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COMPARATIVE STUDY OF PHOTOCATALYTIC ACTIVITY OF ZnO NANOPARTICLES WITH VARIOUS MORPHOLOGIES

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ABSTRACT

Zno has emerged to be one of the most efficient catalyst as far as water detoxification is concerned because it generates H_2O_2 more efficiently, it has high reaction and mineralization rates, along with more number of active sites with high surface reactivity. Here we report synthesis of ZnO nanoparticles (NPs) with various morphologies using a simple and cost effective wet chemical method. Spherical ZnO NPs and ZnO nanowires (NWs) were successfully synthesized by this method. The structure, morphology, and photocatalytic activity of the as synthesized sample were determined using X-ray diffraction, scanning electron microscopy and ultraviolet-visible absorption spectroscopy. The photocatalytic activity of the as synthesized samples were evaluated by the degradation of methyl orange (MO) in aqueous solution under UV light. The potential of the obtained photocatalyst was studied for water treatment under UV irradiation. The photocatalytic results indicate that the as synthesized ZnO NWs show good photocatalytic activity and could be considered as a promising photocatalyst for waste water treatment. ZnO NWs show better crystallinity, high specific area, increased area of contact, and lower transmittance. Hence they are better photocatalyst than ZnO NPs.

Keywords: Chemical Bath Deposition Method, Photocatalytic Activity, Zno Nanoparticles, Zno Nanowires

I. INTRODUCTION

Removal of various organic pollutants from wastewaters is of a great importance nowadays, because these compounds usually are toxic and carcinogenic, posing a serious hazard to aquatic living organisms [1, 2]. Physical methods such as adsorption on various adsorbents, ultra filtration and coagulation only succeed in transferring the pollutants from water to another phase, thus creating secondary pollution [3]. Photocatalysis is a promising process for environmental protection because it is able to oxidize low concentrations of organic pollutants into benign products [4-10]. Photocatalysis utilizes semiconductor photocatalysts to carry out a photo-induced oxidation process to break down organic contaminants and inactivate bacteria and viruses [11-13]. Various photocatalysts, especially metal oxide photocatalysts such as titanium oxide, tin oxide, and zinc oxide are promising materials for degradation of organic pollutants by utilizing UV or solar light [14-21]. High stability, inexpensive and non-toxicity were identified as the main reasons responsible for the wide acceptability of ZnO materials compared to other photocatalysts [22, 23]. ZnO is a semiconductor material with direct wide band gap energy (3.37 eV) and a large exciton binding energy (60meV) at room temperature [24]. ZnO is also biocompatible, biodegradable, and biosafe for medical and environmental applications [25]. ZnO crystallizes in

two main forms, hexagonal wurtzite and cubic zinc blende. Under general conditions, ZnO exhibits a hexagonal wurtzite structure. As to photocatalysis, ZnO is more efficient than TiO_2, the most intensively studied photocatalyst, in the photodegradation of some organic compounds [26-30]. However, the application of ZnO as photocatalyst was limited due to its photoinstability in aqueous solution.

In the present study, we obtained ZnO nanoparticle and ZnO NWs from wet chemical methods. Photocataltytic activity of ZnO nanoparticles and ZnO NWs were investigated by degradation of methyl orange under UV light irradiation. SEM and XRD studies were performed for characterization.

II. EXPERIMENTAL

2.1 Materials

Zinc acetate, Zinc nitrate, absolute ethanol, hexamethylenetetramine (HMTA), NaOH, PVA. Double distilled water was used for the experiments.

2.2 Preparation of ZnO NPs on glass substrate

ZnO NPs were synthesized through hydrolysis of zinc acetate dihydrate in the presence of PVA template prepared in different solvents like ethanol, water and 2-propanol and NaOH. Briefly, 2.19g of zinc acetate dihydrate (0.1M) was dissolved in 100ml of double distilled (DD) water. 50mg of PVA was separately dissolved in10ml DD water with a vigorous stirring at 60° C using magnetic stirrer and then it was added drop vice to zinc acetate solution. For achieving optimum pH around 7–8 during the preparation 0.2M solution of NaOH was added in a similar way. After that glass Substrates were kept in a chemical bath at 95° C.

2.3 Preparation of ZnO NWs on glass substrate

The ZnO seeded layer substrates were kept in a chemical bath at 95°C prepared by dissolving 0.743 gm Zinc nitrate and 0.3504 gm hexamethylenetetramine (HMTA) in 100ml double distilled water. After 2.5 hrs the bath was replenished by fresh source solution and the substrates were kept in the bath for another 2.5hrs. This double bath deposition helped in the growth of densely populated NWs on ZnO seed layer substrates.

III. RESULTS AND DISCUSSION

3.1 Characterization

The XRD diffractogram in Fig.1. Fig.1a) shows the characteristic wurtzite peaks of bulk ZnO corresponding to (101), (002) and (100) planes for as-prepared ZnO NPs. No peaks corresponding to any impurity is detected, showing the purity of the samples prepared.

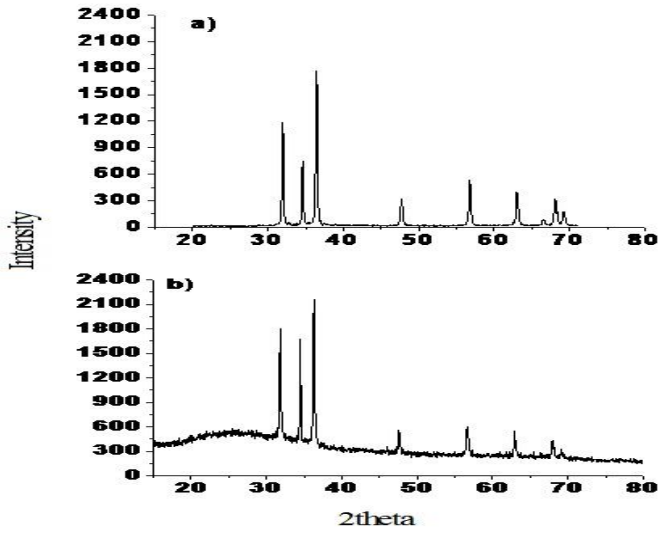

Figure 1: XRD pattern of(a) ZnO NPs and(b) ZnO NWs

Fig 1b) shows the peaks in the XRD spectrum could be assigned to the (100), (002), (101), and (102) crystal planes of ZnO NWs with wurtzite crystal structures. The ZnO seed layers exhibited preferential orientation along (002) plane. Lim et al. suggested that the vertical growth rate of the ZnO NWs is strongly related to the (002) diffraction peak of the seed layer [31]. The intensity of (002) peak on ZnO seed layer resulted in improvement of the crystalline film quality and the highest growth rate in [0001] direction. An average grain size of ZnO NPs is obtainable using the Scherrer's formula for crystallite size broadening of diffraction peaks:

$$D = 0.9\lambda/\beta \cos\theta$$

Where λ is the X-ray wavelength, θ is the Bragg diffraction angle and β is the full width at half-maximum intensity (FWHM) of the diffraction peak [32, 33]. Considering the FWHM of (002) diffraction peaks, crystallite size of 37.1 nm was obtained for ZnO NWs. Whereas the particle size in sample prepared using CBD method was 35 nm. Scherrer's formula was used to calculate particle size.

Fig.2 shows the SEM images of ZnO thin layers produced by CBD method. Fig 2a) shows the spherical ZnO NPs. And fig 2b) shows the vertically aligned ZnO NWs. The Specific area of ZnO NPs is greater than the ZnO NWs. The ZnO NWs is extremely large surface-to-volume ratio as compared to a catalyst deposition on a flat surface [31].

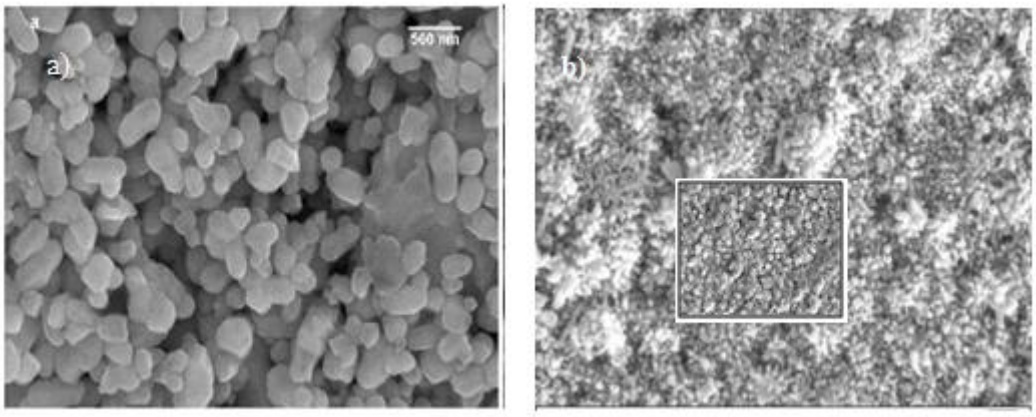

Figure 2: SEM image of ZnO thin film a) Spherical shape ZnO NPs and b) ZnO NWs.

3.2 Photocatalytic activity test

The photocatalytic activity of the ZnO films was evaluated by studying the photo degradation kinetics of MO under UV light irradiation. The thin films with various layers deposited on glass substrates (same substrate area– 4 cm^2) were placed in beakers. Many photo-catalytic experiments were carried out using a home-made photo-reactor (100cm ×100 cm × 100 cm), and using a 340 W mercury lamp for UV irradiation. The distance between the solution surface and the light source was about 12 cm. In a typical experiment, 100 mL of aqueous Methyl Orange (MO) were placed in a beaker, the photo catalyst added and the suspension stirred for 30 min in the dark, at room temperature, to ensure the establishment of the adsorption/desorption equilibrium. The beakers were placed in a photo reactor at 25°C and the UV lamp was turned on. At fixed intervals of time, 3mL of sample were withdrawn, centrifuged, and the supernatant transferred into a spectrophotometer cell for measurement of the absorbance of MO. Absorbance measurements were also recorded in the range of 300-700nm, using a UV-Vis spectrophotometer.

Since the contaminant molecules need to be adsorbed on the photocatalytic surface before the reactions take place, the surface area plays a significant role in the photocatalytic activity. Although NPs offer a large surface area, they have mostly been used in water suspensions, which limit their practical use due to difficulties in their separation and recovery. Moreover, additional equipment is needed for catalyst NPs separation. Photocatalyst supported on a steady substrate can eliminate this issue. One dimensional nanostructures, such as NWs grown on a substrate, offer enhanced photocatalytic efficiency due to their extremely large surface-to-volume ratio as compared to a catalyst deposition on a flat surface. Table 1 compares different ZnO nanostructures for photocatalytic applications. There are many advantages in NWs structures that could be used as photocatalysts [31].

Finally, photocatalytic degradation efficiency (PDE) of MO solutions was calculated with the following formula:

$$PDE(\%) = \frac{A_0 - A}{A_0} \text{ X } 100\% \quad \text{---------- (1)}$$

Where, A0 and A are the UV–Vis absorption of MO solution and MO solutions in suspension after time t.

To evaluate activity of the prepared samples, degradation of MO under UV light irradiation was considered. In Fig. 3, the plots of absorbance versus wavelength for the degradation reaction on ZnO NPs and ZnO NWs. It is

evident that MO has some small absorption peaks in visible range and a large absorption peak in the UV range. Under the light irradiation, intensity of the absorption peaks gradually decreases without any changes in position of the peaks. Fig. 3 shows a typical photocatalytic degradation process of MO using ZnO NPs and ZnO NWs under UV light irradiation. ZnO NWs shows the highest photocatalytic activity, and more than 97% of MO molecule was decomposed in 120 min. For the spherical shape ZnO NPs catalyst, it can be observed that the maximum absorbance at 510 nm had degraded by 22% after irradiation for 20 min, whereas, after 120 min of irradiation, the peak degraded by 89% (calculated by equation (1)) as shown in Figure 3(b). After 20 min of MO degradation by the ZnO NWs catalysts, the peaks had degraded by 20%. However, after the irradiation for 120 min, the peaks nearly disappeared; achieving 97% degradation in this case. The adsorption capabilities of ZnO NWs thin films were performed in the absence of light illumination, and ZnO NPs of the films exhibited 87% removal of the MO from aqueous solution.

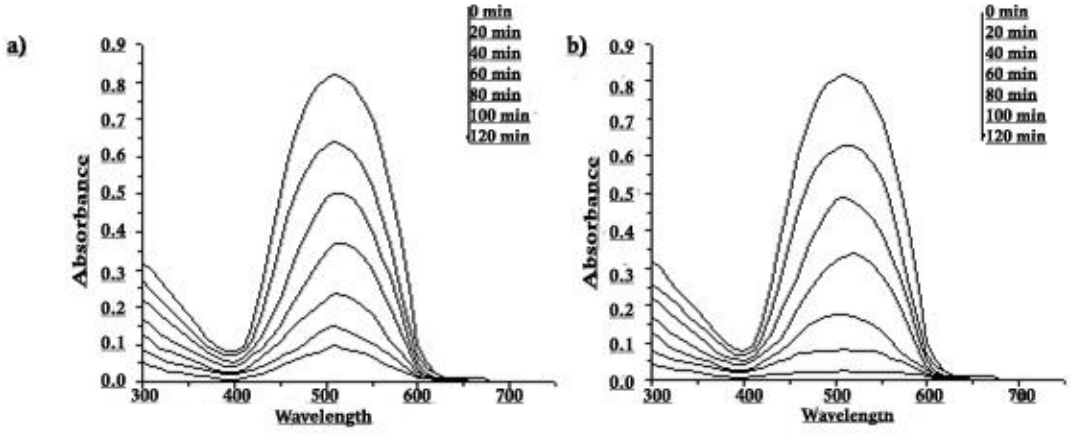

Figure 3: UV-vis spectra in various times for degradation of MO with a) ZnO NPs and b) ZnO NWs.

3.3 Mechanism of Photocatalysis

Fig.4 illustrates the process of photocatalysis. When photons with energies greater than the band gap energy of the photocatalyst are absorbed, the valence band (VB) electrons are excited to the conduction band to facilitate a number of possible photoreactions. The photocatalytic surface with sufficient photo energy leads to the formation of a positive hole (h+) in the valence band and an electron (e−) in the conduction band (CB). The positive hole could either oxidize organic contaminants directly or produce very reactive hydroxyl radicals (OH•). The hydroxyl radicals (OH•) act as the primary oxidants in the photocatalytic system [34], which oxidize the organics. The electron in the conduction band reduces the oxygen that is adsorbed on the photocatalyst. Heterogeneous photocatalysis using semi-conductors is an effective method to destroy a wide range of organic pollutants at ambient temperatures and pressures [35, 36].

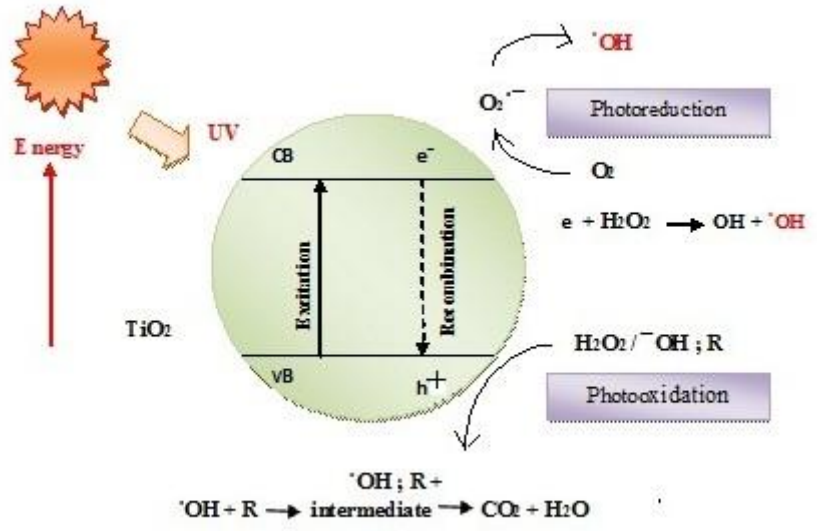

Figure 4: Mechanism of photocatalysis activity [31]

Table 1: Comparison of different ZnO nanostructures used in photocatalytic applications [31].

Nanoparticles		Nanowires	
Advantages	Disadvantages	Advantages	Disadvantages
Could be suspended in a solution	Particle aggregation in a solution leads to a reduced surface area	Growth could be well aligned on most substrates	Growth conditions are more restricted
High performance because of larger surface areas	Post treatment for catalyst removal is required	Offer larger surface area compared to nanothin film	Lower surface area compared to nanoparticle
	Difficult to recover all the catalyst	Post treatment for catalyst removal is not required and Lower crystallinity and more defects	
Efficiency PDE(%) = 87%		Efficiency PDE(%) = 97%	

IV. CONCLUSION

This paper provides of the synthesis, characterization, and applications of ZnO NPs and ZnO NWs. The synthesis method is simple and efficient and it has received increased attention. A mixture of zinc nitrate and hexamine as precursor is the most popular. Due to the unique properties of the material, ZnO NWs are attractive for a number of potential applications such as photocatalysis, solar cells, sensors, and generators. Among the applications of ZnO NWs, photocatalysis is being increasingly used for environmental protection. Further research is needed to improve the quality of ZnO NWs and large-scale produce ZnO NWs for practical

industrial applications. In summary, UV- light responsive ZnO NPs and ZnO NWs were prepared via a CBD method, which exhibited high photocatalytic performance for water treatment under UV- light. ZnO NWs shows the photocatalytic activity 97% of MO molecule was decomposed in 120 min. Therefore, the prepared films exhibit stable photocatalytic properties. Based on this paper, ZnO NWs promise to be one of the most important materials in photocatalytic as well as others applications.

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