic properties of porous ZnO nanosheets, J. Mater. Chem. A 2014,2, 15377–15388.
19. J. Dai, C. Xu, X. Xu, J. Guo, J. Li, G. Zhu, Y. Lin, Single ZnO microrod ultraviolet photodetector with high photocurrent gain, ACS Appl. Mater. Interfaces 2013,5, 9344–9348.
20. Q. Xiang, G. Meng, Y. Zhang, J. Xu, P. Xu, Q. Pan, and W. Yu;Ag nanoparticle embedded-ZnO nanorods synthesized via a photochemical method and its gas-sensing properties; *Sensors Actuators B: Chemical* 2010, 2,635
21. D. H. Lee, K. H. Park, S. Kim, and S. Y. Lee; Effect of Ag doping on the performance of ZnO thin film transistor; *Thin Solid Films* 2011, DOI: 10.1016/j.tsf.2011.04.064 .
22. L. Cao, L. Zhu, J. Jiang, R. Zhao, Z. Ye, and B. Zhao; Highly transparent and conducting fluorine-doped ZnO thin films prepared by pulsed laser deposition; *Sol. Energy Mater. Sol. Cells* 2011, 95, 894.
23. D. R. Sahu and J. L. Huang; Design of ZnO/Ag/ZnO multilayer transparent conductive films; *Material Science and Engineering B* 2006, 130, 295 and Y. Zheng, L.Zheng, Y.Zhan, X.Lin, Q.Zheng, K.Wei, Ag/ZnO heterostructure nanocrystals: synthesis, characterization, andphotocatalysis, Inorg.Chem.2007,46, 6980–6986.
24. I.-S.Hwang,J.-K.Choi,H.-S.Woo,S.-J.Kim,S.-Y.Jung,T.-Y.Seong,I.-D.Kim,J.-H. Lee, Facilecontrol of C_2H_5OH sensing characteristics by decorating discrete Ag nanoclusterson SnO_2 nanowire networks, ACS Appl. Mater. Interfaces 2011,3, 3140–3145.
25. Y. Jin, J. Wang, B. Sun, J.C. Blakesley, N.C. Greenham, Solution-processed ultraviolet photodetectors based on colloidal ZnO nanoparticles, Nano Lett. 2008,8, 1649–1653.
26. H. Kind, H. Yan, B. Messer, M. Law, P. Yang, Nanowire ultraviolet photodetectors and optical switches, Adv. Mater. 2002,14, 158–160.
27. G. Chai, O. Lupan, L. Chow, H. Heinrich, Crossed zinc oxide nanorods for ultraviolet radiation detection, Sens. Actuators A 2009, 150, 184–187.
28. J. Goldberger, D.J. Sirbuly, M. Law, P. Yang, ZnO nanowire transistors, J. Phys. Chem. B 2005, 109, 9–14.
29. Y. K. Mishra, S. Mohapatra, R. Singhal, D. K. Avasthi, D.C. Agarwal, S. B. Ogle, Appl. Phys. Lett., 2008, 92, 043107.
30. S.-T. Kuo, W.-H. Tuan, J. Shieh, S.-F. Wang, Effect of Ag on the microstructure and electrical properties of ZnO, J. Eur. Ceram. Soc. 2007,27, 4521–4527.
31. L. Cao, L. Zhu, J. Jiang, R. Zhao, Z. Ye, and B. Zhao; Highly transparent and conducting fluorine-doped ZnO thin films prepared by pulsed laser deposition; *Sol. Energy Mater. Sol. Cells* 2011. 95, 894.

