

Photocatalytic degradation of dye by Ag/ZnO prepared by reduction of Tollen's reagent and the ecotoxicity of degraded products

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(Received 27 June 2013 • accepted 1 December 2013)

Abstract—A heterostructure of Ag/ZnO powder was prepared by a reduction of $\text{Ag}(\text{NH}_3)_2^+$ ions in a basic solution or Tollen's reagent. From this method, the existence of a metallic Ag coating on the ZnO surface was confirmed by transmission electron microscope and x-ray photoelectron spectroscopy. The photocatalytic activity of the Ag/ZnO powders was investigated by analyzing the degradation of an aqueous methylene blue solution under a blacklight irradiation. Furthermore, the parameters, including Ag content, catalyst loading, initial dye concentration and pH, were also studied. After the methylene blue solution was irradiated for 30 min under a blacklight illumination, total mineralization was not observed as the presence of some carbon compound species was indicated in a mass spectrum. Furthermore, the toxicity of the treated methylene blue solution produced by the Ag/ZnO powders was also investigated by a test for the inhibition of the growth of *Chlorella vulgaris*.

Keywords: Ag/ZnO, Photocatalyst, Tollen's Reagent, *Chlorella vulgaris*

INTRODUCTION

Silver (Ag) is one of the most used coupling metals to enhance the photocatalytic efficiency of many wide energy band gap semiconductor-based photocatalysts such as ZnO and TiO_2 [1-4]. ZnO is an n-type semiconductor in group II-VI with a wide energy band gap and a large free-exciton binding energy. ZnO is widely used for many applications including acting as a photocatalyst for treatment of wastewater or air pollution [5,6]. The textile industry uses these products for treating its wastewater. The textile industry wastewater is often colored and this reduces the light permeability in the water environment and also reduces the photosynthesis of submerged plants. In addition, wastewater containing toxic dye molecules may affect human functions. Photocatalysis is one of the treatment methods that has many advantages such as a high degradation efficiency, can operate in ambient conditions, and solar irradiation can be used for activation. Moreover, the catalyst is inexpensive and environmentally friendly.

The photocatalytic process occurs when the ZnO absorbs photons that have energy equal to or greater than the band gap energy of ZnO and the electrons in the valence band of ZnO (VB_{ZnO}) are promoted to the conduction band of ZnO (CB_{ZnO}). These photogenerated electrons in CB_{ZnO} can react with oxygen to produce a super

anion radical (O_2^-), while the water reacts with the holes (h^+) in the VB_{ZnO} to produce a hydroxyl radical (OH^\bullet). However, the photogenerated electrons in CB_{ZnO} also recombine with h^+ in the VB_{ZnO} and this inhibits the photocatalytic efficiency [7,8]. In a heterostructure such as Ag/ZnO, the Ag metal on the surface of ZnO generates a new Fermi level between the conduction and the valence bands of ZnO, then the photogenerated electron in the CB_{ZnO} can transfer to this level and also react with oxygen to produce the O_2^- species [9]. This furthermore reduces or inhibits the rate of electron-hole pair recombination and enhances the photocatalytic activity of Ag/ZnO. This heterostructure can be prepared by many methods, but mostly by using a chemical reduction because it is simple, does not require high cost equipment, and is easy to control the reaction. The reduction of Tollen's reagent by aldehyde functional groups is one of the methods for preparing Ag coating on metals that provides a silver mirror coating on the substrate. This technique is very popular and well known for the chemical deposition and mass production of Ag coatings on various types of substrates including photocatalyst powders such as TiO_2 [10] and ZnO [11,12].

During the last few decades, many researchers have reported several methods for synthesizing ZnO powders that show a higher photocatalytic activity than a commercial ZnO [13,14]. However, these mentioned techniques mostly need many synthesizing steps, complicated equipment, high cost materials including a stabilizer, solvent and starting material. These also lead to high production costs of the final product, which is a major problem for industrial applications.

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In this work, we report the enhancing effect of Ag on commercial grade ZnO by reduction from Tollen's reagent using glucose as the reducing agent. The photocatalytic activity of the Ag/ZnO heterostructure was studied by the photocatalytic degradation of methylene blue dye in aqueous solution under a blacklight fluorescent tube as an inexpensive UV source. Furthermore, the ecotoxicity of the treated methylene blue solution by the prepared Ag/ZnO photocatalyst was also investigated by testing for the inhibition of the growth of *Chlorella vulgaris* as an ecological indicator.

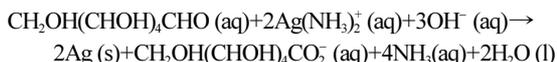
EXPERIMENTAL SECTION

1. Materials

The zinc oxide powder (ZnO, Fluka), silver nitrate (AgNO₃, Merck), potassium hydroxide (KOH, Merck), ammonia solution (NH₃, J.T.Baker), methylene blue (C₁₆H₁₈N₃SCl, Unilab) and glucose (C₆H₁₂O₆) were analytical grade and were used without further purification.

2. Preparation of Ag/ZnO Heterostructure

The Ag/ZnO powders were prepared by reduction from Tollen's reagent. In a typical preparation the required amounts of AgNO₃ were dissolved in distilled water at various concentrations from 0.001 M to 0.05 M. Tollen's reagent was prepared by the dropwise addition of 1 M KOH into the AgNO₃ solution to obtain a brown solid of Ag₂O. After that, concentrated ammonia solution was then added to this suspension until the Ag₂O precipitant was transformed to Ag(NH₃)₂⁺ complex and formed a clear solution. Finally, 1 g of ZnO powder was added followed by the addition of a 1 M glucose solution, and this mixture was continuously stirred for 1 h. The product was filtered, rinsed with distilled water several times, then collected and dried for 1 h. The metallic Ag from the reduction of Tollen's reagent can be produced as follows:



3. Characterization

The structural identification and morphology of the Ag/ZnO powders were carried out by using an X-ray diffractometer (XRD, X'Pert MPD, Philips) with Cu K_α radiation at a wavelength of 0.15406 nm and a transmission electron microscope (TEM, JEM 2010, JEOL), respectively. The elemental analysis of the Ag/ZnO powders was measured by an energy dispersive x-ray spectrometer (EDS, Oxford) coupled with SEM. The oxidation states of Ag and Zn in Ag/ZnO powders were analyzed by X-ray photoelectron spectroscopy (Quantera SXM, Physical Electronics) using Al K_α monochromatic radiation at 1,486.6 eV. The degradation products were characterized by liquid chromatograph-mass spectrometry (LC-MS, 2690-LCT, Waters, Micromass) using an electrospray ionization operating in the positive (ESI⁺) mode.

4. Photocatalytic Degradation of Methylene Blue

The photocatalytic activity was investigated through the degradation of an aqueous methylene blue (MB) solution under irradiation with a blacklight fluorescent tube (15W, Sylvania). This tube efficiently emits UVA at 315–400 nm (peak at 352 and 368 nm, from the data sheet). 100 mg of Ag/ZnO was placed into a 1 × 10⁻⁵ M MB solution. To study the possible adsorption of MB on the surface of Ag/ZnO powders, this mixture was stirred for 30 min in the dark,

and then it was irradiated under a blacklight fluorescent tube. The solution was sampled every 10 min and centrifuged to separate the catalyst powders. The remaining MB concentration for each irradiated period was determined by a UV-Vis spectrophotometer (Lambda 25, Perkin Elmer). The degradation was calculated by the following equation:

$$\text{Degradation (\%)} = [(A_0 - A_t)/A_0] \times 100$$

where A₀ is the absorbance at 644 nm of the MB solution before illumination, and A_t is the absorbance at 644 nm of MB solution after irradiation at the required times.

5. Ecotoxicity Test

The ecotoxicity tests were carried out with the freshwater unicellular green algae *Chlorella vulgaris*. The stock of *Chlorella vulgaris* was cultured in nutrient medium applied from Athibai [15]. All nutrient medium and equipment were sterilized to ensure that there were no contaminating microorganisms. The 100 mL of stock algal cells were propagated in a 500 mL of glass bottle containing 300 mL liquid nutrient medium and kept at 25 ± 2 °C under cool white fluorescent lighting (18 W) with a 12 h light and 12 h dark light photoperiod. Agitation was performed by filtered air bubbling.

The inoculum of *Chlorella vulgaris* provided a concentration of around 2 × 10⁶ cell/mL in each flask that contained 4 mL of methylene blue solution before and after the photocatalytic process. 0.5 mL of inoculated nutrient medium was added into each flask and then incubated at 25 ± 2 °C and continuously shaken (100 rpm). Illumination was provided by white fluorescent light (18 W) following a day/night rhythm of 12 h/12 h for 72 h. To evaluate the cell density, 100 mL of testing solution containing *Chlorella vulgaris* was pipetted into formaldehyde to stop cell division and 10 mL of the resulting solution was pipetted onto a hemacytometer slide, and the number of cells was evaluated using the optical microscope. The data represent the mean ± standard deviation of triplicate measurements from each treatment.

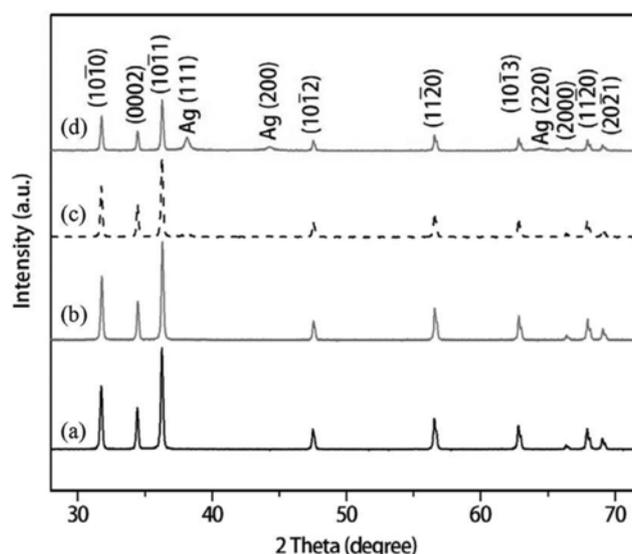


Fig. 1. X-ray diffraction patterns of Ag/ZnO powders prepared from the AgNO₃ concentrations of (a) 0, (b) 0.001, (c) 0.01 and (d) 0.05 M. The four Miller indices correspond to the ZnO phases.

RESULTS AND DISCUSSION

1. Structure and Morphology

Fig. 1 shows the XRD patterns of pure ZnO and Ag/ZnO prepared from the reduction of Tollen's reagent at various initial concentrations of AgNO₃ solutions. For the pure commercial ZnO, all diffraction peaks were well matched with ZnO crystallizing in its wurtzite structure (JCPDS card number 36-1451), while the diffraction peaks corresponding to the (111), (200) and (220) planes of the face-centered cubic (fcc) structure of Ag (JCPDS card number 04-0783) were detected in the Ag/ZnO samples. The peak intensities for metallic silver increased with an increase of the AgNO₃ concentrations, and no other phases were observed such as for Ag₂O in these XRD patterns. Fig. 2 shows the energy dispersive x-ray spectra of Ag/ZnO powders at various initial concentrations of AgNO₃ solutions. There were three signals for the oxygen, silver and zinc elements, and the intensity of the Ag signal was consistent with the initial concentrations of the AgNO₃ solutions. The composition in atoms percentage of Ag and Zn for all samples is reported in Table 1.

Fig. 3 shows the TEM image of Ag/ZnO powders prepared from the 0.03 M AgNO₃ solution. The existence of the Ag particles deposited on the ZnO surface confirmed the heterostructure of Ag/ZnO. Fig. 4 shows the x-ray photoelectron spectra of the Ag/ZnO powders prepared with different initial AgNO₃ concentrations. The metal-

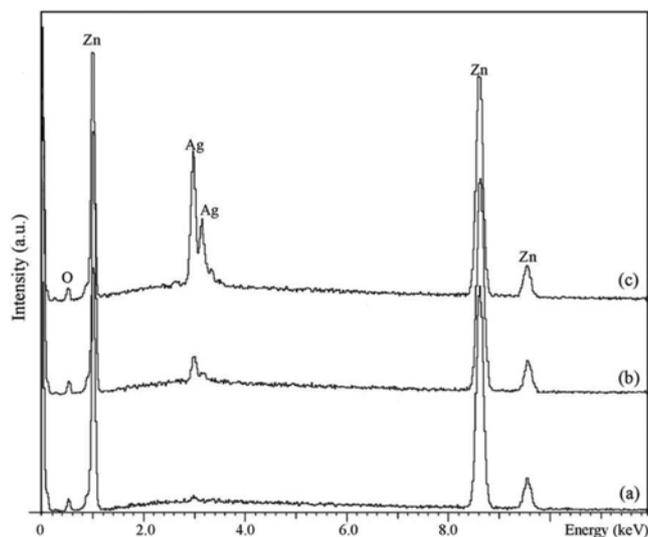


Fig. 2. Energy dispersive x-ray spectra of Ag/ZnO powders prepared from the AgNO₃ concentrations of (a) 0.001, (b) 0.01 and (c) 0.05 M.

Table 1. Elemental composition of Ag/ZnO prepared from various AgNO₃ concentrations

AgNO ₃ concentration (M)	% Composition analyzed by EDS	
	Zn (at%)	Ag (at%)
0.001	99.34 (9)	0.66 (2)
0.005	97.49 (4)	2.51 (6)
0.010	95.12 (7)	4.88 (4)
0.030	87.04 (5)	12.96 (4)
0.050	81.93 (8)	18.07 (7)

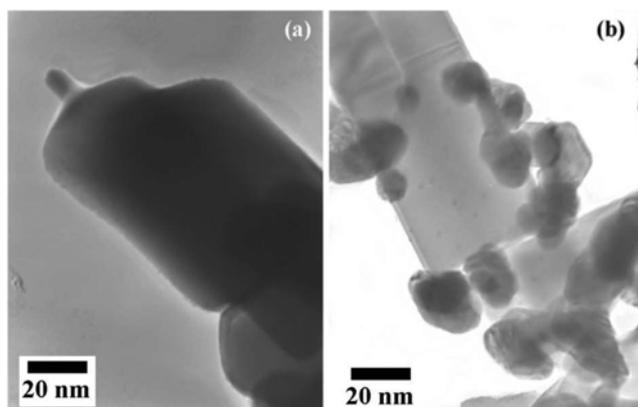


Fig. 3. TEM images of (a) ZnO and (b) Ag/ZnO prepared from 0.03 M AgNO₃.

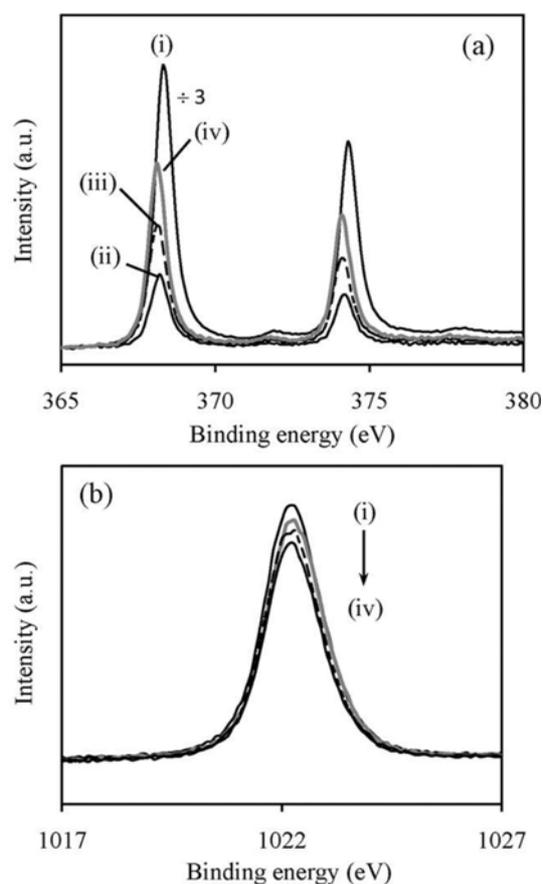


Fig. 4. XPS spectra of (a) Ag 3d for (i) pure Ag and Ag/ZnO prepared from the AgNO₃ concentrations of (ii) 0.01, (iii) 0.03 and (iv) 0.05 M, and (b) Zn 2p for ZnO prepared from the AgNO₃ concentrations of (i) 0, (ii) 0.01, (iii) 0.03 and (iv) 0.05 M.

lic silver prepared from this method without any ZnO powder shows the doublet peaks of Ag 3d at binding energies of 368.30 (Ag 3d_{3/2}) and 374.30 (Ag 3d_{5/2}) eV as same as those reported in the literature (Fig. 4(a) i) [16,17]. Furthermore, the intensities of these peaks also increased with the Ag content in the samples. For the Ag/ZnO, all the binding energies were located at about 368 (Ag 3d_{3/2}) and 374 (Ag 3d_{5/2}) eV (Fig. 4(a) ii-iv), and showed that the Ag on the ZnO

surface was in a metallic form. From the literature the binding energies of Ag^0 , Ag_2O and AgO have been reported to be about 368.2, 367.8 and 367.4 eV, respectively. The binding energy value decreased with a decrease of the electron density of Ag. The binding energy of Ag $3d_{3/2}$ shifted from 368.30 (pure metallic silver) to 368.18 (Ag/ZnO prepared from 0.05 M AgNO_3), and from this it can be concluded that the electrons in the Fermi level of the Ag, most likely transfer to a valence band of ZnO that has a lower Fermi level for Ag [18], or there is a conduction band of ZnO formed by a tunneling effect [19]. The $2p_{3/2}$ peak positions of all Ag/ZnO powders all had nearly the same binding energy of 1022.2 eV (Fig. 4(b)), and this confirmed that the main oxidation state of Zn was +2.

2. Photocatalytic Activity

The effect of Ag loading on the photocatalytic efficiency of ZnO powders was first studied by degradation of the methylene blue (MB) solution (Fig. 5(a)). To ensure that the decrease of methylene blue concentration did not result from adsorption, or self-photodegradation by pure silver, the MB solution with Ag/ZnO powders was stirred in the dark, the MB solution without any photocatalyst was stirred under blacklight irradiation, and with only pure silver powders present in the MB solution was stirred under blacklight illumination, respectively. These results are shown in Fig. 5(b). Although these parameters slightly diminished the methylene blue dye concentrations, these reductions were negligible compared to the photocatalytic effect of the Ag/ZnO powders.

From Fig. 5(a), the photocatalytic activity after irradiation for 10 min increased from 77.3% to 89.6% when the AgNO_3 concentration was increased from 0.0 to 0.03 M. As we know, the deposited Ag particles on the surface of ZnO generate a new Fermi level

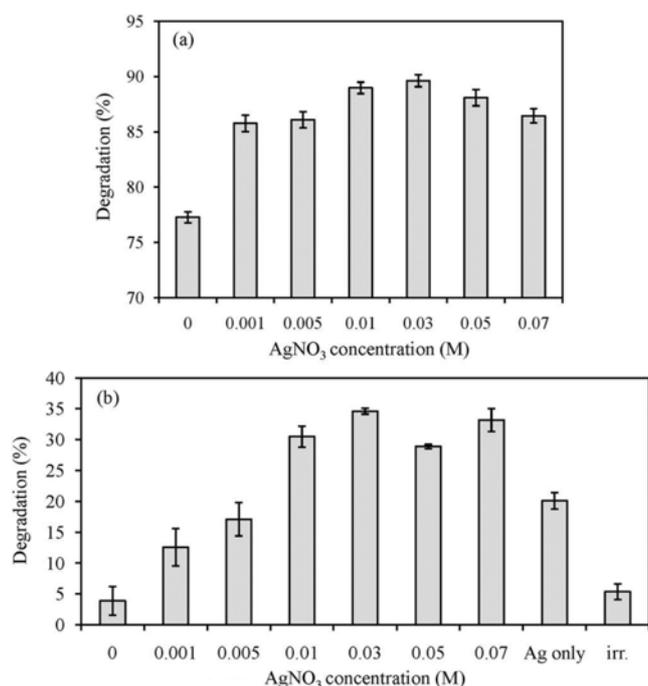


Fig. 5. Efficiency of methylene blue dye degradation by (a) photocatalytic reaction and (b) adsorption of Ag/ZnO powders prepared at various AgNO_3 concentrations. This efficiency is caused from the self-degradation by UV light and adsorption by Ag particles as shown in (b).

that receives the electrons from the conduction bands of ZnO and inhibits or reduces the charge recombination so this enhanced the photocatalytic activity of Ag/ZnO over the pure ZnO [9]. If the AgNO_3 concentration was greater than 0.03 M, the photocatalytic activity of Ag/ZnO tended to decrease. This could be due to the decrease of the ZnO surface area by an increase of the deposited Ag. As only pure Ag particles cannot degrade the MB dye, then it must work in conjunction with ZnO. When the Ag loading was more than the optimum point, the portion of the ZnO surface that absorbs the photons was decreased by the increase of the Ag coverage. Then, the population of electrons in the conduction bands and holes in the valence bands decreased and produced a lower photocatalytic efficiency.

To study the relationship between the catalyst loading and the degradation efficiency, the amount of the Ag/ZnO powder prepared from the 0.03 M of AgNO_3 solution was varied between 50-150 mg in 150 mL of 1×10^{-5} M MB solution. In this range of catalyst loading, the photocatalytic activity of the Ag/ZnO after 10 min of irradiation increased with the amount of the loading of the Ag/ZnO powders (Fig. 6). This could be due to production of a higher population of generated reactive species due to the higher amount of photocatalyst that would absorb more photons and generate more reactive species [20,21]. The amount of the catalyst loadings in this studied range was therefore not overloaded, for in that case some particles

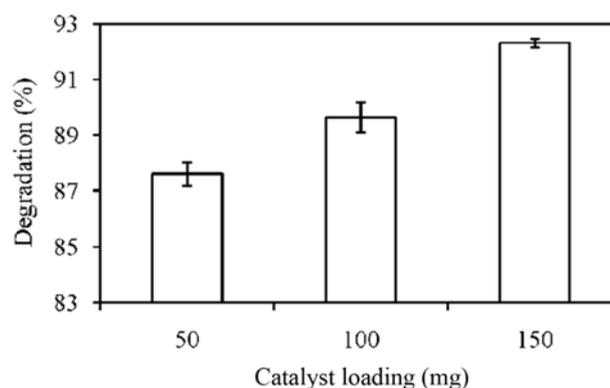


Fig. 6. The efficiency of MB photocatalytic degradation by various amounts of Ag/ZnO prepared from the 0.03 M AgNO_3 .

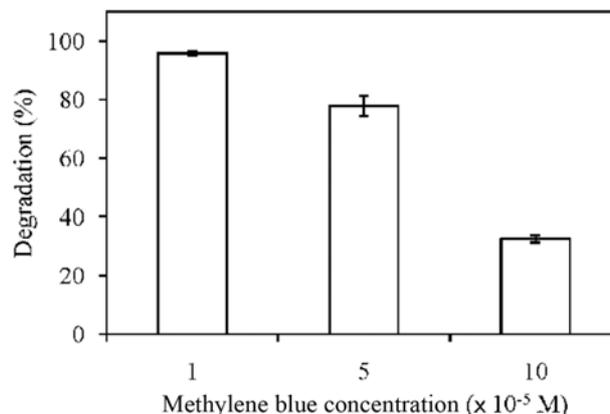


Fig. 7. The efficiency of MB photocatalytic degradation by various initial MB concentrations using Ag/ZnO prepared from the 0.03 M AgNO_3 as a photocatalyst.

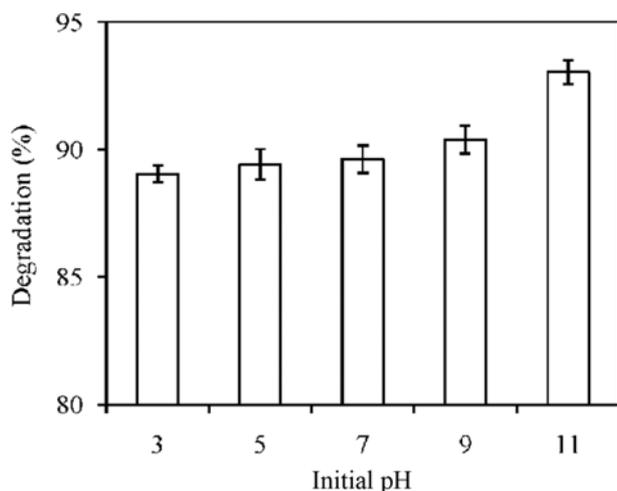


Fig. 8. The efficiency of MB photocatalytic degradation at various initial pH values using Ag/ZnO prepared from the 0.03 M AgNO₃ as a photocatalyst.

may have been shielded by sticking together and this would have reduced the photon flux per surface area.

The concentration of methylene blue was varied between 1×10^{-5} and 1×10^{-4} M to study the effect of the initial dye concentrations on the efficiency of the Ag/ZnO powders. An increase of the initial dye concentration decreased the photocatalytic degradation efficiency (Fig. 7). At high dye concentrations, fewer photons can reach the surface of the Ag/ZnO which reduces the production of reactive species and leads to a decrease in the photocatalytic activity [20,22].

The effect of pH on the MB decolorization was investigated over the pH range of 3-11 using 100 mg of Ag/ZnO powder prepared from the 0.03 M of AgNO₃ solution, in 150 mL of 1×10^{-5} M MB solution (Fig. 8). After 10 min of irradiation, the maximum efficiency of the Ag/ZnO powders was at pH 11. At high pH, there are OH⁻ species in the solution that can adsorb onto the surface of Ag/ZnO powder and produce \cdot OH radicals. Thus, the \cdot OH radicals are more easily generated in an alkaline medium and this increases the photocatalytic degradation efficiency [20,22].

3. Mineralization of Methylene Blue and Ecotoxicity of Treated MB Solution

The degradation of MB by Ag/ZnO under a blacklight illumination was investigated by mass spectrometry with an electrospray ionization (MS-ESI) operating in a positive mode. The mass spectra of the methylene blue before and after irradiation are shown in Fig. 9. The main peak at $m/z=284$ amu was assigned to its cationic structure (MB⁺) [23]. After irradiation for 30 min, total mineralization was not observed because some intermediate species were observed as shown in Fig. 9(b). This was in agreement with a decrease of the total carbon content that decreased from 0.96% (before irradiation) to 0.30% (after irradiation for 30 min). However, the signal of the peak at $m/z=158$ amu (349 counts as in Fig. 9(b)) was very low compared to the signal of the peak at $m/z=284$ amu (2.04×10^5 counts in Fig. 9(a)). It can be implied that the photocatalytic process can convert most of the carbon atoms to CO₂ and leave the small anions such as SO₄²⁻ and NO₃⁻ in the solution [24,25].

Some of the many small molecular products produced by photocatalysis may be toxic. We studied the ecotoxicity of the treated

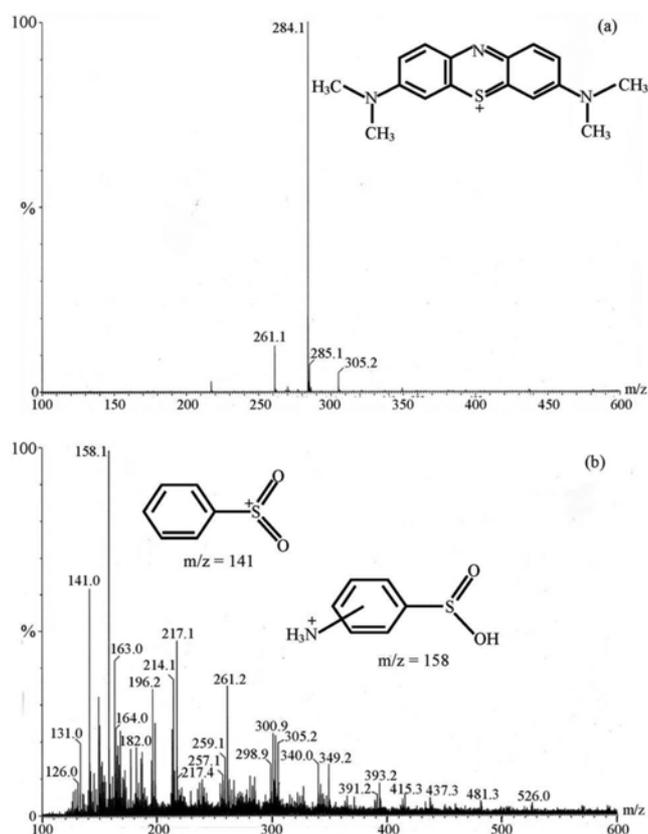


Fig. 9. Mass spectra of the MB solutions (a) before and (b) after photocatalysis.

MB solution by testing for the inhibition of growth of *Chlorella vulgaris* used as an ecological indicator. Although there are many ecological indicators, such as protozoa, fish, crustacean, bacteria, algae and so on, the green algae, such as *Chlorella* sp., are often more sensitive to contaminants or chemicals than the others in the same aquatic environments [26]. Chen [27] used *Vibrio fischeri* as marine bacteria for evaluating the toxicity of reactive orange 16 before and after photocatalytic degradation by TiO₂, but it has not been reported for ecotoxicity of MB after photocatalytic degradation by Ag/ZnO powder. Moreover, *Chlorella* sp. is a suitable ecological indicator more than marine bacteria for testing the toxicity of degraded product in freshwater resource. Fig. 10 shows the density of individual cells

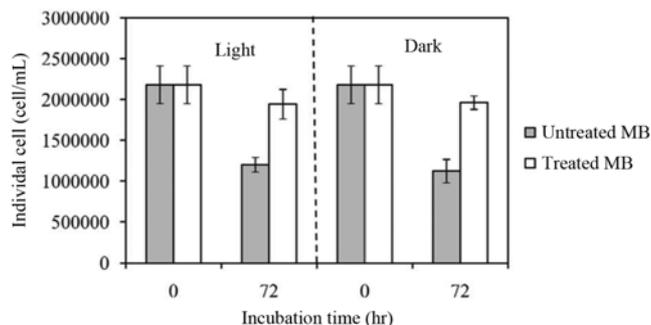


Fig. 10. Individual cells of *Chlorella vulgaris* in a 1×10^{-5} M MB solutions before and after photocatalysis incubated in the dark and under fluorescent light.

(cell/mL) for *Chlorella vulgaris* in 1×10^{-5} M MB solutions before and after photocatalysis. To ensure that any inhibition of growth did not come from the reduction of photosynthesis caused by the colored MB solution, the *Chlorella vulgaris* in two solutions (MB solutions before and after photocatalysis) was incubated for 72 h in dark condition. The results (Fig. 10) confirm that there was no significant change of *Chlorella vulgaris* growth in the dark or under fluorescent light, so the growth inhibition by the effect of light during incubation was also negligible. Thus, any toxicity detected must be due to the presence of toxic chemicals. However, the number of individual cells in the MB solution treated with by Ag/ZnO was higher than those in the initial MB solution. This can be explained by two possible reasons: first, the MB itself was more toxic than the degraded products. Second, the small molecules produced by photocatalysis may be toxic but their concentrations were lower than the initial toxic MB concentration. However, in the same volume, it can be concluded that the water containing the degraded products after photocatalysis was less toxic than the initial MB solution using *Chlorella vulgaris* as the bioindicator.

CONCLUSIONS

A heterostructure of Ag/ZnO powder was successfully prepared by a reduction of Tollen's reagent. The prepared Ag/ZnO showed a better photocatalytic efficiency than commercial grade ZnO. From the XPS results, the Ag on the surface of ZnO was metallic Ag. By increasing the catalyst loading, the photocatalytic activity of Ag/ZnO powders also increased due to an increase of the generated reactive species, but its efficiency decreased with an increase of the MB concentration because of the reduction in the penetration of photons or the penetration of light at the high dye concentrations. At pH 11, the OH⁻ ions were more easily adsorbed on the surface of photocatalyst and led to the production of more reactive species and an increase of the photocatalytic activity. Although the photocatalysis, in this work, did not result in a total mineralization, the treated MB solution had a lower toxicity than the untreated or initial MB solution. This indicated that the treated MB solution was less toxic to *Chlorella vulgaris* cells than the untreated or initial MB solutions.

ACKNOWLEDGEMENT

This research received partial support from the Human Resource Development in Science Project (Science Achievement Scholarship of Thailand, SAST), and the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education is gratefully acknowledged. We would also like to thank Dr. Brian Hodgson for assistance with the English.

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