Journal of Advances in Engineering and Science

(JAES) Volume 13 Issue 02
ISSN.: 0973-9041

Synthesis, Characterization of Doped Zinc Oxide Nanostructure and its Photocatalytic Application

Snehal S. Hande
Department of Chemical Eng.
Sinhgad College of Engineering,
Vadgaon (Bk),
Pune, Maharashtra, India.
pdjolhe@gmail.com

P. D. Jolhe
Department of Biotechnology,
Sinhgad College of Engineering,
Vadgaon(Bk),
Pune, Maharashtra, India.
pdjolhe@gmail.com

V. S. Ashtekar
Department of Chemical Eng.
Sinhgad College of Engineering,
Vadgaon (Bk),
Pune, Maharashtra, India.
vashtekar108@gmail.com

Abstract — Recently titanium dioxide photocatalyst have been used successfully in different fields, for example, air-purification, self cleaning, deodorizing and sterilization. However, the major issue is that with TiO2 photocatalyst we can utilize only the UV light which exhibit only 2-3% of solar light. For the improvement of photocatalytic degradation of pollutants at λ > 400 nm, few types of photocatalysts have been tried such as transition metal ion implanted TiO2, reduced TiO2, dye-sensitized TiO2. Other semiconductors as photocatalysts have been examined by few research groups. In the recent years, ZnO semiconductors, has gotten much attention because of his wide and direct band gap of 3.37 eV at room temperature, minimum cost and environmentally friendly quality. However, the reactivity of ZnO with nanometer dimensions depends essentially on the optical and electronic properties; it is transparent invisible region. Therefore, ZnO semiconductor is broadly used in photocatalytic degradation of organic and inorganic pollutants. Some issues still remain to be solved in its application, such us the quick recombination of photogenerated electron-hole pairs. In this manner enhancing photocatalytic activity by modification has become a interesting topic among researches in recent years. Transition metal doping and coupling semiconductors are the most way. In like manner, several techniques have been used for the synthesis of undoped and doped ZnO. This survey focused on the different synthesis methods of ZnO and its application in dye degradation.

Keywords: zinc oxide (ZnO) nanoparticles; doping; application.

I. Introduction

Recently, transition metal and rare earth doped II-IV semiconductor nanoparticles have gotten much consideration because of modification of optical properties. Normally, semiconducting nanoparticles are known to exhibit physico-chemical properties due to quantum confinement effect. Particularly, doped nanoparticles are predicted to demonstrate enhanced optical properties, viz., luminescence efficiency, band edge emission and delay time with respect to particle size variation. These properties have opened up a number of new ranges of applications, for example, DNA markers, biosensors, light emitting diodes, lasers and in spintronics and photocatalysis.

Semiconductor materials, for example TiO_2, ZnO are the promising competitors in air purification, harmful waste remediation and water purification. In recent years considerable attention is attributable to their photocatalytic capacity in the degradation of different environmental pollutants [1]. Zinc oxide (ZnO) is attracting huge attention due to its fascinating properties like wide direct band gap of 3.37 eV at room temperature with the wurtzite structure and high exciton binding energy of 60 meV [2], high thermal stability and high chemical and mechanical strength [3]. It is also cheap and biocompatible material. Because of its unique properties, ZnO can be used for many of the applications including the manufacture of paint, ceramics, photocatalysis and electronics [4]. ZnO is one of the most encouraging material which is applied to many fields, for examples, laser diodes, transparent conductive contacts, ultraviolet lasers, thin film transistors, solar cells, optoelectronic and piezoelectric applications, organic light-emitting and liquid crystal displays, surface acoustic wave devices, gas sensors etc. TiO_2 and ZnO are the main transition metal oxide semiconductors that have enough stability to photoexcitation. Despite the fact that TiO_2 is universally recognized as the most photo active catalyst, ZnO is a suitable another option to TiO_2 because of same band gap energy (3.2 eV) and lower cost which shows better performance in the degradation of dye molecules in both acidic and basic medium than TiO_2. It is surely understood that ZnO demonstrates the richest scope of morphologies among the wide band gap semiconductors [5]. For a decade now, photocatalytic work has mainly focused on TiO_2 because it is a stable and safe material. However, TiO_2 particles must be energized by high photon energy to start any photocatalytic process. This catalyst has a low quantum yield rate because of its low rate of electron exchange to oxygen thus takes into account a high rate of recombination of energized electrons and holes. Recently, many research groups have focused on the capability of ZnO particles for their photocatalytic activities rather than TiO_2 particles. Despite the fact that photodegradation mechanism and the band gap energy are same, many documents have described that the ZnO photocatalyst had higher photocatalytic efficiency. ZnO has few disadvantages together with the low quantum yield and quick combining rate of photogenerated electron-hole pair in the photocatalytic reactions in aqueous solutions which deter commercialization of the photocatalytic degradation process [4].

In general, the as-prepared ZnO nanoparticles are n-type semiconductors because of the oxygen vacancies and some other native defects, for example, zinc interstitials etc. Such vacancies and imperfections serve as active sites for the adsorption of oxygen and H_2O molecules. However, the presence of such defects in ZnO fundamentally influences the photoluminescence of ZnO. The defects present inside the ZnO strongly depend on the synthesis method and also annealing conditions [2].

Recently, undoped or doped ZnO films widely examined because of their advantageous features, for example, high optical transparency, low electrical resistivity, simple preparation, low cost and non-poisonous quality. Doped ZnO films show moderately higher conductivity, high transmittance when compared with undoped ZnO films. Subsequently, doping with various dopants is generally necessary to enhance the electrical and optical properties of these films. Rare earth metals are known for their ability to trap the electrons, which can be adequetely decrease the combining of photogenerated electron-hole pairs.

II. Methods of Synthesis of Zinc Oxide and Applications

P. Korake, R. Dhabbe, A. Kadam, Y. Gaikwad, K. Garadkar [1] prepared La doped ZnO nanorods using microwave assisted method. They determined that the crystallite size of La-doped ZnO is much smaller when compared with pure ZnO and reduces with increasing La content. They described that the degradation efficiency of meta-systox increases up to 0.5 mol% of La doped ZnO and afterward decreases for higher doping level under UV light irradiation.

X. Xu, Y. Chen, S. Ma, W. Li, Y. Mao [3] produced lanthanum doped ZnO nanofibers with bed like structures by electrospinning technique. They reported that La doping changes the structures of ZnO nanofibers. They found that an appropriate amount of La doping improves the gas sensing properties of ZnO nanofibers. The 1.0 wt% La-doped ZnO had high sensitivity and excellent selectivity, despite its short response time and recovery time.

N. Clament, S, Selvam, V. Judith, J. Kennedy [5] used co-precipitation method for the synthesis of ZnO nanomaterials. Because of the small crystal size distribution, spherical shaped nanocrystals showed superior photocatalytic activity. They observed that when compared with other zinc oxide and TiO_2, 1.5 wt% La-doped ZnO showed better performance in the degradation of BPA. The photocatalytic activities of the catalysts were affected by the morphology, high crystallinity, surface defects produced by La loading into ZnO.

S. Anandan et al. [6] synthesized La doped Zinc oxide with various La contents using co-precipitation method. When compared to pure ZnO they determined that the crystallite size of La-doped ZnO is smaller and reduced with increasing La content and showed that the rate of degradation of monocrotophos increased with increasing in La content up to 0.8 wt% and then reduced. They also found that the doping of La in ZnO helps to accomplish complete mineralization of MCP within a short irradiation time.

For the synthesis of Ag doped ZnO nanoparticles S. Suwanboon et al. [7] used the precipitation method. They examined the effects of Ag doped ZnO nanoparticles on their structural, photocatalytic and antibacterial properties. They described that the particle sizes reduced, and the photocatalytic efficiency for degradation of MB increased.

H. Benhebal, A. Leonard, M. Chaib, S. Lambert, M. Crine [8] demonstrated that when ZnO was doped with 10% lithium, potassium or sodium the band gap energy was reduced because of an increase in its crystallinity. In the degradation of phenol and benzoic acid, it is found that Na- and Li-doped ZnO particles had a superior efficiency than the K-doped ZnO particles.

C. Xu, L. Cao, G. Su, W. Liu, X. Qu, Y. Yu [9] synthesized ZnO nanoparticles by using hydrothermal method. It is observed that the structure of the ZnO powders were hexagonal wurtzite and band gap energy increased along with the reduction of the crystallite size. It is observed that when reacting for 240 min, 78% of methyl orange is degraded by the 3 mol% Co- doped ZnO nanoparticles.

R. Soltani, S. Jorfi, H. Ramezani, S. Purfadakari [10] synthesized and immobilized ZnO nanostructures onto clay like support, named biosilica. Biosilica used as sonocatalyst for the sonocatalytic decolourization of methylene blue dye in the aqueous phase. They concluded that the sonocatalytic action of ZnO-biosilica nanocomposite (77.8%) was higher than that of pure ZnO nanostructure (53.6%). The addition of chloride and carbonate ions negligibly affected sonocatalysis while the addition of persulfate ion increases the color removal from 77.8% to 99.4% during 90min.

For the synthesis of La doped zinc oxide nanoparticles, M. Khatamiana, A. Khandara, B. Divbanda, M. Haghighi, S. Ebrahimiasl [11] used polymer pyrolysis method. Synthesized materials were characterized by various methods, for example, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-vis. When compared with pure ZnO, the particle size of La doped ZnO is found to be smaller. When La, Nd and Sm loading increased up to 4, 4 and 8 wt%, the rate of degradation of 4-NP is increased and afterward reduced. When compared with other catalyst, the 4 wt% Nd-doped Zinc oxide was found to be most active and showing high photocatalytic action.

W. Raza, M. Haque, M. Muneer [12] used sol gel method for the synthesis of pure and doped ZnO. Synthesized materials were characterized by various methods, for example, x-ray diffraction, scanning electron microscopy, energy dispersive x-ray analysis (EDX), UV-vis and fourier transform infrared spectroscopy (FTIR). They found that the nature of the obtained particle were crystalline with hexagonal wurtzite phase. According to the SEM and EDX images it is observed that La and Ce metals efficiently loaded on the surface of ZnO. The thermal stability of pure ZnO was reduced, due to enhancement in the dopant concentration. The photocatalytic activity is measured by evaluating change in concentration of chromophoric dyes which in turn considered as function of irradiation time. By increasing in dopant concentration of La from 0 to 0.9% Ce, the photocatalytic activity of doped ZnO increased from 0 to 2%.

III. Conclusions

This paper represents all inclusive survey of different types of synthesis technique of zinc oxide and its application in dye degradation. ZnO is a suitable different option for TiO_2 because of same band gap energy (3.2 eV) and lower cost which indicates superior performance in the degradation of dye molecules in both acidic and basic medium than TiO_2. Doped ZnO photocatalyst is having more photocatalytic efficiency than pure ZnO.

REFERENCES

[1] P. Korake, R. Dhabbe, A. Kadam, Y. Gaikwad, K. Garadkar, “Highly active Lanthanum doped ZnO nanorods for photodegradation of metasystox”, Journal of Photochemistry and Photobiology B: Biology (2013).

[2] R. Govindaraj, R. Govindan, M. Geetha, P. Anbarasan, “Structural, morphological and luminescence studies on pristine and La doped zinc oxide (ZnO) nanoparticles”, International journal for light and electron optics (2015).

[3] X. Xu, Y. Chen, S. Ma, W. Li, Y. Mao, “Excellent acetone sensor of La-doped ZnO nanofibers with unique-bead-like structures”, Sensors and Actuators B (2015).

[4] S. Suwanboona, P. Amornpitoksuk, A. Sukolrat, N. Muensit, “Optical and photocatalytic properties of La-doped ZnO nanoparticles prepared via precipitation and mechanical milling method”, Ceramics International 39, pp. 2811–2819, 2013.

[5] N. Clament, S. Selvam, V. Judith, J. Kennedy, “Comparative studies on influence of morphology and La doping on structural, optical, and photocatalytic properties of zinc oxide nanostructures”, Journal of Colloid and Interface Science, pp. 407 215–224, 2013.

[6] S. Anandan A. Vinu, K.L.P. Sheeja, L.N. Gokulakrishnan P. Srinivasu, T. Mori, V. Murugesan, K. Ariga[c], “Photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension”, Journal of Molecular Catalysis A: Chemical 266, pp. 149–157, 2007.

[7] P. Amornpitoksuk, S. Suwanboon, S. Sangkanu, A. Sukhoom, N. Muensit, J. Baltrusaitis, “Synthesis, characterization, photocataly- tic and antibacterial activities of Ag-doped ZnO powders modified with a diblock copolymer”, Powder Technology 219, pp. 158–164, 2012.

[8] H. Benhebal, M. Chaib, A. Leonard, S. Lambert, M. Crine, “Photodegradation of phenol and benzoic acid by sol–gel synthesized alkali metal-doped ZnO”, Materials Science in Semiconductor Processing 15, pp. 264–269, 2012.

[9] C. Xu, L. Cao, G. Su, W. Liu, X. Qu, Y. Yu, “Preparation, characterization and photocatalytic activity of Co-doped ZnO powders”, Journal of Alloys and Compounds 497, pp. 373–376, 2010.

[10] R. Soltani, S. Jorfi, H. Ramezani, S. Purfadakari, “Ultrasonically induced ZnO–biosilica nanocomposite for degradation of a textile dye in aqueous phase”, Ultrasonics Sonochemistry 28, pp. 69–78, 2016.

[11] M. Khatamiana, A. Khandara, B. Divbanda, M. Haghighi, S. Ebrahimiasl, “Heterogeneous photocatalytic degradation of 4-nitrophenol in aqueous suspension by Ln (La^{3+}, Nd^{3+} or Sm^{3+}) doped ZnO nanoparticles”, Journal of molecular catalysis A: Chemical 365, pp. 120– 127, 2012.

[12] W. Raza, M. Haque, M. Muneer, “Synthesis of visible light driven ZnO: Characterization and photocatalytic performance”, Applied surface science 322, pp. 215-224, 2014.