

Recent Developments of Zinc Oxide Nanostructures as Solar Photocatalysts

Nandini Sharma¹ and Ranjana Jha²

^{1,2}Research Lab for Energy Systems, Netaji Subhas Institute of Technology, University of Delhi, Delhi.
 E-mail: ¹nandinis304@gmail.com, ²drranjanajha@gmail.com

Abstract—Organic dye pollutants are released from industries that are resistant to environmental degradation and are not completely removed through treatment processes. Their presence in environment can lead to severe health problems to humans and wild-life. Hence, solar photocatalysis process holds a great potential to treat organic dye contaminants. This process is green and eco-friendly for the elimination of dye and secure the obtained clean water for usage. In this perspective, ZnO nanostructures have been shown to be potential candidates as photocatalyst to be used in photodegradation. It involves low-cost, non-toxic and more efficient process in the absorption across a wide fraction of the solar spectrum compared to other metal oxides. There are numerous aspects, yet, required to be taken into consideration for further growth and development. The purpose of this paper is to analyze the photo-degradation processes of organic dye contaminants. This review article covers the recent progress in ZnO nanostructured growth processes and its utilization as a photocatalyst however looking into their future challenges and pathways. Basic factors affecting the photonic efficiency of catalyst have been described. The main bottlenecks for low photonic efficiency and various concepts is reviewed. The role of nanotechnology in field of photocatalysis is presented and related current issues have been pointed out.

1. INTRODUCTION

Since 1974, the rise in prices of oil increased radically and lead to emergent need to develop some alternative energy source[1][2]. It is well known that the solar radiation falling on the surface of earth is more than sufficient to fulfil all the energy demands of human being. Sunrays are blessings of nature and is free of cost[3][4][5]. The task is to gather and transform solar energy to economically viable form and replace the usage of artificial light sources such as lamps by solar photons.

The objective is to devise an inexpensive and energy efficient source of light energy to drive the photodegradation reactions and catalyze the harmful contaminants into harmless products[6][7].

The development of an efficient solar photons assisted catalysis process holds high relevance in today's scenario. Hence, it's a matter of today's need to make use of solar photons in an efficient manner and make the photodegradation process cost effective and feasible. It's a photon induced

degradation of organic contaminant hence, the photocatalyst must be capable of absorbing the photons reaching the earth from solar spectrum[8].

Photocatalysts	Experimental conditions				Degradation efficiency (%)	Ref.
	Catalyst loading (g·L ⁻¹)	Dye	Light source	Irradiation time		
ZnO	0.5	Basic Blue-11	Visible lamp: 2x15 W	24 h.	100%	(Lu et al., 2009)
ZnO	1.25	RemB1 (B)	UV irradiation: 125W Philips Hg lamp	60 min.	90%	(Gouveia et al., 2000)
ZnO	0.5	Rhodamine B	15 W UV lamp	240 min.	100%	(Yu and Yu, 2008)
ZnO: Rod like Rice like Granular	1	Methylene Orange	Photochemical Chamber Reactor containing 16 RPR- 3500 A lamps	60 min.	40% 96% 99%	(Danwittayakul et al., 2013)
ZnO	1	Phenol Red	UV irradiation by 5 UV tubes in UV chamber	60 min.	80%	(Prabha and Lethasree, 2014)
ZnO nanorods	0.5	Phenol	55 W compact Fluorescent lamp	480 min.	71.2%	(Sin et al., 2013)
ZnO	2.5	Acid Brown 14	Solar radiation	180 min.	49%	(Sakthivel et al., 2003)
ZnO	0.5	Acid Red 1	UV radiation	80 min.	100%	(Hameed et al., 2011)
ZnO	1	Acridine Orange	Visible irradiation	180 min.	32%	(Pare et al., 2008)
ZnO	2	EY dye	UV lamp	120 min.	74%	(Chakrabarti and Dutta, 2004)
ZnO nano particles (annealed at 700 °C)	1	EY dye	Solar irradiation	90 min.	78%	Present study

With this important significance of solar energy in assisting photodegradation reactions, it's important to focus on efficient utilization of solar energy for photodegradation reactions[9].

In recent times, many researchers reported papers on fabrication and utilization of photocatalyst due to the advantages of photocatalysis process as listed in Table 1 [JALCOM REFERENCE PUT]. Therefore, a review about the

choice of suitable photocatalyst fabrication approaches to obtain preferred dimension of ZnO nanostructures based on specific use and suitability of solar photocatalytic system should be carried out to ease the implementation of this technology in a bigger scale [10-12].

The main aims of the current review is to estimate the utilization of ZnO nanoparticles as solar photocatalysts, employment of ZnO nanoparticles in water treatment, solar-photocatalysis processes of zinc oxide, growth methods of ZnO nanoparticles, as well as future challenges and perspectives of using ZnO nanoparticles in these processes.

2. FUNDAMENTAL AND MECHANISM OF ZNO ASSISTED SOLAR PHOTOCATALYSIS

ZnO is an n-type semiconductor having a broad direct band gap width (3.37 eV), large excitation binding energy (60 meV) and deep violet-ultraviolet (UV) absorption at room temperature [13-15]. It is an excellent semiconductor oxide that possesses favorable excellent electrical, mechanical and optical properties, similar to TiO₂. Moreover, some studies have confirmed that ZnO exhibits a better efficiency in photocatalytic degradation of some dyes, even in aqueous solution.

As a well-known photocatalyst, ZnO has received much attention in the degradation and complete mineralization of environmental pollutants. Since ZnO has almost the same band-gap energy (3.3 eV) as TiO₂, its photocatalytic capability is anticipated to be similar to that of TiO₂[16]. Moreover, ZnO is relatively cheaper compared to TiO₂ whereby the usage of TiO₂ catalyst is uneconomic for large scale water treatment operations. In addition, ZnO can be a suitable alternative photocatalyst other than TiO₂ since its photodegradation mechanism has been proven to be similar to that of TiO₂. In some cases, ZnO shows higher photocatalytic tendency towards photodegradation and mineralization of environmental organic or inorganic pollutants[17-20].

Photochemical splitting of water into H₂ and O₂ using solar energy is a process of great economic and environmental interest[21].

The key of the process is the ability of photocatalyst to create electron-hole pairs. In a semiconductor photocatalyst, reaction occurs in three steps: (1) the photocatalyst absorbs photon energy and generates photoexcited electron-hole pairs in the bulk, (2) the photoexcited carriers separate and migrate to the surface, and (3) adsorbed species are reduced and oxidized by the photogenerated electrons and holes to produce H₂ and O₂ respectively.

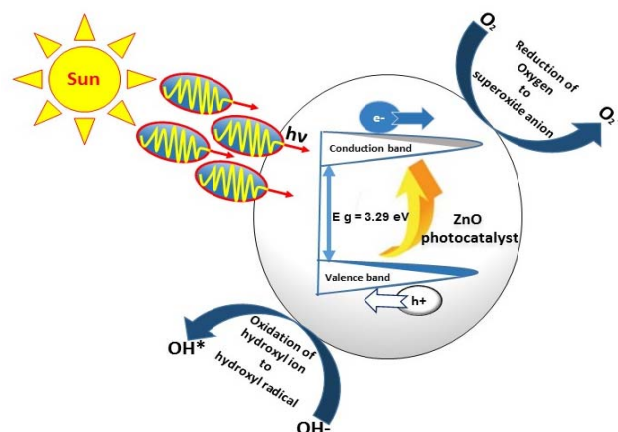


Figure 1 Photodegradation process under solar irradiation [reference]

The available crystallite structures of ZnO crystallization are hexagonal wurtzite and zinc blende. The bonding in hexagonal structure of ZnO is largely ionic and possess radii of 0.074 nm for Zn²⁺ and 0.140nm for O²⁻ [22]. Hence, wurtzite structure formation is preferred over the zinc blende structure.

3. SYNTHESIS ROUTES:

3.1 Co-precipitation route

The synthesis of nanocrystals involved the simultaneous processes of nucleation, growth, coarsening and agglomeration, as shown in Fig.2. The resulting precipitate is generally insoluble species formed under conditions of high super saturation.

Nucleation is a basic step, and huge number of small particles will be generated. Ostwald ripening and aggregation, are secondary processes, which affect the size, morphology, and properties of the resulting products. Chemical reaction results in the conditions of super saturation which is essential to initiate the precipitation process.

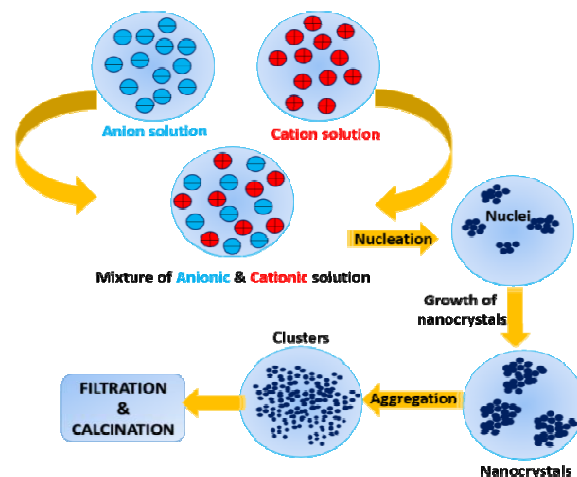


Figure 2: Co-precipitation route for the growth of nanoparticles

3.2 Hydrothermal route

It includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. Hydrothermal method involved synthesis of nanocrystals. The formation of nanoparticles depends on the solubility of elements in hot water under high pressure. The growth is achieved in an apparatus comprising of a steel pressure vessel called an autoclave, inside which teflon lined container is present.[23] This is filled with growth solution upto 60% of the total volume.

The hydrothermal method has several advantages over other methods for the synthesis of nanostructures, such as ability to create crystalline phase which are not stable at the melting point, materials having high vapor pressure. The method keeps a control over their chemical homogeneity and composition [10].

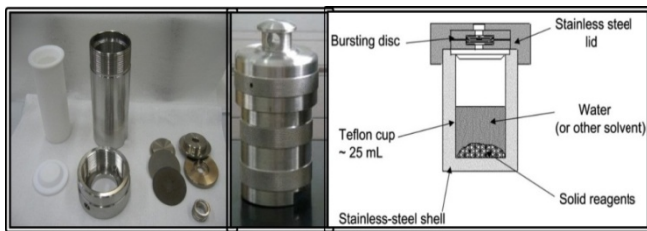


Figure 3: Hydrothermal Unit and its components available at RLES, Department of Physics, NSIT

Hydrothermal crystallisation is defined as transformation of amorphous species in crystalline ones, under the influence of temperature and pressure. It's a simple, fast, low temperature, surfactant-free and carrier solvent assisted interfacial reaction method for preparation of size-controllable nanostructures[12].



Figure 4: Autoclave safety and operation

The crystallization vessels used are Teflon lined stainless steel autoclaves as shown in Fig.3. It provides a pathway for producing mono-dispersed particles with high purity, high crystallinity and controlled physical and chemical features[24].

3.3 Sonochemical route

It is a green route with controlled toxicity, controlled size characteristics and economical. Natural reducing agent (ultrasonic waves in present case) was utilized for nanoparticles synthesis. It involves process free from toxicants, surfactants and capping agents[14].

Ultrasound acts as a significant and green tool for the growth of nanoparticles. When reactant liquids are exposed off to ultrasonic radiations, ultrasonic cavitation is formed. Ultrasonic cavitation involves the bubble formation, growth, and implosive burst of bubbles[15].

Chemical effects of ultrasound improves the rate of reaction and forms highly reactive radical species during cavitation. The resulting ultrasonic cavitation yields a variety of physical and chemical effects, such as high temperature (>5000 K), pressure (>20 MPa), and cooling rate (>1010 K s⁻¹), which offers a unique surroundings for chemical reaction under extreme conditions[16].

When ultrasound is delivered to the reaction solution system, bubbles acts in accordance with the compression/expansion cycle of ultrasound triggering it to follow the cycle of expansion and compression of ultrasonic waves. The energy is released in the form of light and heat at the point of implosion. The high temperatures and pressures created during cavitation leads to release of enough energy to initiate the reaction[17].



Figure 5: Sonochemical process for growth of nanoparticles using Horn type Ultrasonicator, available at RLES, Department of Physics, NSIT

4. EFFECT OF OPERATIONAL PARAMETERS IN SOLAR PHOTODEGRADATION EFFICIENCY

Solar Photodegradation of dyes are effected by numerous factors, such as pH, initial concentration of dyes, photocatalyst particle size and its concentration, reaction temperature, light intensity and the presence of electron acceptors as shown in Figure 2 .

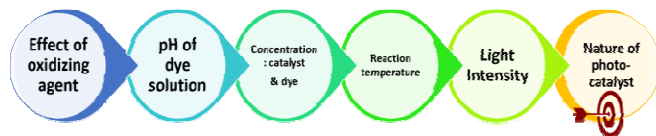


Figure 2 Effect of Various Operational parameters on Solar Photodegradation Efficiency

4.1 Effect of Oxidizing Agent

Presence of Hydrogen peroxide in less amount increases the degradation of organic compounds due such as EY dye molecules, by efficiently generating the hydroxyl radical and inhibiting the process of recombination. Moreover, the solution phase may, at times, be oxygen starved, due to either oxygen consumption or slow transfer. Addition of peroxide in proper amount increases the rate of reaction due to adequate supply of oxygen. In addition, in the presence of high concentration of peroxide, OH⁻ radicals preferentially react with the excess of H₂O₂. This undesirable reaction competes with the degradation of the dye chromophore[28].

4.2 Effect of intensity and wavelength of light

Wide band gap limits absorption in the UV region of solar spectrum. The wavelength and intensity of the UV light irradiation source affects the degradation of dye in aqueous solution using catalyst powder in photocatalytic reactor. The artificial UV irradiation is more reproducible than sunlight and can bring higher efficiency in the degradation of textile dyes. However, solar energy, because of its abundance and non-hazardous nature, is expected to emerge as an alternative cost effective light source.

4.3 Nature of the Solar Photocatalyst

Photocatalytic activity of different photo-catalysts varies with the differences in the lattice mismatch, and BET surface and impurities on the catalyst's surface affect the adsorption behavior of a pollutant and the lifetime and recombination rate of electron-hole pairs. A large surface area can be the determining factor in certain photodegradation reactions, as a large amount of adsorbed organic molecules promote the reaction rate. On the other hand, the predominant way of electron-hole recombination may be different depending on the particle size. Wider band gap is more favorable for driving conjugate reactions involving electrons and preventing recombination [27].

4.4 pH Effect

The interpretation of pH effects on the efficiency of the photodegradation process is a very difficult task because three possible reaction mechanisms can contribute to dye degradation. Dye degradation occurs due to action of hydroxyl radical, direct strong reduction by the electron in the CB. The

contribution of each one depends on the substrate nature and pH [29]. The solution pH modifies the electrical double layer of the solid electrolyte interface, and consequently affects the sorption-desorption processes and the separation of the photo generated electron-hole pairs in the surface of the semiconductor particles. Thus a pH variation can influence the adsorption of dye molecules onto material surface.

5. OBJECTIVES AND CONCLUSIONS OF THIS REVIEW

Photocatalysis is an effective process that converts solar energy into chemical energy which is further used for decomposition of dyes into harmless substances. In the present work, nanostructures are designed for solar energy assisted photocatalysis reactions. The mechanism of photodegradation involves a photocatalyst and a model for a contaminant, usually an organic dye such as Eosin-Y dye in this work in order to evaluate photocatalytic activity. Since the influence of the catalyst properties has been in some cases controversial, it is therefore necessary to study the nature of the sample to be used as a catalyst, as this will provide a clue on the design of photo-catalyst characteristics for an efficient degradation mechanism.

The better understanding of the photo catalytic process and the operative conditions is discussed for the removal of dyes. Nanomaterials have large surface to volume ratio, and require a short distance for photo-excited electrons and holes to diffuse to surfaces, they have the potential for photocatalysis with high photonic efficiency if their structural and optical characteristics are tuned in proper manner.

Certainly, they have to be synthesized by green and clean routes. Hence, carrying out photodegradation experiment and obtaining efficiency under varied experimental conditions has two fold benefit, that is, it enables us to identify the better catalyst for water cleaning under solar irradiation, as well as, it enables us to identify the better photocatalytic material for application in solar cells.

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