

Inhibition of Photocatalytic Activity of Basic Blue-41 by ZnO Modified Surface with Amino Silane

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Abstract. The reduction of the photo catalytic efficiency of ZnO can be achieved by modifying its surface with amino silane, which synthesized through condensation reaction under basic condition. The pH of solution was varied from 8 to 14 during the synthesis and was found that pH 12 was the most suitable pH for the preparation. All of ZMAS were characterized by Elemental Analysis which showed the highest percentage of nitrogen at 3.1064% and IR technique which indicated the Si-O-Zn bond at about 1000 cm⁻¹. The photodegradation property of ZMAS prepared at pH 8-12 toward basic blue 41 was retarded when compared with the unmodified ZnO. Effect of mole ratio of ZnO:APTES (1:0.1, 1:0.5, 1:1, and 1:2) in the preparation of ZMAS was investigated. The photodegradation activity of ZMAS prepared at mole ratio of ZnO:APTES as 1:0.5 to 1:2 toward basic blue 41 was retarded when compared with the unmodified ZnO. The coating of amino silane on ZnO surface did not have much effect on the band gap energy of modified ZnO. The absorption edge of ZMAS was only slightly shifted from 392 to 397 nm.

1. Introduction

The first synthesis dye has been discovered since 1856 by William Henry Perkin. At present more than 10,000 synthesis dyes are available in the market. The textile industry usually uses these dyes to create products. In order to use these dyes, the Textile factories need to improve the quality of the dyes to be durable for various environments such as: sunray, water, temperature etc. When these dyes are dumped into natural water sources, they will pollute and destroy the environment [1]. As a result, more awareness of the effects began to emerge, but the demand for dyes was not exhausted. The natural dyes are another way to reduce the problem because it is a green chemistry. Natural dyes are more environment friendly than synthetic dyes. However, the big problem of to use the natural dyes in the textile industry is the operation cost because it requires a lot of land to produce and they are not durable to the environments such as sunray, water, and temperature [2].

To retard the photodegradation of dyes by UV ray from the sunlight, many kind of UV absorber such as UVA-1, UVA-2, and UVA-3 were integrated into the dyes. In this research, we want to improve the light resistant property of dyes by using UV absorber and light stabilizer. Zinc Oxide can be used to absorb UV radiation with a wide band gap of 3.4 eV. In order to keep the UV absorber properties but prevent the enhancing photocatalytic degradation property, the surface of Zinc Oxide will be modified by amino silane [3]. Amino silane reacts easily on the surface of Zinc Oxide by condensation reaction and the Nitrogen on amino silane chain will trap radicals to prevent the photodegradation of dyes.



2. Experiment and characterization

2.1. Synthesis of modified surface ZnO (ZMAS)

2.1.1. Effect of pH on the synthesis of ZnO modified surface by amino silane. The synthesis of ZnO modified surface by (3-Aminopropyl) triethoxysilane (APTES) was prepared following this process: 2 g of ZnO was stirred in 50 ml of KOH solution for 1 hour (pH was varied from 8-14). Then 2.878 ml (mole ratio of ZnO:APTES was fixed as 1:0.5) of APTES was added and stirred for 24 hours at 60 °C on sand bath. The excess APTES was washed with distilled water. Finally, the white precipitate was dried under vacuum.

2.1.2. Effect of mole ratio of ZnO:APTES on the synthesis of ZnO modified surface by amino silane. The synthesized ZnO modified surface by APTES (ZMAS) was performed as mentioned 2.1.1. but the pH was fixed at pH 12. The mole ratio of ZnO:APTES was varied as 1:0.1, 1:0.5, 1:1, and 1:2, respectively.

2.2. Characterization

The functional group of APTES was analyzed by Fourier Transform Infrared Spectroscopy (FT-IR, Bruker EQUINOX-55). The quantity of APTES on surface of ZnO was recorded by Elemental Analysis (EA, LECO CHNS-932 and VTF-900). The UV absorption property of ZMAS was analyzed by UV-visible Diffuse Reflectance Spectroscopy (UV-DRS, JASCO V-670).

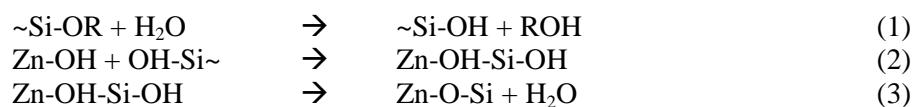
2.3. Photocatalytic study of ZnO modified surface by amino silane

The photodegradation experiment was carried out under UV lamp. Initially, 0.01 g of the ZnO modified surface by APTES (ZMAS) was added into 100 ml of 10 ppm BB41 solution. The degradation reaction was operated under dark condition for half an hour and then operated under UV lamp. The system was first left in the dark in order to attain the absorption equilibrium before the degradation. In this condition, the solution was continually stirred under UV lamp. To monitor the reaction, the sample was collected by a syringe in order to measure the amount of initial (before the addition of the ZMAS) and remaining concentration of BB41 in each period of time. For avoidance of the ZMAS contamination in the collected sample, stirrer was switched off 10 minutes before collecting the sample. Then all of the collected samples were centrifuged for 5 minutes to reduce the dispersion of the fine powdered ZMAS. After that, the centrifugation was transferred into a test tube. Finally, their concentrations were measured by a JASCO 7800 UV-Vis spectrophotometer at wavelength 610 nm.

3. Result and discussion

3.1. Effect of pH on the synthesis ZnO modified surface by amino silane

The hydrated metal oxides can be presented as MOH on the surface, when Zinc oxide was soaked in a basic condition. Then silanol group, which hydrolyzed by the nucleophilic attack of the oxygen contained in water on silicon atom according to the equation 1, will react with the OH group on the metal surface to form ZMAS. However, it was found that the concentration of hydroxide ion at pH 8 and pH 10 were not high enough to change all the surface of Zinc oxide into OH group before the coupling reaction with APTES [4]. Therefore pH 12 and pH 14 were more suitable for the preparation of ZMAS in this experiment. The mechanism of oxalation condensation is stated in equation 2 and 3 respectively.



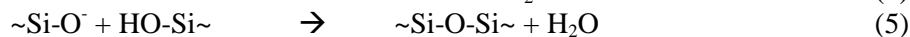
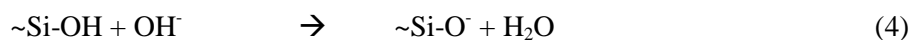
The oxalation condensation occurs from lone pair electrons of oxygen, which act as nucleophile, attack to metal atom through the nucleophilic addition process. Therefore, the metals must have empty orbitals for obtain electrons from nucleophile. The Silicon atom has empty 3d orbitals. So, the hydroxyl group of Zinc is attacking to Si atom followed by H₂O elimination to form Zn-O-Si bond (as shown in equations 2 and 3 respectively).

3.1.1. Characterization

Table 1. Percentage of CHN and IR spectra of ZMAS prepared at various pH when the mole ratio of ZnO:APTES was fixed at 1:0.5.

	Elemental Analysis			Fourier Transform Infrared Spectroscopy		
	Carbon (%)	Hydrogen (%)	Nitrogen (%)	N-H stretching	C-H stretching	Si-O-Zn stretching
ZnO	0	0	0	-	-	-
ZMAS-pH 8	7.1848	2.4147	2.4271	3412, 3381	2924	987
ZMAS-pH 10	7.3647	2.3120	2.5366	3417, 3252	2925	995
ZMAS-pH 12	8.8993	2.4691	3.1064	3428, 3265	2925	1006
ZMAS-pH 14	0.9734	0.1542	-0.1544	-	-	-

The modifying process of ZMAS (pH was varied from 8-12) was successful which confirmed by the percentage of nitrogen in the products as shown in table 1. The amount of nitrogen was related to the amount of silane group on the surface of ZnO. From IR spectra, the Si-O-Zn stretching vibration peak was found at about 1000 cm⁻¹ [5]. At pH 14, most of silanol group are deprotonated and react with itself through the condensation reaction as shown in equation 4 and 5;



As shown in figure 1, the photodegradation property of ZMAS prepared at pH 8-12 toward basic blue 41 was retarded when compared with the commercial ZnO semiconductor but not the ZMAS prepared at pH 14. This indicated that the amino silane can prohibit the catalytic efficiency of ZnO for photodegradation of dyes. There are two possible explanations for the reduction of catalytic efficiency of ZnO when modified by amino silane. Firstly, the silanol group on the surface of ZnO is react with nearby silanol group through condensation reaction to form the polymer of Si-O-Si bond (figure 2). The hydrocarbon chains on silane will prevent water from approaching the ZnO (hydrophobic effect), so the hydroxyl radical is not occurred from water splitting process. Secondly, the radical trapping, nitrogen on amino silane can trap radical, which generated by water splitting proceed. The mechanism is similar to HALS as shown in figure 3. In this work the preparation condition at pH 12 was preferred due to the highest percentage of nitrogen in the product.

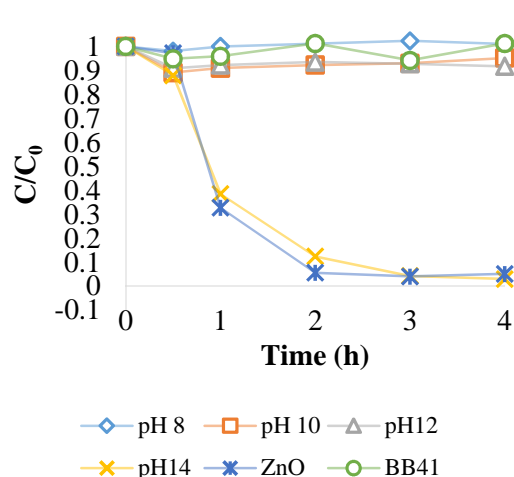


Figure 1. The photodegradation of BB41 under UV irradiation for 4 hours by ZMAS prepared at various pH.

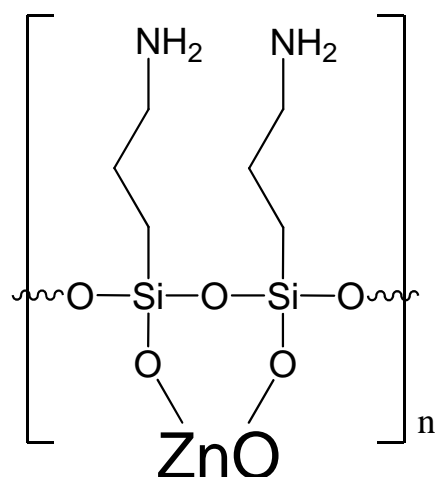


Figure 2. Condensation reaction to form the polymer of Si-O-Si bond at the surface of ZnO.

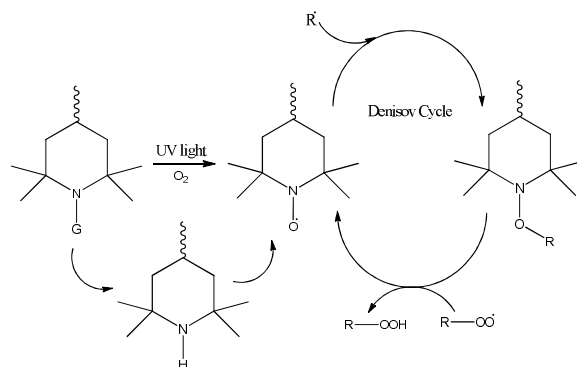


Figure 3. Possible mechanism of HALS activation and radical scavenging.

3.2 Effect of ZnO:APTES mole ratio on the synthesis of ZMAS

The synthesis of ZMAS when the mole ratio of ZnO:APTES were 1:0.1 and 1:0.5 was successful, which did not leave sticky solid on the surface of the reaction vessel, unlike the mole ratio of ZnO:APTES at 1:1 and 1:2. The sticky solid may occurred from the reaction of the excess APTES that can form Si-O-Si bond at the surface of the glass vessel.

3.2.1. Characterization

Table 2. Percentage of CHN and IR spectra of ZMAS prepared at various mole ratio of ZnO:APTES at pH 12

Mole ratio of ZnO:APTES	Elemental Analysis			Fourier Transform Infrared Spectroscopy		
	Carbon (%)	Hydrogen (%)	Nitrogen (%)	N-H stretching	C-H stretching	Si-O-Zn stretching
1 : 0	0	0	0	-	-	-
1 : 0.1	1.1413	0.16855	-004144	-	-	1019 ^a
1 : 0.5	8.8993	2.4691	3.1064	3428, 3265	2925	1006
1 : 1	9.4540	2.6487	3.5290	3268	2929	991
1 : 2	11.687	3.3014	4.3634	3308	2930	994

^avery weak intensity.

The results from the elemental analysis as shown in table 2 show the percentage of nitrogen in the ZMAS was related to amount of silane which came from the increasing concentration of APTES. The IR spectra of All ZMAS products also showed the Si-O-Zn stretching at about 1000 cm^{-1} and only when the mole ratio of ZnO:APTES equal was 1:0.1 the very weak intensity peak was observed. As shown in Figure 4, the photodegradation property of ZMAS prepared at mole ratio of ZnO:APTES various from 1:0.5 to 1:2 with BB41 was retarded when compared with the commercial ZnO but not the ZMAS prepared at mole ratio of ZnO:APTES equal as 1:0.1. As shown in Figure 5, the coating of amino silane on ZnO surface did not have much effect on the band gap of ZnO. The absorption edge of ZMAS was only slightly shifted from 392 to 397 nm. Therefore, ZMAS still has UV absorber property.

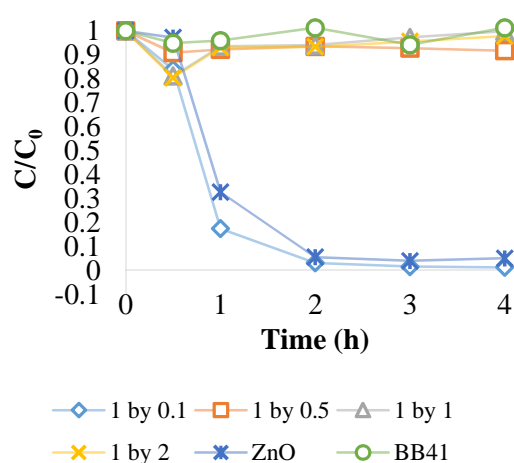


Figure 4. The photodegradation of BB41 under UV irradiation for 4 hours by ZMAS prepared at various mole ratio of ZnO:APTES.

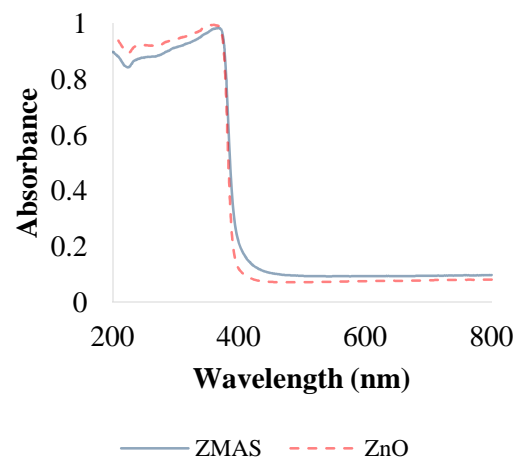


Figure 5. DRS- UV-visible spectra of the ZMAS and ZnO.

4. Conclusion

The suitable condition to prepare ZnO modified surface by amino silane (ZMAS) is at pH 12 with the mole ratio of ZnO:APTES as 1:0.5. The prepared ZMAS can still absorb UV light and can retard the photocatalytic efficiency of ZnO towards BB41. The prepared ZMAS may possible to be used as dye stabilizer for the textile industry.

5. References

- [1] Insaf A, Yasmine S, Ines J, Francisco P and Wissem M 2016 *J. Dev. Drugs* **5**.
- [2] Woo K K, Ngou F H, Ngo L S, Soong W K and Tang P Y 2011 *Am. J. Food Technol.* **6**(2) 140-8.
- [3] Grasset F, Saito N, Li D, Park D, Sakaguchi I, Ohashi N, Haneda H, Roisnel T, Mornet S and Duguet E 2003 *Food Chem.* **360** 298-311.
- [4] Kosmulski M 2009 *J. Colloid Interface Sci.* **337** 439-48.
- [5] Farzi G A, Tayeb R and Naghibinasab S 2015 *Int. J. Nano Dimens.* **6**(1) 67-75.

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