



PHOTOCATALYTIC PROPERTIES OF SEMICONDUCTIVE OXIDE NANOPARTICLES. FROM FUNDAMENTALS TO APPLICATIONS

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ABSTRACT

Photocatalysis is a promising technology that demonstrated important applications in environmental systems such as air purification, pollution removal, self-cleaning and antimicrobial. Semiconductive oxides (e.g., ZnO, TiO₂, CuO) are important photocatalytic materials that can act as sensitizers for light based redox processes due to their electronic structure, which is characterized by the conduction-band with electrons (good reductants) and the valence band with holes (powerful oxidants). Excitation of electrons from the conduction-band and valence-band holes can react with electron donors and electron acceptors adsorbed on the semiconductor surface and electric double layer around the particles. The band gap value determines the semiconductive behavior of oxide nanoparticles. The absorption of UV-Vis radiation is an important tool for evaluating photocatalytic behavior of the obtained semiconductive nanoparticles. In this paper we present the correlation between the band gap value, particle size and the photocatalytic activity of ZnO nanoparticles prepared via an aqueous solution chemical method.

KEYWORDS: ZnO nanoparticles, band gap, photocatalysis, antimicrobial activities

1. Introduction

Semiconductor photocatalysts such as TiO₂ and ZnO nanoparticles have attracted much attention in recent years due to their various applications to the photocatalytic degradation of organic pollutants in water and air and dye sensitized photovoltaic solar cell [1-3].

Among these semiconductor photocatalysts, TiO₂ is the most commonly used owing to its stable, harmless and inexpensive properties. However, two typical defects including only exciting by high energy UV irradiation and a low quantum yield rate resulted from a low rate of electron transfer to oxygen and a high rate of recombination between excited electron/hole pairs, limit the photo-oxidation rate of TiO₂ nanoparticles. In order to improve the photocatalytic efficiency of TiO₂ nanoparticles, most

studies have been focused on the modification of TiO₂ doped by metal ions, especially transition metal ions, which make it possible for TiO₂ to absorb visible light by increasing the charge separation [4, 5]. In addition, combination of different kinds of semiconductor also photocatalysts is a promising way to improve the photocatalytic efficiency [6]. The substitution of TiO₂ by ZnO used for photo-degradation is ascribed to the photo-degradation mechanism of ZnO being similar to that of TiO₂ [3, 13]. When photocatalyst e.g. semiconductor TiO₂ or ZnO was irradiated with UV-light, electron (e⁻) from the valence band was excited to the conduction band resulting in the formation of holes (h⁺) in the valence band. Both excited state electrons (in conduction band-CV) and holes (in valence band-VB) can recombine, but if suitable scavenger for electrons or holes is available, recombination is prevented [14].



Example, in an air environment, the photogenerated holes and electrons can react with water molecule which are adsorbed on the surface or react with oxygen molecule to form hydroxyl and superoxide radicals.

ZnO nanoparticles can be synthesized by various approaches including sol-gel processing [15, 16], homogeneous precipitation [17], mechanical milling [18], organometallic synthesis [19], microwave method [20], spray pyrolysis [21, 22], thermal evaporation [23] and mechanochemical synthesis [24].

However, ZnO nanoparticles fabricated by the abovementioned methods are prone to aggregate due to the large surface area and high surface energy. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles.

The present study focuses on the solvothermal synthesis of ZnO nanopowders and the effect of concentration of the precursors and the utilization of ZnO nanoparticles for photocatalytic process for textile treatment.

The solvothermal synthesis of ZnO powders has four advantages (1) powders with nanometer-size can be obtained by this method (2) the reaction is carried out under moderate conditions (3) powders with different morphologies by adjusting the reaction conditions and (4) the as-prepared powders have different properties from that of the bulk.

The influence of surface coating on the photocatalytic degradation of methylene blue was studied, since the photocatalytic activity of ZnO nanoparticles in form of both colloidal solution and textile coating material was evaluated in normal laboratory environment and after UV irradiation.

2. Experimental details

The preparation procedure was basically similar to that of Spanhel [25]. The procedure consists of two major steps. First the suspension of the precursor and second the hydrolysis of the precursor to form the zinc oxide nanoparticles. Zinc acetate dihydrate ($(\text{ZnAc})_2 \cdot 2\text{H}_2\text{O}$) (Sigma Aldrich) and isopropanol (Sigma Aldrich), were used to prepare the precursor before lithium hydroxide (LiOH-Merk) was used to hydrolyze the precursor.

A two neck round bottom distillation flask was used to suspend 0.035M; 0.045M; 0.11M of $(\text{ZnAc})_2 \cdot 2\text{H}_2\text{O}$ in 500mL 2-propanol by reflux heating 82°C (boiling point) for three hours. 0.035M (1:2) lithium hydroxide was dissolved in 500 mL isopropanol at room temperature by vigorous magnetic stirring.

The $(\text{ZnAc})_2 \cdot 2\text{H}_2\text{O}$ suspension was cooled down to 0°C before the lithium hydroxide solution was added drop wise under vigorous stirring.

The ZnO sol was stored at $\leq 4^\circ\text{C}$ for 24 hours.

For separating ZnO nanoparticles and to remove the residual products, high-speed centrifugation 4000rpm/20min was used followed by several alcoholic washes. After which it is dried in an oven at 60°C to obtain powder can be weighed and finally resuspended in alcohol to be ready for application to the textile.

The finishing solutions were prepared: zinc oxide nanoparticle solution (100mL), 3-Glycidoxypropyl)methyldiethoxysilane (GPTMS) sol, Tetraethyl orthosilicate (TEOS) and 0.01N hydrochloric acid (HCl) were mixed together for 2h by magnetic stirring. The final formulation was applied to the fabrics (cotton 100%) by a pad-dry-cure method. After padding samples were dried in ventilated oven at 130°C for 30min. Finally the fabrics were washed with distilled water and dried at ambient temperature.

The size of the ZnO nanoparticles was measured by dynamic light scattering (DLS), using Zetasizer, Nano-S produced by Malvern. The crystal structures of the product were identified by X-ray diffraction patterns DRON -3 diffractometer system (Burevestnik, USSR) with $\text{CoK}\alpha$ radiation, $\lambda=1.789 \text{ \AA}$.

The crystallite size of the particles was calculated with Debye-Scherrer formula:

$$D = \frac{0.94 \cdot \lambda}{\beta \cos \theta} \quad (1)$$

The value of interplanar distance (d) was calculated with Bragg's equation:

$$2d \sin \theta = n \cdot \lambda \quad (2)$$

and lattice parameters:

$$\frac{1}{d^2} = \frac{4(h^2 + h \cdot k + k^2)}{3a^2} + \frac{l^2}{c^2} \quad (3)$$

The calculation is based on the measurement of full-width at half-maximum (FWHM) values in the corresponding XRD pattern.

Band gap energy value for ZnO nanoparticles was calculated with formula [26]:

$$E = h \cdot \frac{c}{\lambda} \quad (4)$$

UV/Vis Absorption measurements for that material are being carried out using a Cary 5E UV-VIS-NIR Spectrophotometer, Varian Deutschland GmbH with integrating sphere.

3. Results and discussions

Figure 1 shows DLS measurements of ZnO nanoparticle as prepared at different concentrations.

The results showed that the size of the nanoparticles increases (from 6nm to 322nm) with the increasing concentration of the solution (from

0.025M to 0.11 M). Crystal structure of the particles prepared was characterized by the XRD (Figure 2). The peaks at $2\theta = 37.48^\circ, 40.37^\circ, 42.87^\circ$ were assigned to (100), (002), (101), of ZnO planes, indicating the wurtzite structure. No characteristic peaks of any impurities were detected, suggesting that high-quality ZnO nanoparticles were synthesized.

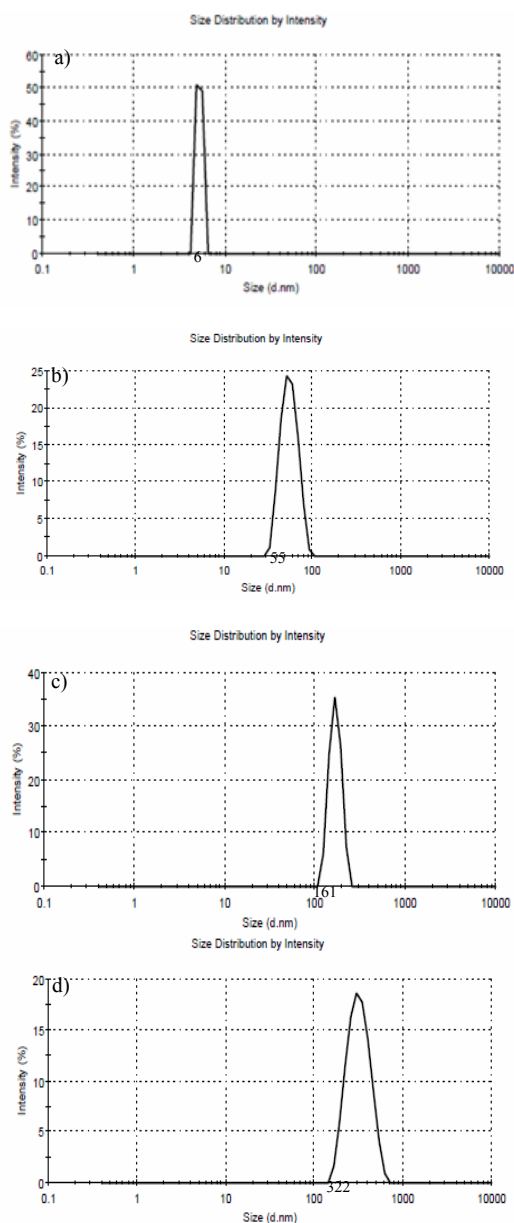


Fig. 1. Histograms of ZnO nanoparticles with different concentration by DLS: ZnO-1(0.025M) a), ZnO-2(0.035M) b), ZnO-3(0.045M) c) and ZnO-4(0.11M) d)

Accordingly, the crystallite size calculated from XRD patterns using the Scherrer equation (Scherrer size) shows the same variation peak intensity.

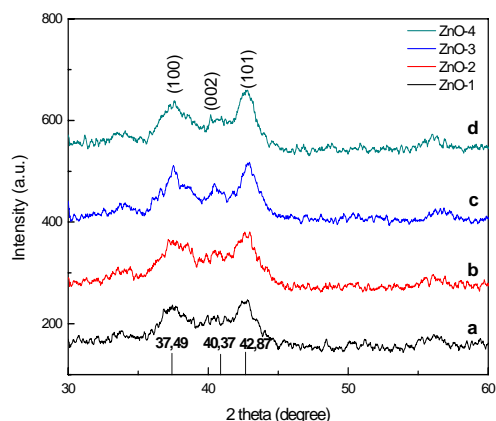


Fig. 2. XRD patterns for ZnO nanoparticles with different concentration: ZnO-1(0.024M) a), ZnO-2(0.035M) b), ZnO-3(0.045M) c) and ZnO-4(0.11M) d)

Table 1. Crystallite size, interplanar spacing and lattice parameters for ZnO nanoparticles with different concentration

Solution concentration	Crystallite size	c	a
[mol/L]	[nm]	[Å]	
0.025M	2.4	5.286	3.2823
0.035M	5.2		
0.045M	8.1		
0.11M	7.5		

For the study of the band gap was used optic absorption spectrum. When a semiconductor absorbs photons of energy larger than the gap of the semiconductor, an electron is transferred from the valence band to the conduction band, an abrupt increase in the absorbency of the material occurs to the wavelength corresponding to the band gap energy. The value of the band gap energy for the sample ZnO-0.035 M was 3.16eV, which resulted from absorption at 392nm. The photocatalytic properties of ZnO nanoparticles on degradation of methylen blue (MB) were studied using ZnO nanoparticles with different size. It can be seen that nanoparticles obtained from the solution with 0.035M concentrations are most effective (Figure 3).

From Figure 4, we can see the comparison with untreated fabrics and treated fabrics between ZnO nanoparticles. The extent of photocatalytic degradation was determined by the reduction in absorbance of the solution. As a result of the reaction between ZnO nanoparticles (through the reactive oxygen species on its surface) and MB dye, the rate

of decolourization was changed as the size of ZnO nanoparticles changed.

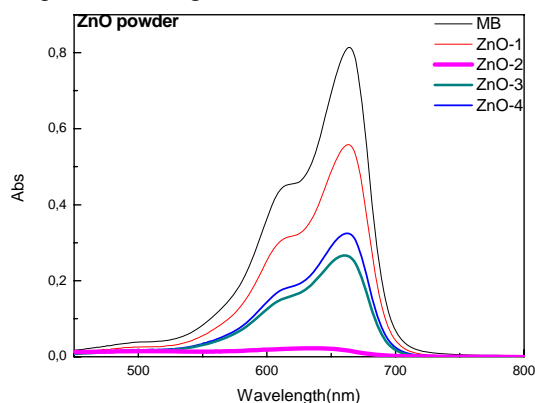


Fig. 3. UV-Vis absorption spectra of methylene blue in presence by different size of ZnO nanoparticles (powder) after UV-irradiation, 1h in normal laboratory environment

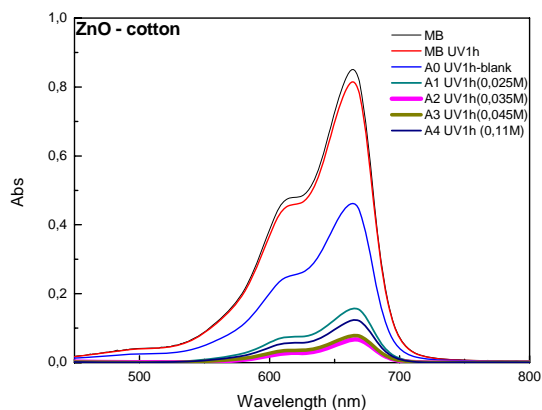
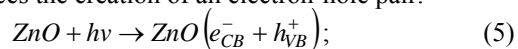


Fig. 4. UV-Vis absorption spectra of methylene blue in presence by different size of ZnO nanoparticles (applied on cotton 100%) after UV-irradiation, 1h in normal laboratory environment

As indicated in figure 3 and figure 4 the rate of decolourization increased as the size of ZnO nanoparticles decreased. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The major peak was observed at λ_{max} , i.e., 663nm.

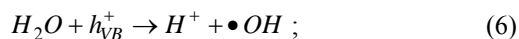
The photocatalytic processes involve several numbers of possible reactions [27]:

- photoexcitation of a semiconductor surfaces induces the creation of an electron-hole pair:



- separation of electrons and holes
- surface reactions

The remaining holes contribute to the oxidation reactions by generating $\bullet OH$ radicals, either to the decomposition of water



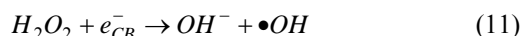
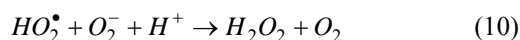
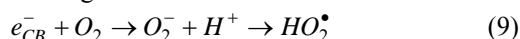
or by the reaction with adsorbed OH^-



The hydroxyl radical species alone is a strong oxidant for the partial or complete degradation of the dye:



While, on the surface of the catalyst, oxygen is reduced as an electron acceptor to superoxide and this leads to production of $HOO\bullet$ radical which finally plays a strong oxidant role



- degradation of dyes

So, all these possible reactions contribute to increase the degradation of MB dye by decreasing the size of ZnO nanoparticles.

4. Conclusions

ZnO nanoparticles are prepared using a solvothermal process at temperature of 82°C. The XRD measurement confirms that ZnO consists of würtzite-type nanocrystallites with different crystalline orientation, and (101) the dominating peak. The photocatalytic activity of different ZnO nanoparticles (powder) and with ZnO nanoparticles treated fabric has been demonstrated by the decoloration of MB dye, after irradiating for 60min with ultraviolet light. As a result of the reaction between ZnO nanoparticles and MB dye, the rate of decolorization changed when the size of ZnO nanoparticles changed.

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