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 (·OH and O₂⁻) 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 (Eg). Some interesting facts from oxide semiconductors, its Eg 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$_2$O) might be broadens the light absorption up to the visible region. Ag$_2$O 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$_2$O 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$_2$O nanocomposites towards methyl orange as attained by precipitation method. Yet, the photocatalytic studies of Ag$_2$O/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$_2$O/ZnO nanocomposites with various ratio of Ag$_2$O 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$_2$O/ZnO nanocomposites had been done to support the exhibition of photocatalytic improvement.

2. Experimental section

2.1. Synthesis and characterizations of Ag$_2$O/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 ZnSO$_4$.7H$_2$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 ~ 120°C for 5 hours in vacuum. In order to confirm qualitatively the concentration ratio of Ag$_2$O in ZnO, crystal phase intensity ratio was executed by peak indexing from x-ray diffraction. The Ag$_2$O/ZnO nanocomposite properties were further investigated using diffuse reflectance spectroscopy.

2.2. Photocatalytic experiments

Nano-hybrid Ag$_2$O/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$_2$O/Ag sample with different silver contents was dispersed in 100 ml MB solution (20 mg-L$^{-1}$) under constant pH of 13. Prior to the illumination, the suspensions of Ag$_2$O/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-Ag$_2$O 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 $2\theta$ 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 Ag$_2$O was introduced to the ZnO, intensively crystallographic planes of (111) and (200) cubic-Ag$_2$O phase begin to appear at $2\theta$ 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 Ag$_2$O to ZnO (see Table 1 and Table 2). It is indicating quite-well proportionality of molar ratio percentages with the yielded products of Ag$_2$O/ZnO nanocomposites by one-pot process in this study.

Figure 2 shows the optical reflectance characteristics of Ag$_2$O/ZnO nanocomposites with various percentages. A contrast trend among pure Ag$_2$O (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 Ag$_2$O/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 Ag$_2$O/ZnO of 25% to 100%, gradual increment was seen. Ag$_2$O 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 Ag$_2$O 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 Ag$_2$O 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 Ag$_2$O (100%) had
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 Ag$_2$O/ZnO with MR of 50% as unveiled in Figure 3.

The photodegradation rate enhancement on Ag$_2$O/ZnO nanocomposites might be attributed to the p-n heterojunction structure that formed between p-type Ag$_2$O to n-type ZnO [10], [11]. A simple schematic energy band diagram for isolated p-Ag$_2$O 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-Ag$_2$O 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

Table 1. Crystal properties of ZnO in Ag$_2$O/ZnO nanocomposites.

| Ag$_2$O (x%) | Cry. Phase (ZnO) | <D> (nm) | Rel. Intens (%) | Center (˚) | FWHM (˚) | Int. Area (%) |
|--------------|-----------------|----------|----------------|------------|----------|----------------|
| ZnO (100%–x) | (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          |
|              | (100)           | 12.3     | 21.47          | 32.03      | 0.792    | 24.62          |
| 25%          | (002)           | 21.5     | 21.74          | 34.63      | 0.507    | 15.98          |
|              | (101)           | 14.2     | 35.07          | 36.47      | 0.708    | 35.94          |
|              | (100)           | 8.5      | 9.57           | 31.97      | 1.094    | 19.38          |
| 50%          | (002)           | 13.3     | 8.69           | 34.25      | 0.747    | 12.01          |
|              | (101)           | 16.1     | 15.31          | 36.14      | 0.638    | 18.09          |
|              | (100)           | 11.3     | 4.18           | 32.02      | 0.855    | 8.05           |
| 75%          | (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 Ag$_2$O in Ag$_2$O/ZnO nanocomposites.

| Ag$_2$O (x%) | Cry. Phase (Ag$_2$O) | <D> (nm) | Rel. Intens (%) | Center (˚) | FWHM (˚) | Int. Area (%) |
|--------------|----------------------|----------|----------------|------------|----------|----------------|
| ZnO (100%–x) | (111)                | -        | -              | -          | -        | -              |
|              | (200)                | -        | -              | -          | -        | -              |
| 0%           | (111)                | 13.9     | 6.4            | 32.83      | 0.716    | 6.64           |
|              | (200)                | 13.2     | 15.32          | 38.34      | 0.758    | 16.82          |
| 25%          | (111)                | 31.4     | 41.03          | 32.66      | 0.384    | 29.17          |
|              | (200)                | 25.2     | 25.4           | 37.95      | 0.454    | 21.35          |
| 50%          | (111)                | 37.9     | 62.26          | 33.01      | 0.339    | 47.47          |
|              | (200)                | 20       | 20.9           | 38.3       | 0.54     | 25.41          |
| 75%          | (111)                | 25.8     | 67.85          | 32.84      | 0.441    | 67.04          |
|              | (200)                | 24.9     | 32.15          | 38.15      | 0.458    | 32.96          |

The photodegradation rate enhancement on Ag$_2$O/ZnO nanocomposites might be attributed to the p-n heterojunction structure that formed between p-type Ag$_2$O to n-type ZnO [10], [11]. A simple schematic energy band diagram for isolated p-Ag$_2$O 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-Ag$_2$O 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
tends to absorb more photon energy rather than Ag$_2$O. The photogenerated electrons from ZnO site are preserved in CB while the photogenerated holes migrated to the VB of Ag$_2$O 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 Ag$_2$O site. Excited electrons from Ag$_2$O are transferred to the CB of ZnO and the remained holes are left in VB of Ag$_2$O that later on can be reacted directly to the organic dyes or water molecules.

4. Conclusion

The photocatalyst of Ag$_2$O/ZnO nanocomposites was successfully prepared by microwave-assisted colloidal synthesis. XRD results described the incorporation of Ag$_2$O in ZnO as followed by an increase of MR. Optical reflectance studied the influence of Ag$_2$O incorporation in ZnO. It showed the photo-absorption improved from visible to UV ranges. The photocatalytic activities of Ag$_2$O/ZnO nanocomposites under visible-light increased with increasing MR of Ag$_2$O to ZnO, while the opposite trends observed under UV light irradiation. Overall, the photocatalytic efficiency of Ag$_2$O/ZnO nanocomposites under UV- and visible-light irradiation is better than those of bare-Ag$_2$O as well as bare-ZnO due to p-n heterojunction structure well-formed in Ag$_2$O/ZnO nanocomposites.

5. References

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