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STUDY PHOTOCATALYST PROPERTY OF ZnO FOR METHYLENE BLUE

Bui Hong Van[1], Pham Van Ben[1] and Tran Minh Thi[2]
[1]*Faculty of Physics, Hanoi University of Science, Vietnam National University*
[2]*Faculty of Physics, University of Education, Vietnam National University*

Abstract. The commercial nanoparticles ZnO with C_{6v}^4- $P6_3mc$ hexagonal structure, particle size of hundreds of nanometer and band gap energy about of 3.26 eV have been used on photocatalyst for methylene blue. The results showed that: as increasing irradiated time from 30 minutes to 120 minutes by 365 nm radiation of Narva LT 18W ultra - violet lamp, the color of methylene-blue and ZnO mixture were depleted gradually, in which the absorptance and photoluminescence intensity were also decreased. The cause of these phenomena has been studied and explained. The role of ZnO nanopowder photocatalyst for Van Phuc dye wastewater (Ha Dong district, Hanoi city) has been tested by the first step.

Keywords: Nanoparticles ZnO, methylene blue, photocatalyst.

1. Introduction

Methylene blue is an organic pigment with the molecular formula $C_{16}H_{18}N_3SCl$ and the graphic formula present in Figure 1, including 3 aromatic rings containing the color group -C = C, -C = N, -C = S and the support group color -N (CH_3) 2 [1]. This pigment is quite stable, imperfect with base, has strong redox and oxidation properties, so it is widely used in chemistry, biology and medicine [1]. However, methylene blue is also very toxic because it contains aromatic rings, so after being discharged, it will pollute the environment and cause bad effects on plants and human health.

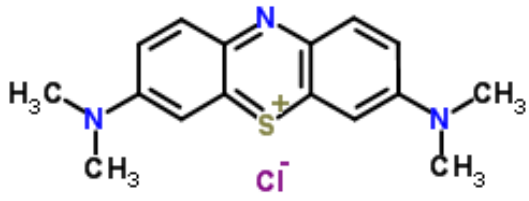

Figure 1. Stuctural formula of methylene blue

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Contact Tran Minh Thi, email address: tranminhthi@hnue.edu.vn

For the treatment of organic pigments and methylene blue in wastewater, some traditional chemical and biological methods such as ozonation, absorption, adsorption [1-3] can be used. In recent years, it has also used photocatalytic properties caused by the surface effects of undoped and doped TiO_2, ZnO, ZnS nanoparticles to decompose organic pigments into non-toxic products, there are H_20 and CO_2 [4-6]. Among these nanoparticles, ZnO has good photocatalytic ability for organic pigments under the effect of radiation in the ultraviolet region or in the visible region [5]. However, up to now, the photoluminescent spectra have almost no papers mentioned in investigated process of photocatalytic properties for methylene blue.

This paper presents the researching results the PL spectra and UV spectra and photocatalyst ability of commercial ZnO nanoparticles for methylene blue under the effect of ultraviolet radiation. These results are base to study the preparation of ZnO nanoparticles, doping with some non-metallic such as C, N, or ZnO/CNTS (ZnO/carbon nanotube composites) to use in photocatalyst method in wastewater treatment under solar radiation.

2. Content

2.1. Experiments

Photocatalyst process for methylene blue by commercial ZnO nanoparticles (Merck) as follows. Dissolving 5 mg MB and 500 mg ZnO into 2 times distilled water, separately, then magnetic stirring for 30 minutes. Mixing two mixtures in the ratio of 1:1 and magnetic stirring for 60 minutes. The obtained mixture solution (denoted as: MB-ZnO) were simultaneously magnetic stirred and irradiated by 365 nm wavelength of Narva LT 18 W ultraviolet lamp for 30 to 120 minutes. All magnetic stirring and irradiating were conducted in dark room. After irradiating the obtained mixture solution were centrifugated in order to get precipitation ZnO.

The crystalline phases of these ZnO nanoparticles were examined by XRD patterns on XD8 Advance Bukerding diffractometer with Cu K_α (λ = 1.5406 Å, $2\theta = 10^o$ - 70^o) incident radiation at room temperature. The crystal size and mophology of these nanopaticles were observed by TEM (JEM 1010). Uv-Vis spectra of ZnO nanoparticles, MB solution and mixture of MB and ZnO (ZnO-MB) solution were recorded on 5000 UV-Vis-NIR Cary spectrometer. The photoluminescence (PL) spectra at 300 ^{o}C of ZnO nanopowders, the mixture of ZnO powders diffused in the second time distilled water, mixture of MB and ZnO were excited by 325 nm of He-Cd laser and recorded on 2300i spectrometer.

2.2. Result and discussion

2.2.1. Crystalline structure and optical property of ZnO nanoparticles

Figure 2 presents XRD patterns of ZnO nanoparticles. There are peaks (010), (110), (013), and (112) in which (011) peak is strongest intensity. XRD pattern shows that ZnO nanoparticles are single phase, polycrystalline with $\boldsymbol{C_{6v}^4}$- $P6_3mc$ hexagonal

structure and lattice crystalline constant of a = b ≈ 3.2428 Å, c ≈ 5.203 Å. These values are as the same as standard ones of ZnO (JPC Card. N_o 036-1451; a = b = 3.2490 Å, c = 5.2066 Å). The D average crystal size of ZnO nanoparticles were estimated from XRD patterns and using Debye-Scherrer formula: $D = \frac{0{,}9\,\lambda}{\beta cos(\theta)}$, in which D (Å) is the crystal size, λ is the X-ray wavelength of CuK_α, β (rad) is the full width of diffraction peak, θ (rad) is the diffraction peak. The results show that average crystal size of ZnO is about of 100 nm. While TEM image shows that ZnO nanoparticles are mainly quasi-sphere shape possessing average crystal size of 200 - 400 nm. This value is bigger than that from XRD pattern and Debye-Scherrer. The difference is due to Ostwald ripening and Vander Waals interaction agglomerating nanocrystal together to form a bigger crystal in preparation produce [7, 8]. Figure 4 presents UV-VIS spectra of ZnO nanoparticles. There is only a wide band with absorption band edge at 352 nm related to absorption transition near the band gap of ZnO crystal [9]. Base on the absorption spectra, plot the dependence of $(\alpha hv)^2$ on photon energy (hv) (the insert of Figure 4), the band gap energy of ZnO is determined to be about of 3.260 eV, this value is consistent with references [9].

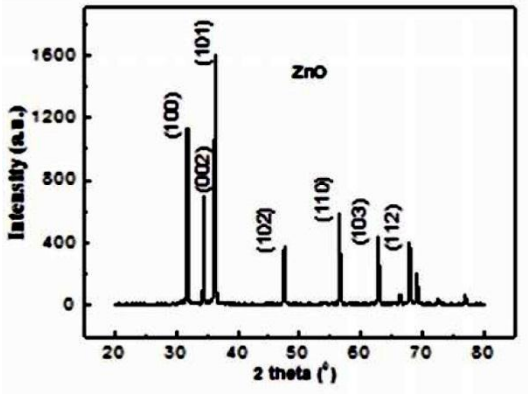

Figure 2. XRD patterns of ZnO nanoparticles

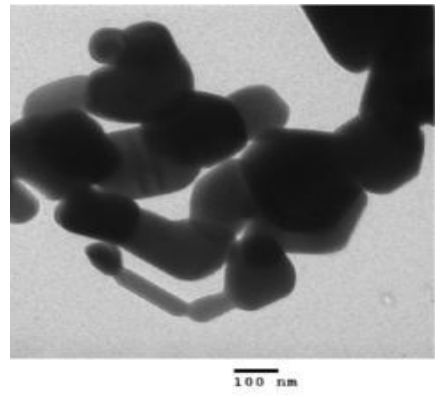

Figure 3. TEM image of ZnO nanoparticles

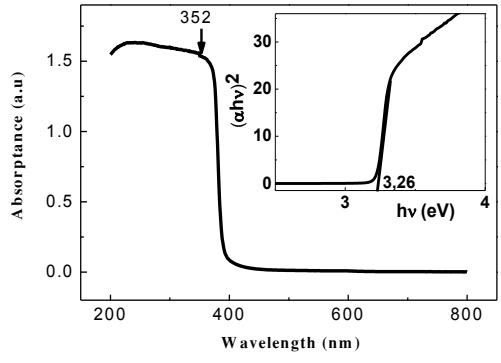

Figure 4. UV-VIS spectra of ZnO nanoparticles

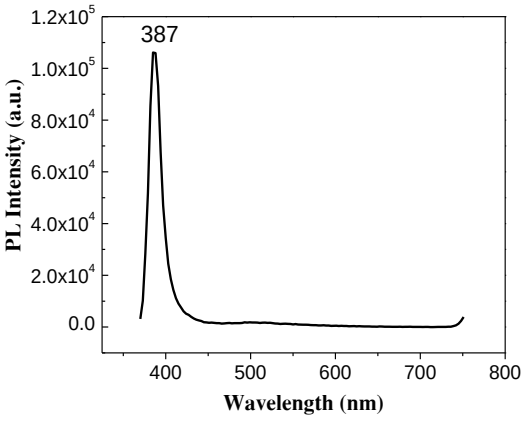

Figure 5a. PL spectraof ZnO nanopowders

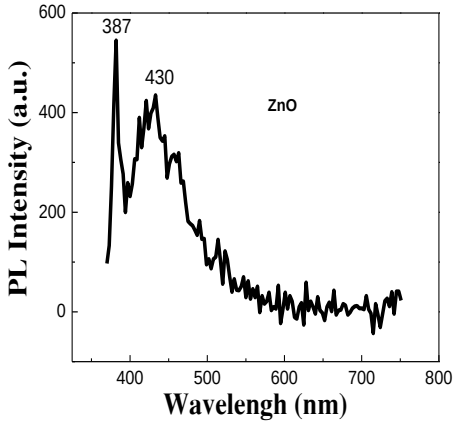

Figure 5b. PL of the mixture of ZnO powders diffused in the second time distilled water

Figures 5a, 5b show photoluminescence spectra of ZnO powder and the mixture of ZnO powders diffused in the second time distilled water. Photoluminescence spectra of ZnO powder (Figure 5a) mainly present a strong intensity peak at about 387 nm (3.202 eV). This peak can be assigned to radiation of free exciton combination in ZnO with binding energy of 58 meV [10]. In photoluminescence of the mixture of ZnO powders diffused in distilled water, besides exciton peak, there is a wide band in the range of 400 – 600 nm with maximum at 430 nm (Figure 5b). This band can be assigned to the defects on surface of ZnO nanoparticles after ZnO powders were diffused in distilled water [11]. However, the intensities of these peaks are low because density of ZnO nanoparticles is small. The appearance of the peak of 387 nm also assigned to free exciton combination, nearly absorption band edge, so the crystal structure and morphology show that commercial ZnO nanoparticles have good quality that can be applied in photocatalyst for organic pigment.

2.2.2. Photocatalyst of ZnO for methylene blue

Figure 6 shows images of MB-ZnO mixture solution with difference irradiation time. When non-irradiating, the color of ZnO-MB mixture solution is blue (Figure 6a). As irradiating with the time of 30, 60 minutes, the color of ZnO-MB mixture solution gradually depleted (Figure 6b-c), then completely depleted as irradiated for 90, 120 minutes. This gradual depletion shows that ZnO nanoparticles act as photocatalyst for MB. This effect was investigated by UV-VIS and photoluminescence spectra of MB-ZnO mixture solution.

Figure 7 is the UV-VIS spectra of MB solution and MB-ZnO mixture solution irradiated with difference time. In the UV-VIS spectra of MB, there presents 2 peaks at 250, 290 nm in the ultra violet region and 2 bands at about 610, 656 nm in the visible region, in which 610 nm band has the strongest intensity (Figure 7a). These bands in the ultraviolet band is assigned to π- π^*absorption transition in coloured groups of MB.

Bands in visible region belong to n - π^* absorption transition also in coloured groups of MB, in which, notably the group of –C=N [12].

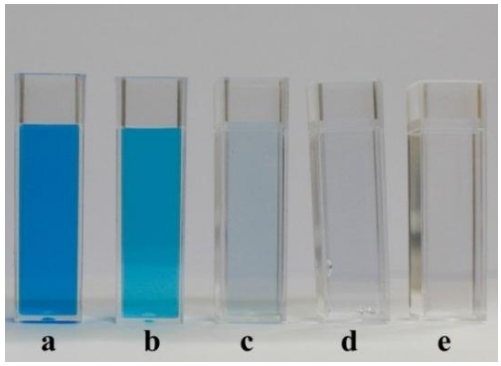

Figure 6. MB-ZnO mixture solution irradiated a. 0 minute, b. 30 minutes, c. 60 minutes, d. 90 minutes, e. 120 minutes

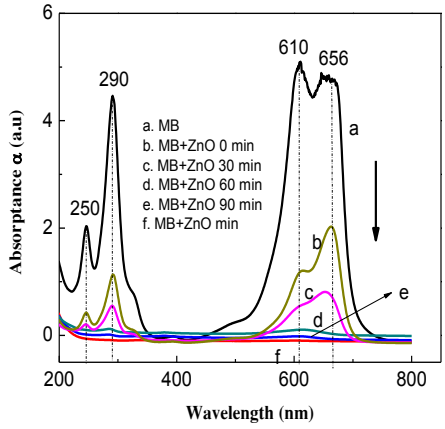

Figure 7. UV-VIS spectra of MB solution non irradiated and MB-ZnO mixture solution irradiated for different time

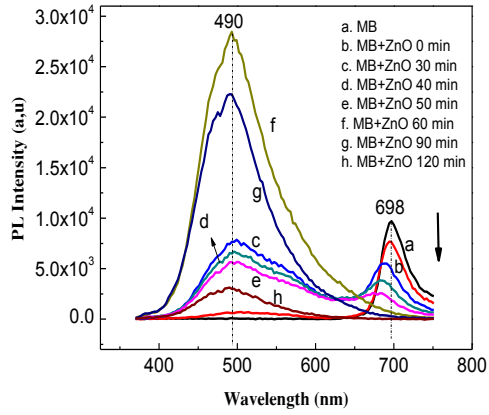

Figure 8. PL spectra of MB solution non irradiated and MB-ZnO mixture solution irradiated for different time

With MB-ZnO non-irradiated, in UV-VIS spectra, there peaks and bands characterized to coloured groups in the same position as MB solution but the absorptance reduced remarkablely. The 610 nm band is reduced more than 656 nm band (Figure 7b). The absorptance decreasing of bands, peaks and the change in correlation between 610 nm and 656 nm band can be by N atoms of MB, which may be due to adsorb on ZnO nanoparticles surfaces coordinate bonded to Zn^{2+} ions. This bound may be form complexes to reduce absorption transition ability of electrons between orbitals in coloured group of MB [13]. When irradiating MB-ZnO mixture solution for 30, 60, 90 minutes, the absorptance of peaks and bands reduce gradually, their position are unchanged (Figure 7c-e). For 120 minutes irradiation, the UV-VIS spectra distinguish. Using UV-Vis spectra and formula: $C = C_0 e^{-kt}$ in which, C_0, C are concentration of MB in (MB+ZnO) mixture solution as unirradiated and irradiated for different time, the rate of concentration attenuation k of MB for 663 nm band can be determined [14, 15]. The results show that k ≈0.03 $minute^{-1}$, this value is consistent with ones in references [3].

Figure 8 presents photoluminescence spectra of MB-ZnO solution non-irradiated and irradiated for difference time. In PL spectra of MB solution (curve in Figure 8), there is only red band at 698 nm with strong intensity. This band can be assigned to absorption transition of electrons from anti -binding π^* orbital to n binding orbital of coloured groups in MB. As the same as UV-VIS spectra, when non-irradiation, PL spectra of MB-ZnO mixture solution also appeared the red band at 698 nm assigned to MB, at the same time appeared a blue band in the range of 400-600 nm with maximum at 490 nm (Figure 8b). This blue band can be related to surface defects of ZnO nanoparticles in distilled water [11]. In comparison to PL spectra of the mixture of ZnO powders diffused in distilled water (Figure 5), this blue band shifted towards to the longer wavelength of 60 nm (the red shift) The decreasing of red band in PL spectra of MB-ZnO mixture and the red shift by the surface defects of ZnO nanoparticles are also the evidence of coordinated binding between N atoms of MB and Zn^{2+} ions on the surface of ZnO nanoparticles to form complex compound. Thus, when MB-ZnO mixture irradiated for 30, 40 minutes, the PL intensity of red band decreases but its position shifted towards to the shorter wavelength (the blue shift) from 698 to 676 nm (Figure 8c-d) and extinguish as irradiated for 90, 120 minute (Figure 8e-f).

Therefore, when increasing irradiated time the absorptance and PL intensity of peaks and bands assigned to coloured group of MB in UV-VIS spectra and PL spectra also decrease gradually and extinguish. However, the peak position of band in PL spectra shifts towards to the shorter wavelength. The decreasing of the absorptance, PL intensity and the peak shift are due to decomposing gradually of MB versus irradiated time. This decreasing is caused by photocatalyst of ZnO nanoparticles for MB: Under the effect of radiation with photon energy larger or equal to band gap energy of ZnO, the free electrons (e^-) in conduction band and free holes (h^+) in valance band are created. Holes can oxidize H_2O or OH^- to OH* radicals [1]:

$$h^+ + H_2O \rightarrow H^+ + OH^*$$
$$h^+ + OH^- \rightarrow OH^*$$

Electrons can deoxidize O_2 adsorbed on ZnO nanoparticles surfaces to form anion group O_2^-*:

$$e^- + O_2^- \rightarrow O_2^-{}^*;$$
$$O_2^-{}^* + e^- + 2H^+ \rightarrow H_2O_2$$

or:
$$2O_2^-{}^* + 2H^+ \rightarrow H_2O_2 + O_2 \ ;$$
$$H_2O_2 + e^- \rightarrow OH^* + OH^-$$

The OH-radical has a strong oxidation, which decomposes MB into intermediate products and eventually into H_2O and CO_2 [1]:

$OH^* + MB \rightarrow$ intermediate products $\rightarrow H_2O + CO_2$

Besides the good effect on MB, the commercial ZnO nanoparticles also test photocatalyst ability for Van Phuc dye wastewater (Van Phuc village, Ha Dong district, Hanoi city). The 500 mg of ZnO nanopowders are dissolved in 500 mL two time

distilled water and mixed with Van Phuc dye wastewater in the ratio of 1:1. The result showed that as un-irradiated, this mixture is strong red (Figure 9a), yellow, light- yellow as irradiated for 30, 60 minutes (Figure 9b-c). Finally, this mixture almost fades as irradiated for 90, 120 minutes (Figure 9 d-e). The detailed study of organic ingredients in this textile wastewater will be mentioned in subsequent studies, as this belongs to a relatively larger national research topic.

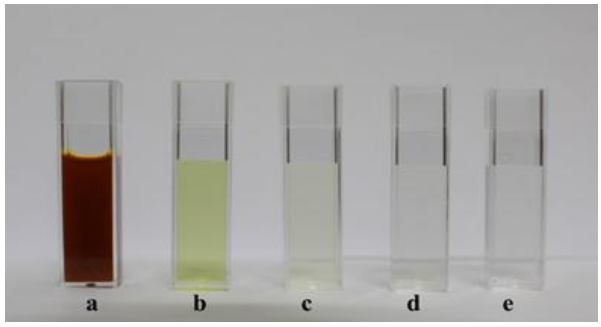

Figure 9. Van Phuc dye wastewater-ZnO mixture solution with different irradiation times a. un-irradiated; b. 30 minutes; c. 60 minutes; d. 90 minutes; e. 120 minutes

3. Conclusions

The commercial nanoparticles ZnO (Merck) with hexagonal structure have average particle size about of some nanometers and good absorption propertier. The absorption, the photoluminescence characteristic, especially the PL of free exciton combinations at 387 nm has relation to an organic pigment treatment as photocatalyst agent. Van Phuc dye wastewater was tested by the commercial nanoparticles ZnO. These results promises to apply a transition metal doped ZnO nanoparticles in photocatalyst treatment for harmful pigment in wastewater.

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