PREPARATION OF NANO-STRUCTURED CRYSTALLINE ZNO AND ITS PHOTO-CATALYTIC PROPERTIES

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Abstract
Nano-structured crystalline ZnO was prepared with zinc nitrate and modified gelatin by the sol-gel method. The result of transmission electron microscope (TEM) and X-ray diffraction (XRD) spectroscopy showed the average particle size of it was about 20 nm. The photo-catalytic activity was studied in diluted methyl orange solution under UV-lamp radiation and in sunlight respectively. The test result demonstrated that the photo-catalytic reaction is a pseudo first order reaction, and there is positive correlation between the apparent rate constant k and some factors including original concentration of methyl orange, the concentration of catalyst and absorbed intensity of radiation I_{abs}.

Keywords: Nano-structured crystalline ZnO, sol-gel method, photo-catalytic reaction.

Nano-structured material has been given more consideration because of its special physical properties, such as quantum size effect, surface effect, thermodynamic property, optical properties and magnetism property, and chemical properties such as catalysis property in light. Nano-structured material is playing an important role in modern industrial, military equipment and high technology fields. Nano-structured Zinc Oxide can absorb ultraviolet radiation, reflect infrared ray and shield static electricity when it is added into coating system. Because of its large specific surface area and strong surface activity, ZnO can be used in chemical sensor and biologic sensor to inspect DNA, peptide, protein and antibody. Compared with other nano-structured materials, nano ZnO has obvious strength, nontoxic, anti-microbial, antivirus, and low cost. So the prospect of its application in the function textile is very good.

There are two methods to prepare Nano-structured material, physical method (including laser method, spraying method and so on) and chemical method (including depositing method, micro emulsion method, sol-gel method and solid chemical reaction method). The size, shape and other property of the particles are depended on the preparation technology.

Nowadays, the importance of environment protecting is well known. The decontamination of amount of wasted water and gas is becoming an important issue for some department and most of dying plants. To treat these wastes effectively and low cost. It's a good method to use nano-structured titanium dioxide and zinc oxide. The energy band gap of nano titanium dioxide or nano zinc oxide is 3.2eV. When the nano zinc oxide absorbs ultraviolet rays, hydroxyl radical will generate, which is a powerful oxidant, it will attack organic substance and generate CO_2, H_2O and other simple non-toxic compound. This complicated photo-catalytic process consists of a series of reactions. To study the reaction velocity, helianthin B is always used as the feculence and hydrogen peroxide is used as oxidant in lab. As to the catalysis of nano zinc oxide, the reaction mechanism is very complex, it is a pseudo first order reaction and the apparent rate constant will change according to the particle size of nano zinc oxide. So it has connection with the technology of preparation.

Because gelatin cross-linked with formaldehyde will form net structure, the particle size of the product is small and narrow distribution. The research of preparing nano titanium dioxide with this method is reported. In this article, zinc nitrate and gelatin cross-linked with formaldehyde are used to prepare nano zinc oxide by sol-gel method. XRD and TEM are used to characterize the crystal structure and the particle size. In order to discuss its photo-catalytic properties, the solution of helianthin B is irradiated with ultraviolet radiation and sunlight respectively to obtain its oxidant velocity.

1．Experiment

1.1 Reagent：

Zinc Nitrate(A.P.)，Formaldehyde (aqueous solution, 36 % by weight, A.P.), Gelatin (C.P.).

1.2 Apparatus:

XRD-- C/max-B (Cu Kαradiation，V = 40kV，I = 40mA.), Rigaku Corporation.

TEM -- JEM-100CX, Japan Electronics Corporation, Ltd..

Ultraviolet-visible light dual beam spectrophotometer—Shanghai analysis apparatus company.

Ultraviolet lamp--12W, Shanghai Precision & Scientific Instrument Co.,Ltd.

Spectrophotometer –722s, Shanghai Precision & Scientific Instrument Co.,Ltd.

1.3 Method of preparation：

prepare 0.5mol·dm^{-3} zinc nitrate（A）. Add appropriate amount formaldehyde to the gelatin solution to prepare the modified gelatin solution (B), the ratio of formaldehyde : gelatin = 0.l3 mol ：100 g. Agitate the zinc nitrate solution in the warm water bath, add appropriate amount of (B), and condensate it by evaporation at 80ºC. When cool, it becomes gel. Dry the gel at 120 ºC, and put it into muffle furnace. After calcinations at 600 ºC, the white Nano ZnO is obtained.

1.4 Methods of characterization:

The information of the structure of zinc oxide is obtained by XRD. The particle size is measured by XRD and TEM. The absorbency of zinc oxide film is measured by Ultraviolet-visible light dual beam spectrophotometer.

1.5 Preparation of TEM sample:

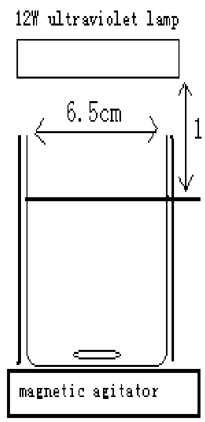
Grind the zinc oxide with agate mortar in the presence of some distilled water, acetylacetone and Triton X100. Then add water to prepare 0.1g/dm^3 transparent solution, disperse the solution by ultrasonic. The solution is used as sample (a). Then dilute part of sample (a) with water to half concentration and add one drop of 0.01% methylene blue solution to be sample (b).

1.) Preparation of the ZnO film:

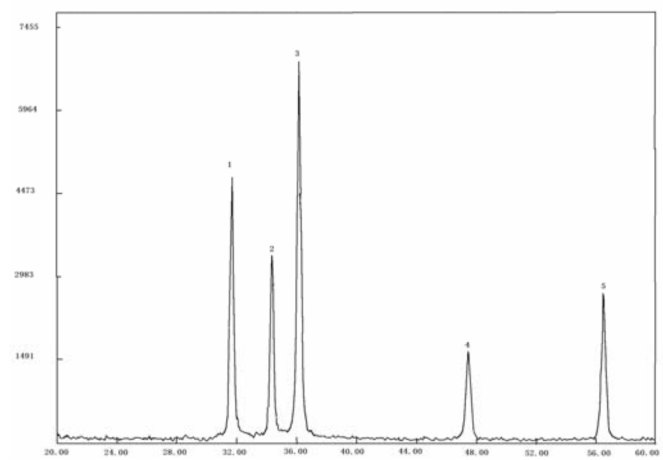
Dip the glass sheet into the solution, draw up and dry it to make the film. It is the sample for testing the absorbency of ultraviolet and visible light. A blank glass sheet is used for reference.

1.7 Experiment of light catalysis:

The light source is from the 12W ultraviolet lamp (the device is showed in picture1); the absorbency of the helianthin B solution is measured by 722s spectrophotometer, the length of wave is 460nm. The catalyst is 2% H_2O_2.



Pic. 1 the device of light catalysis



Gra.2 XRD spectrum of nano ZnO

2. Result and discussion:

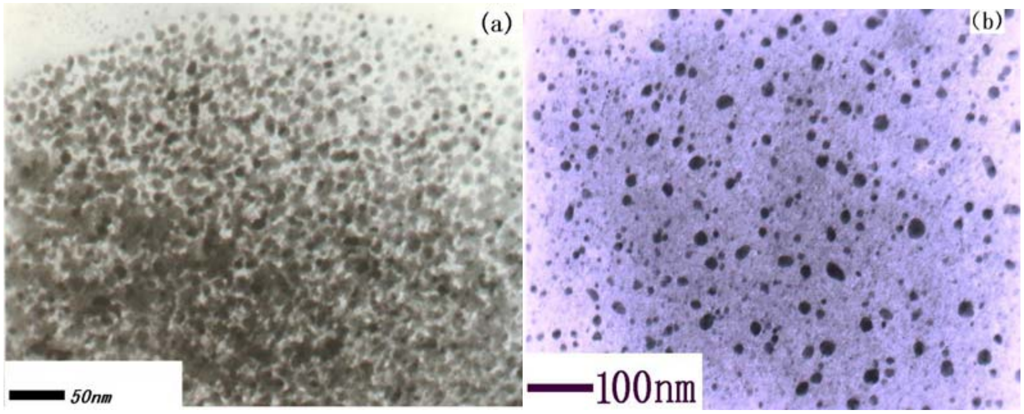
（A）structure and particle size

The XRD spectrum of the sample is showed in Gra. 2; it can be seen from the picture that ZnO is wurtzite crystal;

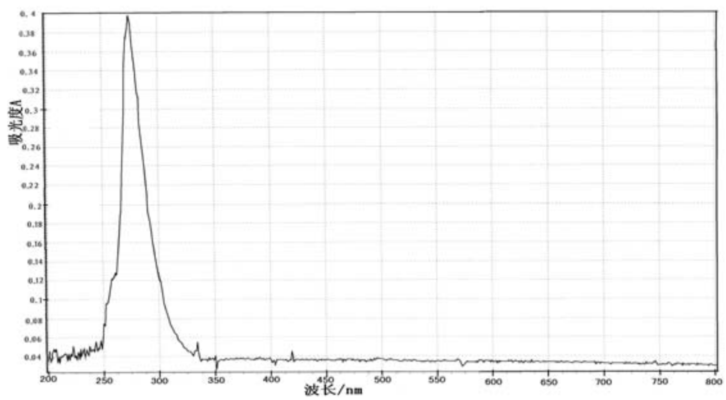
From Scherrer formula： $D = \frac{K\lambda}{B\cos\theta}$

in the formula *D—particle size*;*λ—wave length; K*=0.89;*B—Full Wave at Half Maximum*;*θ—Bragg angle;*

From calculation the particle size is 20.4nm. The picture 3 is the photo of TEM, and the particle size is similar to the calculation. So the particle of nano zinc oxide is single crystal.



Pic.3.the TEM photo of nano zinc oxide (pic.b is the transparent solution diluted and added one drop of 0.01% methylene blue solution)



Graph.4 the spectrum of ultraviolet-visible light absorbency of nano zinc oxide

（B）the spectrum of ultraviolet-visible light absorbency of nano zinc oxide(Gra. 4) shows that nano zinc oxide only absorbs ultraviolet.

（C）Experiment of light catalysis:

(1) The relationship between the order of reaction, rate constant of the light catalysis reaction, and the initial concentration of the reactants:

The device seeing picture 1.Add different volume of 0.04 g/dm^3 helianthin B solution into the beaker, 10mL 0.1 g/dm^3 nano zinc oxide solution, add 10mL 2%H_2O_2 and add distilled water to 50mL. The result is seen in picture 5. Because the solution only absorbs ultraviolet light, it is radiated by ultraviolet lamp. Measure the absorbency (A) of the sample every 1h with the 722s spectrophotometer, and measure the helianthin B concentration. Pack black paper outside the beaker in order to avoid the disturbing. LnA varies directly with the time (t). If there is not zinc oxide or ultraviolet light in the system, it is stable. It seems there is not reaction.

Photo-catalytic reaction is consisting of a series of reactions. The catalytic theory of the semiconductor like ZnO and TiO_2 is when the energy of photon (hν) is higher than or equal to the energy band gap of the semiconductor, the electron obtains energy to be motivated to conduct band from value band, and a hole is left in value band. The electron and the hole is apart under the charge layer, the hole moves to the surface of the semiconductor and reacts with –OH and generate OH·radical. OH·can oxidizes the organics absorbing on the surface of ZnO because of its strong oxidability. However, the electron can react with the hole(h_{vb}^{+}) and return to the initial state and relief the excrescent energy as heat and light[3, 4]。:

$$ZnO+h\nu \rightarrow ZnO(e^{-}_{cb}+h^{+}_{vb}) \ ;$$

$$e^{-}_{cb}+h^{+}_{vb} \rightarrow Q \ ;$$

$$ZnO(h^{+}_{vb}) + HO^{-}_{ads} \rightarrow ZnO + HO^{*}_{ads};$$

$$H_2O_{2ads} + e^{-}_{cb} \rightarrow HO^{*}_{ads} + HO^{-}_{ads};$$

$$D+h\nu \rightarrow D^{*};$$

$$D^{*} + ZnO \rightarrow D^{*}_{ads}(ZnO);$$

$$HO^{*}_{ads} + D^{*}_{ads} \rightarrow CO_2 + H_2O + \cdots\cdots$$

D^{*}_{ads} is the active organic absorbing on the surface of the catalyst, and the kinetics control step of the reaction is [4];

$$HO^{*}_{ads}+D^{*}_{ads} \rightarrow CO_2+H_2O+\cdots\cdots$$

The absorption of the helianthin B on the surface of zinc oxide is single molecular when the content is low.θ_D means the fraction of coverage of D^{*}_{ads} on the surface of the solid catalyst. $\theta_{H_2O_2}$ means the fraction of coverage of H_2O_2 on the surface of the solid catalyst.

Langmuir isotherm:

$$\theta_D = \frac{b_D C_D}{1 + b_D C_D + b_{H_2O_2} C_{H_2O_2}} \ ; \ \theta_{H_2O_2} = \frac{b_{H_2O_2} C_{H_2O_2}}{1 + b_D C_D + b_{H_2O_2} C_{H_2O_2}};$$ C_D means the concentration of the organic in the solution, namely helianthin B.

$$-\frac{dC_D}{dt} = kC_{D^{*}_{ads}} C_{HO^{*}} = k'\theta_D \theta_{H_2O_2}$$ when $b_{D*}C_{D*}+b_{H2O2}C_{H2O2}<<1$;

$$-\frac{dC_D}{dt} = kC_{D*}C_{HO^{*}} = k'\frac{b_{D*}C_{D*}}{1 + b_{D*}C_{D*} + b_{H_2O_2}C_{H_2O_2}} \bullet \frac{b_{H_2O_2}C_{H_2O_2}}{1 + b_{D*}C_{D*} + b_{H_2O_2}C_{H_2O_2}} = k''C_D C_{H_2O_2} \ ;$$ The concentration of H_2O_2 can be seen as fixed when it is excessive. Thus the reaction is pseudo first order reaction: $-\frac{dC_D}{dt} = k_{ap}C_D$。

The smaller of the particle size, the bigger of the specific surface area, and the more of the photons are absorbed. When C_{H2O2} is fixed, the stronger of light strength, the more photons is supplied, and the more OH· is generated. So their relation is $C_{OH\cdot}$□SI_A□$C_C I_A$; And the apparent rate constant (k_{ap}) has connection with intensity of the light absorbed and the specific surface area of catalyst, therefore, has connection with the particle size.

The absorbency of diluted solution is direct proportional with the concentration of the solute according to Lambeer-beer. When the concentration of helianthin B is low,

$\ln(A_0 / A) = \ln(C_{D0} / C_D) = k_{ap} t$; The apparent rate constant (k_{ap}) can be obtained from the absorbency.

A_0 means initial absorbency. C_{D0} means initial concentration of helianthin B. C_D means the concentration during the reaction process. A means the absorbency during the reaction process. Picture 5 is the graph of ln$A$ against t.

Picture 5 indicates this photo-catalytic reaction is pseudo first order reaction. When the concentration of helianthin B increases, the slope decreases. It means the apparent rate constant (k_{ap}) has connection with the initial concentration of reactant. When the intensity of light and concentration of catalyst is fixed, the apparent rate constant (k_{ap}) will decrease according to the increase of the initial concentration of fhelianthin B. This is because of the quench of exited dye molecular absorbing on the surface of zinc oxide[4]. Heat occurs when the exited dye molecular interact each other. When the concentration of dye in the solution increases, the dye molecular absorbing onto the surface of zinc oxide increases too, and also the probability of the interaction among the dye molecular increases. Therefore, the probability of quench of exited dye molecular increases. Then the apparent rate constant (k_{ap}) decreases.

(2) the relationship of the dose of catalyst and the degradation proportion of feculence(helianthin B)：

0.04g/dm^3 fhelianthin B solution 20mL, add appropriate amount 0.1 g/dm^3 nano ZnO sol, 2% H_2O_2 10 mL, and distilled water, total volume is 50mL.Put into a beaker which diameter is 6.5mm. The other step is the same as step (1). The result sees table 1.

Table 1. Effect of the consistence of ZnO against the degradation proportion of fhelianthin B：

consistence of ZnO C/g • dm^{-3}	0. 03	0.04	0.05	0.06	0.1
The degradation proportion after 4h C%	15. 63	18. 75	30	30	30
The rate constant /h^{-1}	0.04246	0.05190	0.08917	0.08917	0.08917

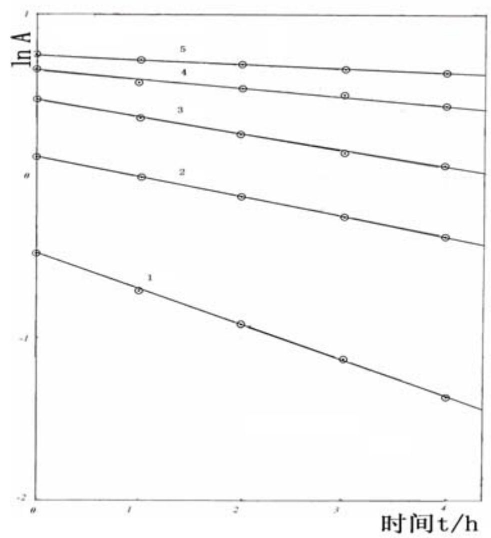
The table shows, when the concentration of ZnO is lower than 0.05 g/dm^3, the degradation proportion increases with the concentration of catalyst. However, when it is higher than 0.05 g/dm^3, the degradation proportion is fixed. It maybe because the power of ultraviolet is too weak (12W), which simulates the sunlight. When the intensity of light in unit time is fixed, according to the Einstein law of photochemistry, one mole of photons activates one mole of molecular, the excess photocatalyst almost don't affect the reaction.

(3) The result of sunlight radiation experiment.(seeing table 2 and graph 6)

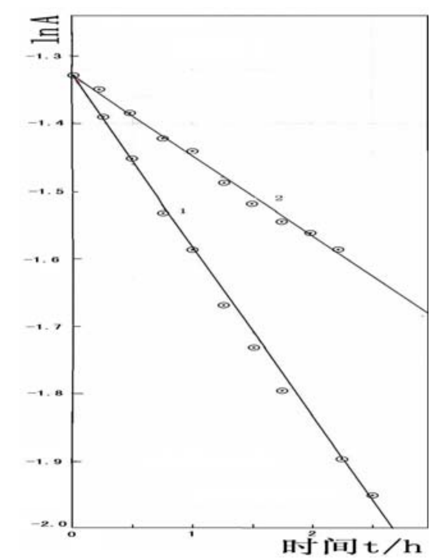
Table 2. The result of sunlight radiation experiment：

code	Consistence of ZnO /g • dm^{-3}	Addition of ZnO / mL	Addition of fhelianthin B （0.004 g/dm^3） /mL	Addition of H_2O_2 （2%） / mL	Addition of H_2O / mL	Code in graph 6	rate constant /h^{-1}
1	0.05	50	10	20	20	1	0.248
2	0.004	4	10	20	66	2	0.117

Graph 6 shows, nano zinc oxide has strong catalytic property under the nature sunlight, and the addition of catalyst affects the catalytic velocity obviously.



graph 5. Absorbency –time when the initial concentration of helianthin B changes.



graph 6. Absorbency of helianthin B-time under sunshine

note： concentration of helianthin B-time /g • dm^{-3}:1-0.004;2-0.008
3-0.0012 ; 4-0.016;5-0.020

3. Conclusions

（1）It's available to prepare nano zinc oxide from zinc nitrate and modified gelatin.

（2）It is a pseudo first order reaction that helianthin B is oxidized when nano zinc oxide act as catalyst and when the concentration of fhelianthin B is low enough. The apparent rate constant (k_{ap}) of the reaction has connection with the initial concentration of helianthin B and nano zinc oxide, and physical property including particle size. The rate constant increases when the initial concentration of helianthin B decreases.

（3）The nano zinc oxide prepared by this method has obvious photo-catalytic property under the weak ultraviolet strength, so it offers a simple and cheap way for dying and finishing plant to treat waste water.

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