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Preparation and characterization of supported ZnO photocatalyst by zincate method

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ABSTRACT

Supported ZnO film photocatalysts are prepared on glass and ceramic substrates by zincate method. Prepared ZnO films are seen rather strongly durable. They resist to chemical dissolution in a broad range of pH from 3 to 10. Various physical tests are conducted to measure the relevant characteristics of the films. Band gap of ZnO film is calculated as 3.24 eV. SEM analysis shows that the ZnO film has granular morphology with uniform particle size about 300–400 nm. The film thickness is calculated as 1.41 μm after twenty coating cycles and the thickness of the thin film per cycle was approximately 70 nm. Photochemical activity tests are performed by measuring photodecolorization rate of methyl orange solution. First order rate constants are correlated to principal process parameters. The results show that ceramic is the preferable supporting material with high activity. According to simulation study, the photocatalytic activity of film coated on ceramic ring of 8 mm diameter is nearly equal to the activity of powder ZnO slurry of 120 mg/dm^3 density. It carried out about decolorization 65% in 3 h. The calculations show that it is possible to prepare ZnO film on ceramic ring with similar activity as powder ZnO.

1. Introduction

Thus, the preparation of supported catalyst is of practical importance. Semiconductor assisted photocatalysis has gained an important place among various advanced oxidation methods for wastewater treatment. The most widespread used photocatalyst is TiO_2, but in recent years ZnO with a similar band gap (3.2 eV) has attracted special attention owing to its low cost [1–3]. The form of the photocatalyst has strong impacts on the process performance and economy. Nano-sized catalyst powder slurries in wastewater have a high solid to liquid contact area which is beneficial for a high rate of reaction. But, the separation and recycling of the powder photocatalyst from slurry in photocatalytic wastewater treatment is a difficult and costly process. Thus, depositing the catalyst on a suitable support is preferred, despite the decrease in the contact area.

The catalyst support and the coating method influence greatly the activity, the technical life and the preparation cost of the catalyst as well as the photoreactor design. The support should be inexpensive, easily accessible and inert in the wastewater medium. Nevertheless, the catalyst should strongly adhere onto support surface to resist to mechanical degradation and photo-corrosion. Various properties at atomic scale such as chemical and crystal structures, surface energy of the support and of the catalyst directly affect the adherence of the catalyst film on the support surface. On the other hand, surface roughness is a microscopic property which can influence the film properties. At macroscopic scale, geometric form of support which determines catalyst surface to reactor volume ratio is another variable of interest. A literature survey have shown that various materials of different shapes have been proposed as catalyst support among which glass fiber and bead, aluminum foil sheet, plastic fiber-optic cable may be mentioned.

On the other hand, the coating method should be simple, cheap, and convenient for the production at industrial scale and easily adapted to process control for reproducible catalytic properties. In recent years, various methods have been proposed to obtain supported zinc oxide films, such as thermal oxidation deposition [4–6], electron beam evaporation [7], spray pyrolysis [8–10], different forms of sputtering [11], chemical vapor deposition [12], anodizing [13], heat attachment method [14], sol–gel [15–19] and chemical deposition [20–23]. Among these methods, the chemical deposition of thin oxide films from an aqueous solution is a very promising method on account of its simplicity and relative low cost.

The aim of this paper is to develop a chemical deposition method and select suitable supporting material and its type for ZnO photocatalyst. ZnO films are deposited by a modified dip-coating method using ammonium zincate solution. However, some variations of the proposed method are also tried. Three classes of materials are con-

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Table 1
Superficial ZnO loading and first order rate constant of various supports.

Support	ZnO loading (mg/cm^2)	Catalytic surface/reactor volume (S_v) (cm^2/cm^3)	k (h^{-1})
Broken glass pieces	0.19	11.4	0.07
Glass bead (1 mm)	0.24	72	0.56
Glass bead (3 mm)	0.27	30	0.42
Glass ring (6 mm)	0.23	8.1	0.45
Glass ring (8 mm)	0.18	7.1	0.35
Ceramic ring (6 mm)	0.25	8.3	0.82
Ceramic ring (8 mm)	0.21	4.2	0.87
Waste ceramic pieces	0.23	9.2	0.77

sidered as support namely, glass bead, glass ring, and porcelain ring of different sizes.

In this study, photocatalytic decolorization of methyl orange as a model organic compound investigated by means of ZnO coated photocatalysts. The pseudo first order rate is used as a criterion for the assessment of the activity of the supported catalysts in a differential photoreactor system by monitoring on-line the concentration of methyl orange dye solution.

2. Experimental

2.1. Materials

Methyl orange (MO) (Fig. 1a) is chosen as a model compound to test the photocatalytic activity. The UV–visible spectrum of this dye in aqueous medium is shown in Fig. 1b. The peak at 464 nm is used to monitor the photocatalytic degradation of MO.

Some important specifications of the catalyst supports used in this study are summarized in Table 1. A chemical deposition method is applied to coat various glassy and ceramic materials with ZnO film, by dipping in an ammonium zincate solution followed by a thermal treatment step for the formation of ZnO film. The method is economical, energy efficient and easy to apply. Glass and ceramic materials are chosen due to their chemical and mechanical resistances and low costs.

2.2. Apparatus

The following tests are made for catalyst film characterization: microstructural properties by SEM (Philips XL30 SFEG), roughness by AFM (Digital Inst.), crystal structures by XRD (Rigaku Dmax 2200), hydrophilicity of the catalyst film was calculated by measuring contact angle using KSV 200 Cam. Band gap value of ZnO films is calculated by monochromator (Triax 550). On the other hand, MO concentrations are measured using UV/vis-spectrometer (PerkinElmer, model Lambda 35).

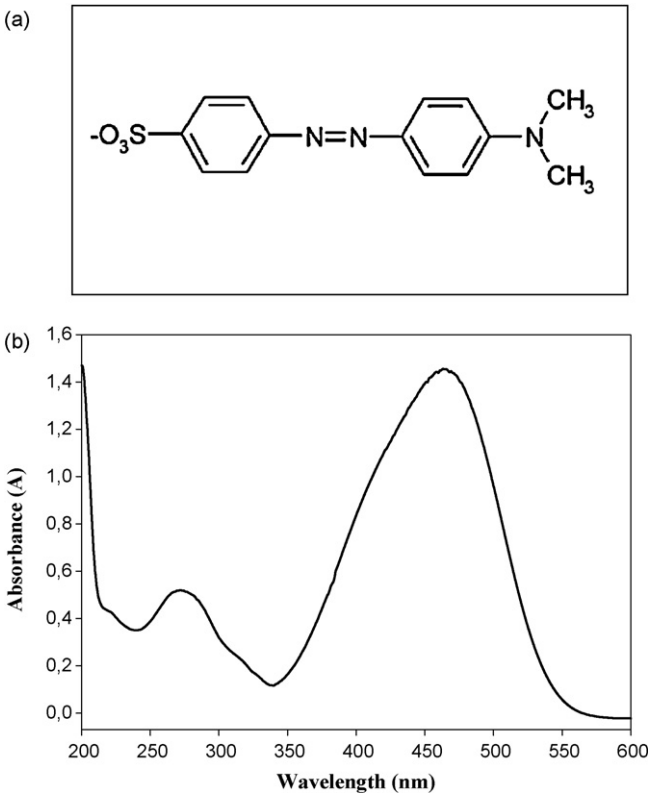

Fig. 1. (a) The structural formula of methyl orange and (b) the UV–visible spectrum of MO.

2.3. Photoreactor test system

The experimental set-up of the microphotoreactor system is shown in Fig. 2. Standard test conditions are given in Table 2. The film quartz reactor, containing the catalyst supporting materials, is surrounded by six UV-A lamps which predominantly emit at 365 nm (6W, General Electric F6T5/BLB), positioned so as to ensure homogenous radiation field inside the reactor.

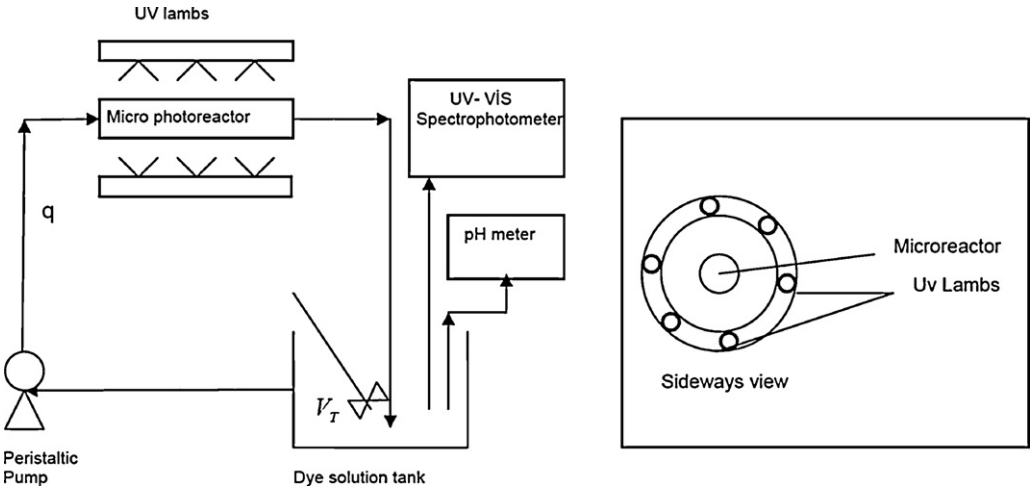

Fig. 2. The experimental set-up of the microphotoreactor system.

Table 2
Experimental conditions of the thin film reactor system.

Parameter	Value
Quartz microreactor volume	5.5×10^{-2} dm^3
Supported catalyst mass in the reactor	50–75 g
UV-A light intensity	528 mW/dm^3
Initial dye concentration	20 mg/l
Total dye solution volume	0.1 dm^3
Liquid circulation velocity	1.2 dm^3/h

Air is blown into the solution tank by an air pump through a diffuser placed below the impeller tip, to maintain the solution saturated with oxygen during the course of the reaction. Prior to irradiation, the dye solution is circulated for 30 min in dark to establish adsorption–desorption equilibrium. Then, MO solution is circulated under UV light for 2 h during which the progress of photocatalytic decolorization is monitored by measuring on-line the absorbance of the dye solution in the tank using the fiber-optic probe of UV–vis spectrophotometer. The pH and the temperature of the tank solution are also measured and no significant changes are observed during the course of the reaction. On the other hand, experiments are also conducted with slurry batch reactor using ZnO powder, placed in the same UV illumination system to ensure the same UV irradiation intensity. Liquid samples are withdrawn at 5 min intervals and filtered immediately for spectrophotometric analysis. The experimental results of both reactor systems are used to compare the activity of ZnO films to the activity of ZnO powder.

2.4. Photocatalyst preparation

2.4.1. Preparation of the ammonium zincate solution

The zincate solution is prepared according to the following reaction:

$$Zn(OH)_2 + 2NH_4OH \leftrightarrow (NH_4)_2ZnO_2 + H_2O \quad (1)$$

Commercial ZnO or $Zn(OH)_2$ presented some dissolution problems for the preparation of the ammonium zincate solution according to reaction (1). Thus, freshly precipitated $Zn(OH)_2$ is prepared by dropping concentrated ammoniacal solution (25% by weight) into well mixed zinc acetate solution until the final pH is 8

$$ZnSO_4 + 2NH_4OH \leftrightarrow Zn(OH)_2\downarrow + (NH_4)_2SO_4 \quad (2)$$

Then, the precipitate is filtered, transferred into another vessel, slurred in a little water, and while stirred magnetically, concentrated ammoniacal solution is added rapidly to obtain a clear ammonium zincate solution. The final pH of the solution is adjusted easily to the desired value (11.0 ± 0.1) by slowly evaporating the excess NH_3 by heating the solution. In this way, the purity of the solution is conserved without the addition of foreign ions by acidic neutralization. Finally, Zn concentration of the solution is checked by complexometric analysis, which is adjusted to the desired value if necessary.

2.4.2. Catalyst deposition

Some initial coating experiments are performed by depositing ZnO film on microscope slides, in order to observe films properties such as film adherence and film homogeneity by naked eye and under optical microscope. The effect of the chemical composition of the zincate solution is investigated by using sodium zincate solution instead of ammonium zincate solution, and by adding various chemicals in the zincate solution. On the other hand, various heating methods, such as UV, IR, and MW (microwave) heating, are tried to dry films and to convert $Zn(OH)_2$ to ZnO. But, no important improvements in the film properties are detected between various techniques. So, it is decided to use pure ammonium zincate solution and a conventional mini electrical furnace for heating purpose.

The catalyst film formation on support surface occurs by a two-step process; a dip-coating step where a liquid film is formed by adhesion on the support surface, and a thermal treatment step where liquid film drying and hydrolysis (the reverse of reaction (1)) occur simultaneously below 100 °C followed by a solid phase transformation of $Zn(OH)_2$ to ZnO above 125 °C.

The removing of any impurities from the support surfaces is of great importance to obtain repeatable catalytic properties by ensuring good adherence of the catalyst layer on the supporting material. For this purpose, a standard cleaning procedure is performed prior to the deposition step; supporting materials hold in chromic acid for 2 days are washed amply by distilled water, hold in an ultrasonic bath for 30 min in alcohol solution, and dried at 105 °C. Moreover, equipments are also cleaned according to the same procedure. For dip coating, a rotating drum made of stainless steel is used. The interior volume of the drum is divided into four equal sections to allow supporting material to rotate freely in the drum. The revolution rate of the drum is electronically controlled. On the other hand, a small electrical furnace is used for the thermal treatment step.

A standard deposition procedure is carried out as follows; a known amount of supporting material is put in the drum and dipped into 0.2 M ammonium zincate solution, where it is rotated for 1 min. Then, the drum is ascended above the solution tank and held for 1 min to allow excess liquid to drain into the solution tank. Later, the drum is placed into the oven preheated to the selected temperature. To ensure a uniform heating of the material, the drum is continued to rotate inside the furnace for 10 min, during which the temperature is controlled at 150 ± 0.1 °C using a thermocouple located near the drum. In this way, one coating cycle is completed. At the end of twenty coating cycles, the final heating is accomplished at 300 °C for 10 min to guaranty the formation of a strongly adherent ZnO film.

2.4.3. Zinc analysis

Zn concentration in zincate solution is determined by means of complexometric method using 0.1 M EDTA solution and indicator buffer tablet. The surface concentration of ZnO is analyzed by atomic absorption spectrophotometer using the solution prepared by dissolving a known amount of supported catalyst in HCl solution.

3. Results and discussion

In this work, various microscopic, structural, optical and photocatalytic activity tests are conducted to characterize ZnO film coated by chemical deposition method.

3.1. Physical characterization of ZnO film

XRD spectrums given in Fig. 3a and b, reveal that both ZnO film and commercial powder ZnO exhibit the same crystal wurtzite (zincite) structure. Besides, the amorphous nature of the film ZnO is easily detected.

General morphology and grain structure of ZnO film coated on glass and ceramic rings are examined by SEM images and are shown in Fig. 4a and b, respectively. The particle mean diameter of ZnO grains on ceramic and glass surfaces is about 300–400 nm.

The thickness of film is estimated by SEM image analysis given in Fig. 5. It is calculated as 1.41 μm after 20 coating processes. The thicknesses are also calculated by solving the ZnO film in concentrated acid solution and analyzing ZnO content by AAS, and similar results are obtained. From these results, it is concluded that each coating cycle contribution to the film thickness is about 70 nm.

Atomic force microscope (AFM) images are taken to discover the structural morphology of ZnO films prepared on glass substrate. The

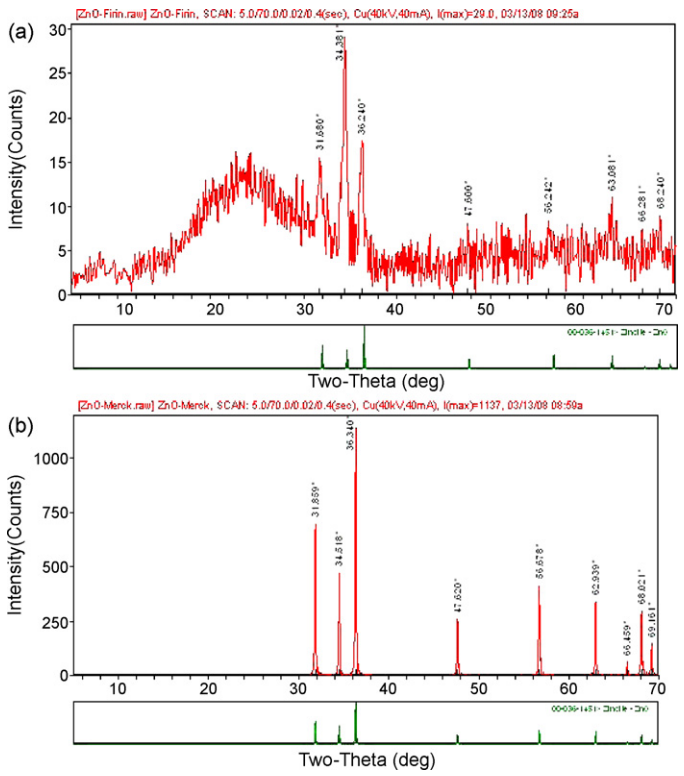

Fig. 3. XRD spectrums of (a) ZnO film on glass plate and (b) commercial ZnO powder.

three-dimensional AFM image is given in Fig. 6, according to which average ZnO crystallite size is calculated as 72 nm.

Surface hydrophilicity is an important property for an efficient contact of the liquid phase and the catalyst film. This property is evaluated by water contact angle measurements. Fig. 7 shows the water contact measurement for heat treated ZnO film. Interestingly, the film exhibits highly hydrophilic behavior (left 36.59°–right 30.96°), as water contact angle is less than 90°. Small angle differences between left and right sides are accepted to the presence of film roughness. The value of water contact angle is less than reported values in the literature [24,25]. This may be due to conical surface morphology on account of they had used different coating methods. Besides, it is found that hydrophilicity is inversely related to the annealing time. In view of this, 300 °C is accepted as a maximum value for the final annealing temperature.

Band gap value is the principal physical characteristic of semiconductor material. The theory of optical absorption gives the relationship (3) between the absorption coefficient α and the photon energy $h\nu$ for direct allowed transition, as in the case of ZnO

$$\alpha h\nu = A(h\nu - Eg)^{n/2} \quad (3)$$

This equation gives the band gap (Eg), when straight portion of $(\alpha h\nu)^2$ against $E(h\nu)$ plot is extrapolated to the point $\alpha = 0$. This is shown in Fig. 8 from which the band gap is calculated as 3.24 eV. Commercial ZnO samples have band gap values between 3.00 and 3.30 eV, and the reported usual value is 3.17 eV. The difference between various band gap values may be due to presence of zinc hydroxide which can remain unconverted during the heat treatment [26], or due to the existence of defect levels after heat treatment, a common phenomena observed in chemically deposited films [27,28].

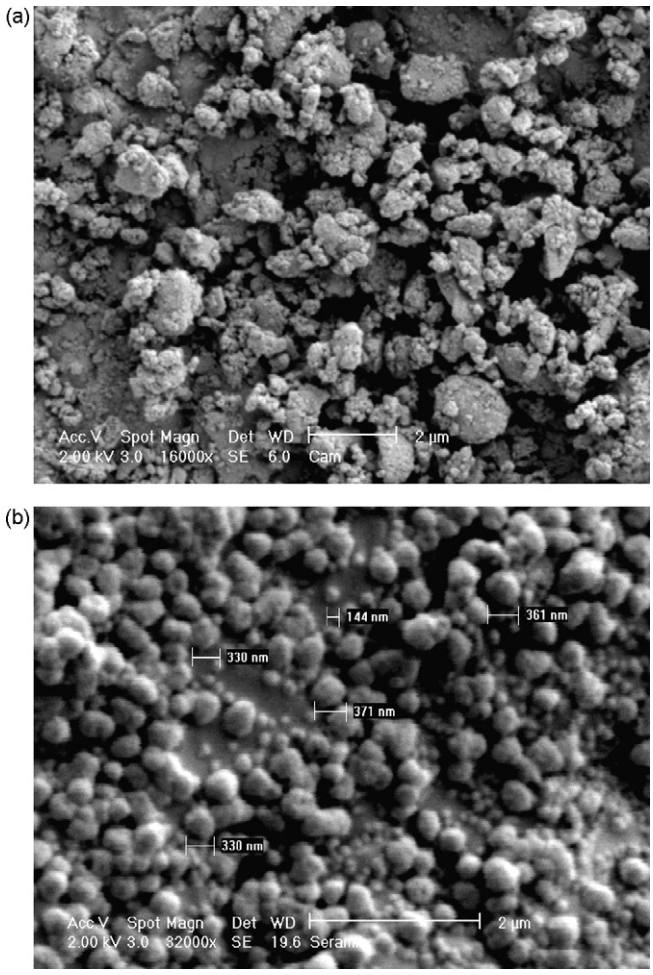

Fig. 4. SEM image of ZnO film surface (a) glass ring (6 mm) and (b) ceramic ring (6 mm).

3.2. Photocatalytic activity of ZnO film

All the supporting materials used in this study have no catalytic effect as demonstrated by blank experiments performed by irradiating MO solution in contact with uncoated supporting materials. Methyl orange is selected as commonly used model organic matter to test the photocatalytic performance.

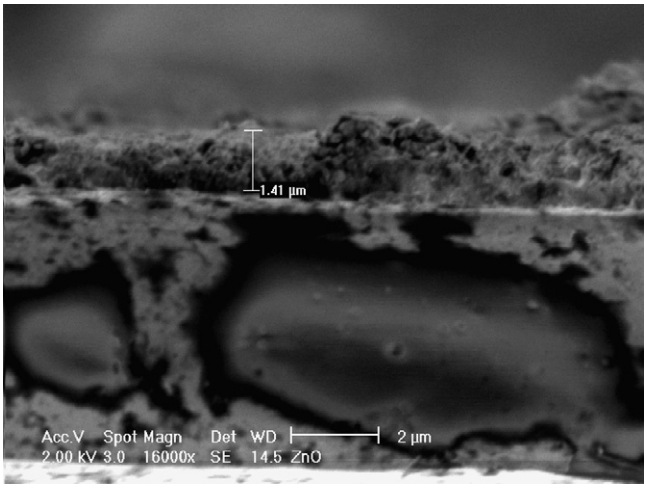

Fig. 5. SEM image of film ZnO cross-section glass ring.

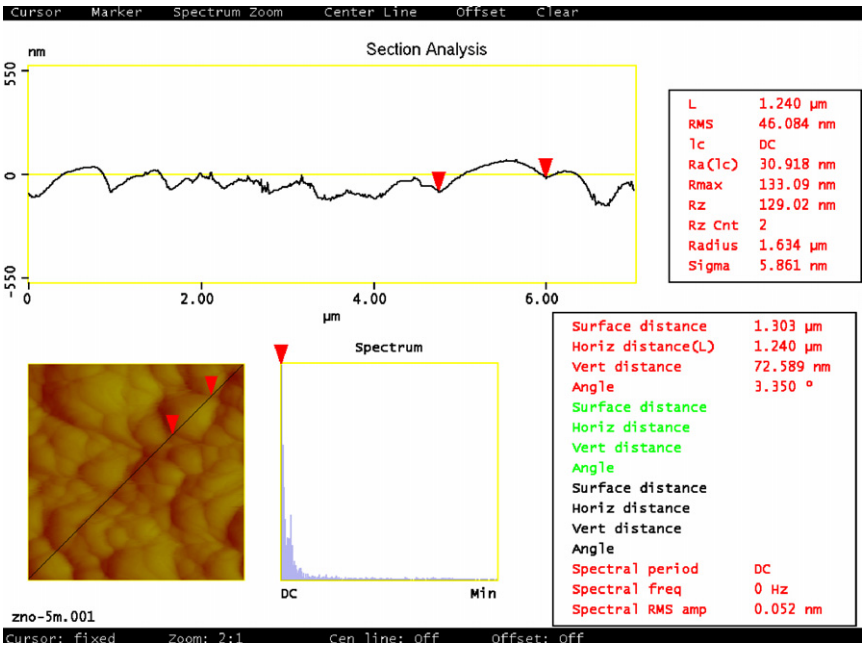

Fig. 6. Atomic force microscope (AFM) images of ZnO film.

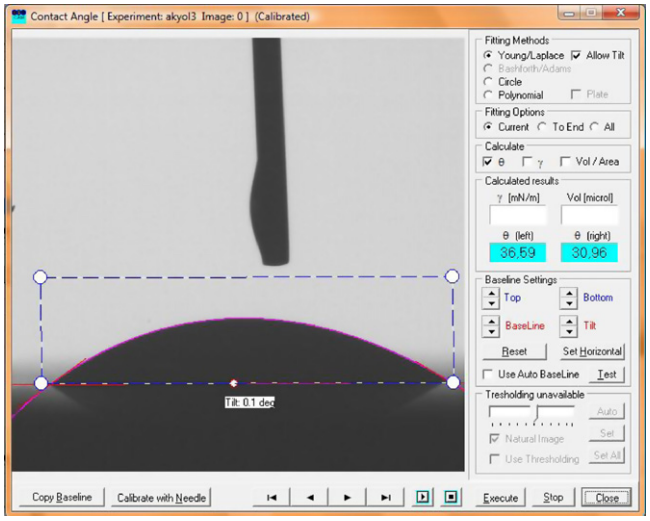

Fig. 7. Contact angle calculation of ZnO film.

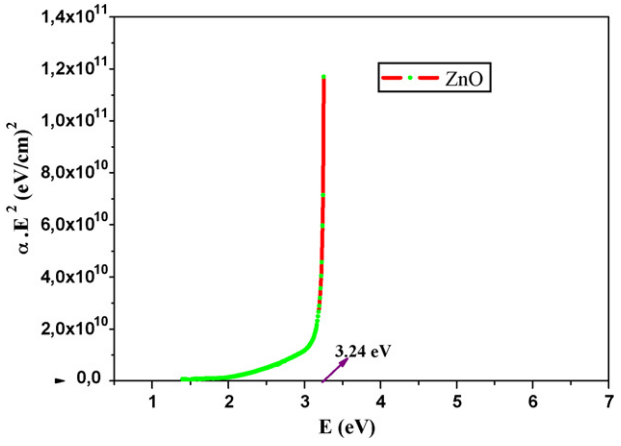

Fig. 8. Band gap calculation of ZnO film ($E{\cdot}\alpha^2$ and E (eV)).

Kinetic analysis is applied for activity measurements. The first order reaction rate constant is used to compare the photocatalytic activity of the supported catalysts, as photocatalytic reactions comply generally with pseudo first order kinetic model

$$-\ln\left(\frac{C}{C_0}\right) = k \cdot t_f \tag{4}$$

where t_f, the photocatalytic reaction time, is calculated from the processing time, t, according to Eq. (5) by applying a correction factor

$$t_f = t\left(\frac{V_t}{V_r}\right) \tag{5}$$

where V_t is the total liquid volume in the system V_r is the active liquid volume in the reactor in contact with UV radiation field.

In the calculation of the rate constant by means of linear regression, on-line absorbance data comprising approximately 100–300 samples is used. On the other hand, in slurry reactor experiments, at least ten kinetic data is used in regression analysis.

On the other hand, photocatalytic rate depend on diverse process parameters as well as the catalyst type, such as; UV wavelength or type (such as UV-A), initial organic dye concentration C_0, light intensity or volumetric photon absorption velocity (mW/dm^3) or (Ei/s m^2), volumetric catalyst loading m (mg/dm^3) (or surface loading (mg/cm^2) for film). To compare the activity performances of various catalyst forms, the rate constant must be correlated to these process parameters. The power law model (Eq. (6)) is usually applied for this purpose [29]

$$k = a \cdot m^b \cdot C_0^c \cdot I^d \tag{6}$$

The model parameters, a, b, c, d are determined by linear regression analysis after suitable logarithmic transformations.

To test the reproducibility of catalyst activity values, the percent relative experimental error on the rate of reactions is estimated using the results of three replicate experiments and it is calculated as 5% which is of acceptable level when the complexity of various physical–chemical processes occurring during the whole process is taken into account.

The solution pH, air flow and temperature are held constant at 6.5, 12 dm^3/h and 25 °C, respectively in all experiments. The same

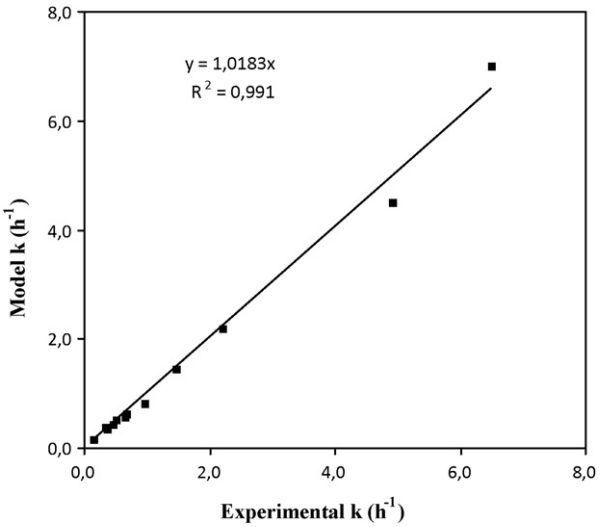

Fig. 9. Fit between model and experimental rate constants with ZnO powder.

parameter ranges applied in the whole kinetic study are as follows:

$$C_0 : 0.03 - 0.065\ \text{mM}, \qquad I : 176 - 528\ \text{mW/dm}^3$$

Base experimental conditions are as follows: $C_0 = 0.065$ mM, $I = 528$ mW/dm^3 (36 W light intensity).

3.2.1. Kinetic modeling with powder ZnO photocatalyst

In slurry reactor experiments, the air flow rate and the stirring rate are held constant as 12 dm^3/h and 300 rpm, respectively. The base catalyst loading value, m, is 75 mg/dm^3 and it is investigated in the range 10–1500 mg/dm^3.

The regression analysis according to Eq. (6) gives the following statistical results:

$$k = 1.20 \times 10^{-5} \cdot m^{0.99} \cdot C_0^{-1.29} \cdot I^{0.48} \quad (7)$$

data number = 12, $R^2 = 0.992$, $s = 0.048$.

The fit between model and experimental "k" is shown in Fig. 9. Exponent of I is approximately equal to 0.5 as found frequently. Furthermore, exponent of C_0, −1.29, which is quite higher than the usual value −1, results primarily from the reduction of the path length of photons entering the solution by increasing dye concentration, according to the Lambert Beer law.

3.2.2. Kinetic modeling with ZnO film coated materials

A literature survey reveals the practical importance of the preparation of supported film photocatalyst; diverse geometrical forms of broad classes of materials such as aluminum [30], glass [5,31–33], and carbon [34] are investigated for this purpose. This research is particularly focused on glass and ceramic bead, ring and irregular piece as cheap and inert materials, to investigate the effect of geometrical form and material type on the photocatalytic activity of supported ZnO films.

ZnO loading of various materials are given in Table 1. These values are between 0.19 and 0.27 mg/cm^2 depending on geometrical form and support type. Table 1 shows that ceramic materials have generally higher photocatalytic activity than glass materials. Between all glass materials, 1 mm bead exhibits higher photocatalytic activity. No direct correlation is deduced between superficial ZnO loading and the photocatalytic activity, due to the difficulties in controlling the homogeneity of films coated on curved and irregular surfaces of these materials.

Ceramic ring ($\phi = 8$ mm) exhibits higher photocatalytic activity than the others as seen in Table 1. S_v value of this material is the smallest of all materials, and it has the best activity per surface area. To make a clear comparison between material types, glass and ceramic materials of the same geometrical form and size (ring of 8 mm diameter) are selected for further kinetic calculations.

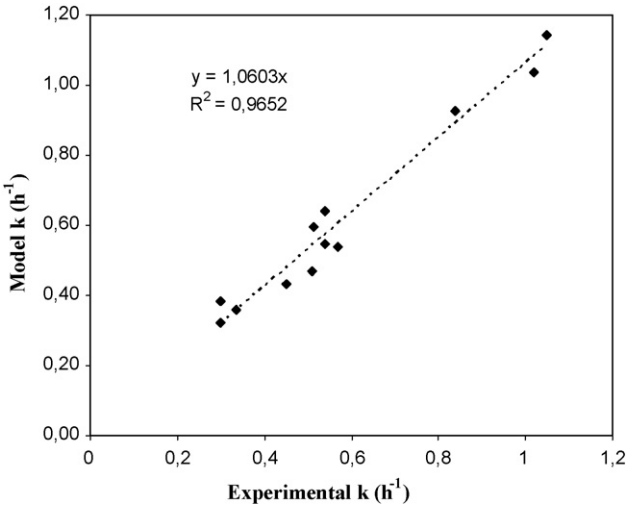

Fig. 10. Fit between model and experimental rate constants with ceramic ring.

The first order kinetic rate constant are calculated for ceramic rings and are correlated according to model Eq. (6). The regression analysis gives the following statistical results:

$$k = 7.3 \times 10^{-5} \cdot C_0^{-0.91} \cdot I^{1.04} \quad (8)$$

data number = 12, $R^2 = 0.946$, $s = 0.039$.

Fit between model and experimental k values is shown in Fig. 10.

The same procedure is applied for glass rings and the following statistical results are obtained

$$k = 9.1 \times 10^{-4} \cdot C_0^{-0.90} \cdot I^{0.62} \quad (9)$$

data number = 11, $R^2 = 0.895$, $s = 0.071$.

Fit between model and experimental "k" is shown in Fig. 11.

3.3. Simulation results

Model Eqs. (7)–(9) along with rate expression (4) may allow now to compare the photocatalytic activity of ZnO coated glass and ceramic materials and powdered ZnO under the same process conditions.

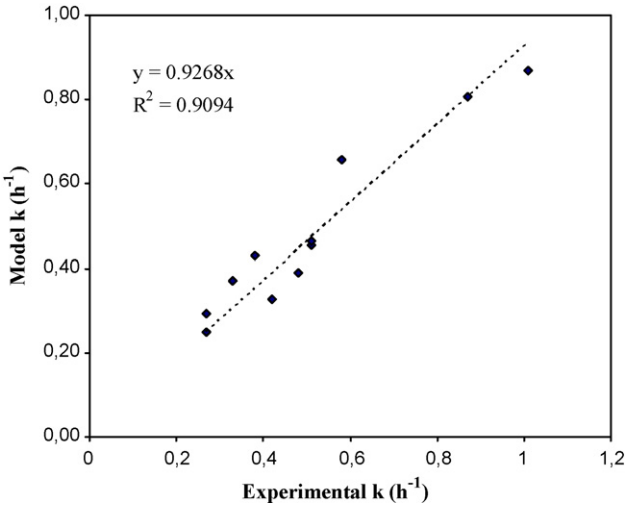

Fig. 11. Fit between model and experimental rate constants with glass ring.

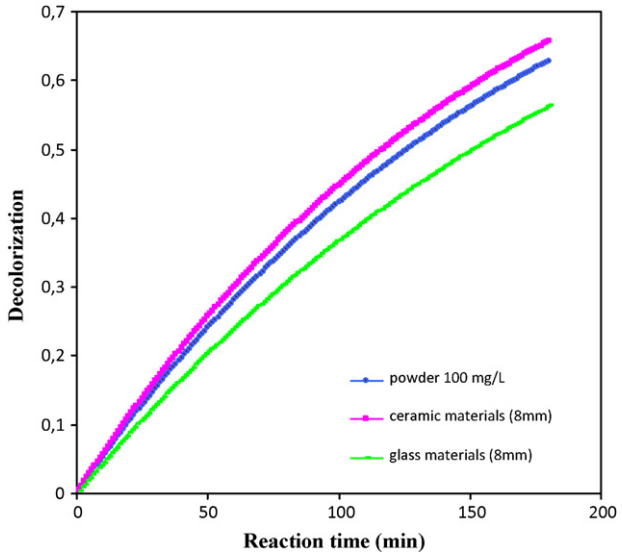

Fig. 12. Decolorization–time simulation curves with glass and ceramic materials on photocatalytic decolorization of MO.

For the simulation study, the following process conditions were selected; initial methyl orange concentration: 40 ppm (0.1223 mM), volumetric photon absorption velocity: 528 mW/dm^3. Various catalyst loadings are tried in the case of slurry reactor to obtain the decolorization efficiency vs. time curves which match those of the supporting materials. Typical curves are given in Fig. 12. The simulation study shows that the photocatalytic activity of ZnO film coated on ceramic ring is similar to that of powdered ZnO slurry of 120 mg/dm^3, and that of glass ring is similar to that of powdered ZnO slurry of 85 mg/dm^3.

The performance comparisons may be further conducted according to S_v values, which is the total active surface of catalyst per reaction liquid volume. This parameter is calculated as 4.2 cm^2/cm^3 for ceramic ring as seen in Table 1. On the other hand, based on particle size distribution analysis, the specific optic surface of powder ZnO is calculated as 3.47 m^2/g which is determined by particle size analysis. Total specific optic surface of powder ZnO slurry of 120 mg/dm^3 density is about 4.16 cm^2/cm^3. Thus, the ZnO film on ceramic ring has the similar intrinsic activity with powder ZnO. On the other hand, the same approach can be applied for glass ring; for glass support S_v is 7.1 cm^2/cm^3 and total specific optic surface of powder ZnO catalyst loading of 85 mg/dm^3 is 2.95 cm^2/cm^3. Thus, the intrinsic activity of catalyst film on glass ring is nearly 45% of powder ZnO.

4. Conclusion

A chemical deposition method is applied to coat various glassy and ceramic materials with ZnO film with high photocatalytic activity. The method is applied in two steps as; a dipping step in an ammonium zincate solution to form a liquid film on support surface and a thermal treatment step for the formation of ZnO film. The method uses low cost chemicals such as an inorganic Zn compound dissolved in ammoniacal solution. It is energy efficient, as it does not require high annealing temperature. Furthermore, it is easily applied on glass or ceramic materials of various forms. The results show that ceramic is preferable as supporting material with high activity. According to the simulation study, the photocatalytic activity of film coated on ceramic ring of 8 mm diameter is nearly equal to the activity of powder ZnO slurry of 120 mg/dm^3 density. The calculations show that it is possible to prepare ZnO film on ceramic ring with similar activity as powder ZnO. On the other hand, the intrinsic activity of catalyst film on glass ring is approximately equal to 45% of powder catalyst.

Nomenclature

A	surface area (m^2)
C	concentration (mmol/dm^3)
Eg	band gap value (eV)
I	volumetric photon absorption velocity (mW/dm^3)
k	first order rate constant (min^{-1})
m	catalyst loading (mg/dm^3)
V	volume (dm^3)

Subscripts

r	reactor
s	surface
t	tank
v	volumetric

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