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To cite this article: S. P. Prakoso *et al* 2016 *J. Phys.: Conf. Ser.* **776** 012051

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The influence of narrow optical gap silver oxide on zinc oxide nanoparticles produced by microwave-assisted colloidal synthesis: photocatalytic studies

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Abstract. This paper reports a photocatalytic study on wide band gap zinc oxide (ZnO) incorporated by narrow band gap silver oxide (Ag₂O), namely Ag₂O/ZnO nanocomposites, which were prepared by colloidal synthesis with microwave supports. The Ag₂O/ZnO nanocomposites were prepared with three different molar ratios (MR) of Ag₂O to ZnO (MR: 0.25, 0.5 and 0.75). In order to confirm qualitatively the concentration ratio of Ag₂O in ZnO, crystal phase intensity ratio was executed by peak indexing from x-ray diffraction. The Ag₂O/ZnO nanocomposites properties were further investigated using diffuse reflectance spectroscopy. The nanocomposites were tested for the degradation of organic dyes solutions under visible and UV light irradiations. The photocatalytic activity of Ag₂O/ZnO nanocomposites under visible light increased with increasing molar ratio of Ag₂O to ZnO, while the opposite trends observed under UV light irradiation. The improvement of photo-absorption together with photocatalytic activities might be suspected due to the p-n heterojunction structure in Ag₂O/ZnO nanocomposites. The corresponding mechanism will be discussed in detail.

1. Introduction

In deteriorating water pollutants like organic dyes from waste water of textile industries, researchers have been attempting to find a way by photodegradation process. Photocatalysts in this process are assisting in disintegrating heavy and harmful organic molecules into environment friendly and harmless species. By the aid of oxide semiconductor as a photocatalyst, radical groups ($\cdot\text{OH}$ and O_2^-) that are produced by photogenerated electron-hole pairs attack the organic pollutants [1]–[3]. Hence, oxide semiconductors are deemed as a suitable material for photocatalyst owing to their optical gap energies in absorbing photon energy.

Light absorption efficiency rather depends on electronic structure of its semiconductors which is correlated to the band gap energy (E_g). Some interesting facts from oxide semiconductors, its E_g could be tailored in several ways as follows: doping [4], compositing [5], thermal treatment [6], plasma treatment [7], and so on. Composites are the simple one from synthesis point of view among of aforementioned. Moreover, composites are consisted of two or more compounds mixed together in



certain comparable amounts for every composer. Thus, normally composites exhibit their combination properties instead of the enhancement from one composer. In regards with the improvement of light absorption for photocatalyst, the unification within wide and narrow band gap oxide semiconductor is a quite strategy. A well-known n-type oxide semiconductor and having wide band gap about 3.3 eV [8] named zinc oxide (ZnO) is widely deployed in the diverse applications. Nevertheless, due to its wide optical gap property, the range of photon energies that could be promoting photogeneration of electron-hole pairs is limited to nearly around UV area. Despite of the broad wavelength that provided from solar spectrum, only small part could be absorbed by ZnO. Therefore, the presence of narrow band gap oxide semiconductors i.e. silver oxide (Ag_2O) might be broadens the light absorption up to the visible region. Ag_2O is possessing an optical gap about 1.4 eV and constitute of hole carrier which is remarkably compatible with ZnO whether as a composite or to form the p-n junction [1], [9]–[11]. In addition, the photogeneration of electron-hole pairs usually come along with annihilation process. This recombination is principally declining photocatalytic activities as well as reducing the production of radical groups. The structure of p-n junction is one of many options to overcome the recombination issue that has been reported recently. Photodegradation rate of ZnO/ Ag_2O heterostructures obtained by photochemical synthesis had been showing 27.4 and 15.6 times faster than pure ZnO under UV and visible irradiation, respectively [10]. Whereas, Kadam et al. [11] had been presenting similar results for higher photodegradation rate of ZnO/ Ag_2O nanocomposites towards methyl orange as attained by precipitation method. Yet, the photocatalytic studies of Ag_2O /ZnO produced by colloidal synthesis with aid of microwave in one-pot are scantily available and constitute a facile way to obtain nanoparticles. Photocatalytic activities of Ag_2O /ZnO nanocomposites with various ratio of Ag_2O to ZnO were performed in this study. UV and visible light were utilized in photodegradation performance to reduce the concentration of methylene blue in water. Furthermore, characterizations of Ag_2O /ZnO nanocomposites had been done to support the exhibition of photocatalytic improvement.

2. Experimental section

2.1. Synthesis and characterizations of Ag_2O /ZnO nanocomposites

All of precursors were used directly as received without any further purification. In proper chemical reaction, a certain amount of mineral salts (AgNO_3 and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were mixed in 200 ml distilled water. Sodium dodecyl sulphate (SDS) was incorporated into the solution as a stabilizing agent in 1:1 ratio to the mineral ions. This mixed-solution then stirred for 10 min to saturate the reaction. Afterward, the mixed-solution was heated-up through microwave heating with irradiation power of 800 W for 90 s. The precipitate then washed three times with distilled water and alcohol to remove the unwanted reaction products. The sample powders were acquired by drying the precipitate at temperature $\sim 120^\circ\text{C}$ for 5 hours in vacuum. In order to confirm qualitatively the concentration ratio of Ag_2O in ZnO, crystal phase intensity ratio was executed by peak indexing from x-ray diffraction. The Ag_2O /ZnO nanocomposite properties were further investigated using diffuse reflectance spectroscopy.

2.2. Photocatalytic experiments

Nano-hybrid Ag_2O /Ag catalysts were implemented to degrade methylene blue (MB) which is chosen as a model of organic pollutant in water. Such a 0.03 g of Ag_2O /Ag sample with different silver contents was dispersed in 100 ml MB solution ($20 \text{ mg}\cdot\text{L}^{-1}$) under constant pH of 13. Prior to the illumination, the suspensions of Ag_2O /Ag photocatalysts in the MB solution were magnetically stirred in the dark chamber for 30 min to assure the steady state of adsorption/desorption MB on the surface of catalyst particles. After that, the mixtures were illuminated by visible-light with power of 40 W for 120 min long. The sampling process was taken for every 15 min and the degraded MB solutions were centrifuged to separate the catalyst. The quantitative analysis of MB in the degraded MB solutions was evaluated by UV-Vis spectrophotometer (Hitachi UH5300) which is recorded the absorption spectrum in the range of 450 – 750 nm.

3. Results and discussion

The transformation of XRD spectra from hexagonal wurtzite-ZnO to cubic-Ag₂O with an addition of MR percentage is obviously observed in Figure 1. At 0%, diffraction pattern can be indexed merely pure ZnO phase which has three main peaks at 2θ of 31.7°, 34.3°, and 36.1° in accordance with hkl indices Miller plane of (100), (002), and (101) wurtzite structure [8], respectively. As the Ag₂O was introduced to the ZnO, intensively crystallographic planes of (111) and (200) cubic-Ag₂O phase begin to appear at 2θ of 32.8° and 38.2° [10], [11], respectively. In addition, either relative intensity or integrated area, they show an opposite trend following the MR percentages of Ag₂O to ZnO (see Table 1 and Table 2). It is indicating quite-well proportionality of molar ratio percentages with the yielded products of Ag₂O/ZnO nanocomposites by one-pot process in this study.

Figure 2 shows the optical reflectance characteristics of Ag₂O/ZnO nanocomposites with various percentages. A contrast trend among pure Ag₂O ($x = 100\%$) and pure ZnO ($x = 0\%$) is shown according to the recorded lowest and highest reflectance of 12.3% and 26% at 800 nm, respectively. The observable abrupt transition ca. 375 nm for Ag₂O/ZnO of 0% to 75% is owing to the excitation in ZnO region as well-known as ZnO has a wide band gap energy [8]. On the higher wavelength range for Ag₂O/ZnO of 25% to 100%, gradual increment was seen. Ag₂O was probably responsible for this transition due to its narrow window gap [9]. Both transition are obviously observed after deploying Kubelka-Munk function [8] as represented on inset Figure 2. Interestingly, those two stages were taken place solely on nanocomposites of 25% to 75%. As can be expected from nanocomposites which the Ag₂O and ZnO are resided as revealed from diffraction patterns (see Figure 1). Moreover, an increase of percentages, lower energy transition was blueshifted (1.34 eV to 1.71 eV) while higher energy transition redshifted (3.24 eV to 3.14 eV). Thus, an emerging of Ag₂O into ZnO gave some affections to their optical properties as demonstrated in Figure 2 and structural properties as listed in Table 1.

Figure 3 displays the photocatalytic activities toward methylene blue for different MRs of photocatalyst nanocomposites during exposure to (a) UV- and (b) visible-light at a given period. The maximum photodegradation rate under UV- and visible-light irradiation could be noticed for MR of 25% and 75%, respectively. Indeed, those photocatalysts showed exceptional performance for each UV- and visible-light irradiation. However, the photocatalyst nanocomposite with MR of 50% exhibits quite-well performance in both UV- and visible-light exposure. Pure ZnO (0%) and Ag₂O (100%) had

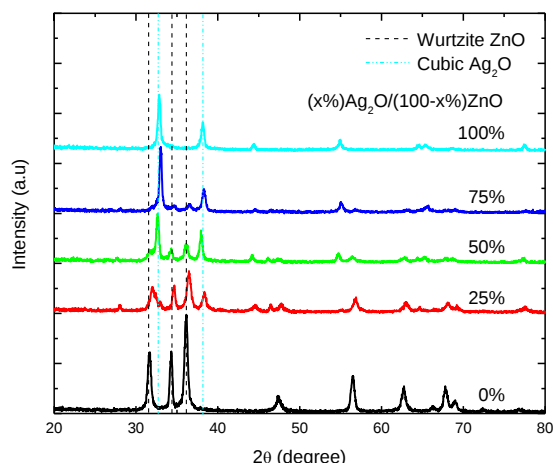


Figure 1. X-ray diffraction patterns from Ag₂O/ZnO nanoparticles with different composition percentages.

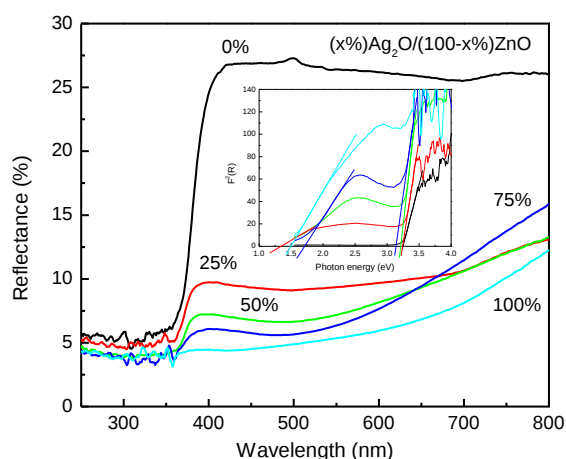


Figure 2. UV-Vis diffuse reflectance of Ag₂O/ZnO nanocomposites with various percentages (inset: Kubelka-Munk function).

Table 1. Crystal properties of ZnO in Ag₂O/ZnO nanocomposites.

Ag ₂ O (x%) ZnO (100%-x)	Cry. Phase (ZnO)	Crystal Properties				
		<D> (nm)	Rel. Intens (%)	Center (°)	FWHM (°)	Int. Area (%)
0%	(100)	22.8	27.79	31.65	0.482	28.79
	(002)	30.8	26.13	34.3	0.39	21.89
	(101)	22.1	46.08	36.13	0.498	49.31
25%	(100)	12.3	21.47	32.03	0.792	24.62
	(002)	21.5	21.74	34.63	0.507	15.98
	(101)	14.2	35.07	36.47	0.708	35.94
50%	(100)	8.5	9.57	31.97	1.094	19.38
	(002)	13.3	8.69	34.25	0.747	12.01
	(101)	16.1	15.31	36.14	0.638	18.09
75%	(100)	11.3	4.18	32.02	0.855	8.05
	(002)	14.5	5.38	34.65	0.694	8.4
	(101)	15.8	7.29	36.5	0.65	10.66
100%	(100)	-	-	-	-	-
	(002)	-	-	-	-	-
	(101)	-	-	-	-	-

Table 2. Crystal properties of Ag₂O in Ag₂O/ZnO nanocomposites.

Ag ₂ O (x%) ZnO (100%-x)	Cry. Phase (Ag ₂ O)	Crystal Properties				
		<D> (nm)	Rel. Intens (%)	Center (°)	FWHM (°)	Int. Area (%)
0%	(111)	-	-	-	-	-
	(200)	-	-	-	-	-
25%	(111)	13.9	6.4	32.83	0.716	6.64
	(200)	13.2	15.32	38.34	0.758	16.82
50%	(111)	31.4	41.03	32.66	0.384	29.17
	(200)	25.2	25.4	37.95	0.454	21.35
75%	(111)	37.9	62.26	33.01	0.339	47.47
	(200)	20	20.9	38.3	0.54	25.41
100%	(111)	25.8	67.85	32.84	0.441	67.04
	(200)	24.9	32.15	38.15	0.458	32.96

slightly lower photocatalytic activities than nanocomposite of 50% under UV- and visible-light, respectively. Nevertheless, they showed the worst photodegradation under reversely light source in accordance with their working optical gap energies. Optical studies in Figure 2 corroborated the efficiency of photocatalytic activities in Figure 3 as well as its photoabsorption. Concisely, wide wavelength optical absorption was achieved by photocatalyst Ag₂O/ZnO with MR of 50% as unveiled in Figure 3.

The photodegradation rate enhancement on Ag₂O/ZnO nanocomposites might be attributed to the p-n heterojunction structure that formed between p-type Ag₂O to n-type ZnO [10], [11]. A simple schematic energy band diagram for isolated p-Ag₂O and n-ZnO is depicted in Figure 4a. The appropriate light source is exciting electrons at valence band (VB) edge to the conduction band (CB) and created electron-hole pairs. And so does to the spontaneous recombination was taken place after illuminating source is shut-off. On the other hand, in case the p-n heterojunction is formed (see Figure 4b), it will cause to the band alignment of Fermi level energy due to the charge balance [12]. The energy band at p-Ag₂O site then bended upwards and at n-ZnO site tends to downward after the equilibrium state accomplished. Upon the photocatalytic activities under UV-light irradiation, ZnO

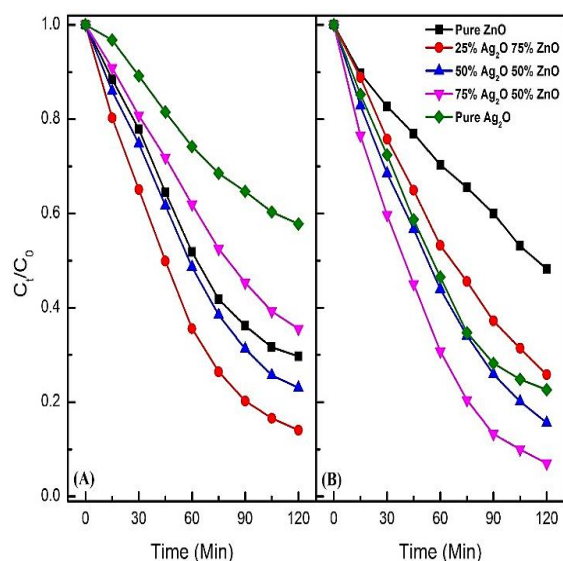


Figure 3. Photocatalysts performance in the reduction of methylene blue during exposure to p-Ag₂O/n-ZnO heterojunction in case of (A) (a) UV- and (b) visible-light.

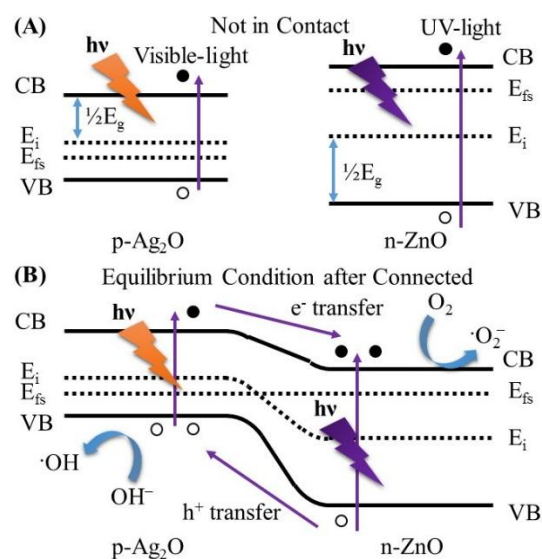


Figure 4. Schematic energy band diagrams of p-Ag₂O/n-ZnO heterojunction in case of (A) isolated p-Ag₂O and n-ZnO and (B) when p-Ag₂O/n-ZnO heterojunction established.

tends to absorb more photon energy rather than Ag₂O. The photogenerated electrons from ZnO site are preserved in CB while the photogenerated holes migrated to the VB of Ag₂O site since lower energy barrier exists within the depletion layer [10], [11], [13]. Therefore, the prolonged charge separation could be effectively improved by p-n heterojunction and lead to the enhancement of photocatalytic activities. Similar photogenerated carrier transport mechanism is happened in case the photocatalytic activities work under visible-light illumination as described in Figure 4b. In this case, the electron-hole pairs are generated dominantly in Ag₂O site. Excited electrons from Ag₂O are transferred to the CB of ZnO and the remained holes are left in VB of Ag₂O that later on can be reacted directly to the organic dyes or water molecules

4. Conclusion

The photocatalyst of Ag₂O/ZnO nanocomposites was successfully prepared by microwave-assisted colloidal synthesis. XRD results described the incorporation of Ag₂O in ZnO as followed by an increase of MR. Optical reflectance studied the influence of Ag₂O incorporation in ZnO. It showed the photo-absorption improved from visible to UV ranges. The photocatalytic activities of Ag₂O/ZnO nanocomposites under visible-light increased with increasing MR of Ag₂O to ZnO, while the opposite trends observed under UV light irradiation. Overall, the photocatalytic efficiency of Ag₂O/ZnO nanocomposites under UV- and visible-light irradiation is better than those of bare-Ag₂O as well as bare-ZnO due to p-n heterojunction structure well-formed in Ag₂O/ZnO nanocomposites.

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