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PREPARATION AND CHARACTERIZATION OF Ag NANOPARTICLES DECORATED WITH ZnO MICROSTRUCTURES FOR THE CATALYTIC PHOTODEGRADATION OF METHYLENE BLUE DYE UNDER UV LIGHT IRRADIATION

(Penyediaan dan Pencirian Ag Berstruktur Nanopartikel Diubuahsuai dengan ZnO Berstruktur Mikro untuk Penurunan Fotokatalisis Pewarna Metilena Biru di bawah Sinar UV)

Hartini Ahmad Rafaie[1]*, Nur Azmina Mohemaed Safian[2], Roslan Md Nor[2], Yusof Mohd Amin[2]

[1]*Faculty of Applied Sciences,*
Universiti Teknologi MARA Pahang, 26400 Bandar Tun Abdul Razak Jengka, Pahang,Malaysia
[2]*Physics Department, Faculty of Science,*
Universiti Malaya, 50603 Kuala Lumpur, Malaysia

**Corresponding author: hartinirafaie@pahang.uitm.edu.my*

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Abstract

Ag nanoparticles (AgNPs) decorated with ZnO microstructures was prepared by sol-gel method at different Ag concentration. The structures, composition and morphology of the samples were characterized by X-ray diffraction (XRD), electron dispersive X-ray spectroscopy (EDS) and field emission scanning electron microscope (FESEM). FESEM images shows that the samples were composed of Ag and ZnO with the particles size ranging from 100 to 500 nm. EDS analysis confirmed that atomic % increases as higher molar concentration applied with value of 5.6 at.% and 16.1 at.% for sample 0.05M and 0.1M AgNPs decorated ZnO microstructures. Methylene blue (MB) dye was used as a representative of dye pollutant to conduct the catalytic photodegradation activity. The AgNPs decorated with ZnO particles exhibited a better photocatalytic activity than the pure ZnO particles. The results show that an increasing of photodegradation rate constant, *k* was obtained when higher concentration of Ag was applied to the ZnO with value of 0.016, 0.026 and 0.032 min^{-1} for pure ZnO, 0.05M AgZnO and 0.1M AgZnO nanoparticles, respectively. The increased of *k* value in the presence of Ag was due to the prolonged lifetime of the photogenerated electron hole pairs in ZnO as a result of Ag nanoparticles acting as electron sink.

Keywords: Ag nanoparticles, zink oksida, sol-gel, photodegradation, methylene blue

Abstrak

Ag berstruktur nanopartikel (AgNPs) diubahsuai dengan ZnO berstruktur mikro pada kepekatan berbeza telah dibuat menggunakan teknik sol-gel. Sifat-sifat struktur, komposisi dan morfologi sampel diperincikan menggunakan pembelauan sinar-X (XRD), spektroskopi Sinar-X sebaran elektron (EDS) dan mikroskop elektron pancaran medan (FESEM). Analisis FESEM menunjukkan sampel terdiri daripada Ag dan ZnO yang mempunyai saiz partikel antara 100 – 500 nm. Analisis EDS pula membuktikan bahawa peratusan atomik meningkat apabila kepekatan Ag yang lebih tinggi digunakan dengan nilai 5.6 at.% dan 16.1 at.% bagi sampel 0.05 M dan 0.1 M ZnO berstruktur mikro diubahsuai dengan Ag berstruktur nanopartikel. Pewarna metilena biru (MB) digunakan sebagai contoh pencemaran warna untuk mengkaji aktiviti penurunan foto pemangkin. ZnO berstruktur mikro diubahsuai dengan Ag berstruktur nanopartikel menunjukkan aktiviti penurunan foto yang lebih baik daripada ZnO tulen. Keputusan menunjukkan bahawa peningkatan dalam pemalar kadar penurunan foto, *k* diperoleh apabila kepekatan Ag lebih tinggi digunakan pada ZnO dengan nilai 0.016, 0.026 dan 0.032 min^{-1} untuk ZnO tulen, 0.05 M dan 0.01 M ZnO berstruktur mikro diubahsuai dengan Ag berstruktur nanopartikel. Peningkatan nilai *k* dengan kehadiran Ag disebabkan oleh jangka hayat berpanjangan penghasilan foto oleh pasangan lubang dan elektron di ZnO hasil daripada Ag nanopartikel yang bertindak sebagai penerima elektron.

Kata kunci: Ag berstruktur nanopartikel, zink oksida, sol-gel, penurunan foto, metilena biru

Introduction

Recently, Zinc Oxide (ZnO) has been widely investigated as one of the important material for photocatalytic applications due to its large initial rates of activities and having active sites with higher surface reactivity [1]. Combined with the advantages of non-toxicity, high sensitivity, stability, cost effective and environmental safety, ZnO has become a potential photocatalyst for remediation of environmental problem [2]. It is reported that, ZnO photocatalyst also presents some challenges such as fast recombination rate of the photogenerated electron-hole pair and low quantum efficiency, which resulting low photocatalytic efficiency reaction in the system [3, 4]. Therefore, in order to improve the photocatalytic activities, researchers have been found that doping is one of the alternative ways to improve the photocatalytic properties. For instance, Changle Wu et al. reported that Cu doped ZnO can enhance the photocatalytic efficiency of ZnO under visible light irradiation [5], and Jing Zhao et al. reported that Ni-doped ZnO nanorod exhibited higher photocatalytic activity than un-doped ZnO [6]. Incorporating and modifying silver in ZnO have been attract much interest in photocatalytic application due to more effective electron–hole separation of the Ag/ZnO composite and Ag will increase the electron transfer process [7 – 9]. In this work, the photocatalytic activities of the pure ZnO and AgNPs decorated microstructured ZnO act as photocatalyst prepared by sol-gel method were studied by the degradation of methylene blue (MB) under ultraviolet irradiation.

Materials and Methods

Synthesis of the photocatalyst

ZnO and Silver nitrate ($AgNO_3$) were used as the starting materials for the synthesis of AgNPs decorated with ZnO microstructures by sol-gel method. Methylene blue dye (MB) was used as a representative organic pollutant in water. All materials used were of analytical grade and were used without any further purification. The stock solution was prepared by dissolved 5 g of ZnO powder that mixed with $AgNO_3$ and HMTA at 0.05 M and 0.1 M concentration in 100 ml of deionized water. The stock solution was then heated at 95 °C for 6 hours. After completion, the obtained white-greyish precipitates were rinsed repeatedly with deionized water and finally dried at 300 °C for 2 hours.

Characterization methods

The structural properties of the prepared samples of AgNPs decorated with ZnO microstructures were characterized by X-ray diffraction (XRD) recorded by PANalytical diffractometer using Cu Kα (λ = 1.5406 Å), while the surface morphology of the samples was studied using field emission scanning electron microscope (FESEM). The composition analysis was performed by electron dispersive X-ray spectroscopy (EDS) attached to the FESEM. The optical absorbance properties of the catalyst were characterized by UV–Vis spectrophotometer.

Photocatalytic measurement

The photocatalytic activities of the samples were carried out by monitoring the photocatalytic degradation of MB dye in aqueous solution. 30 mg of pure ZnO, 0.05M and 0.1M AgNPs decorated microstructures ZnO act as a catalyst were placed into a beaker containing 10 mg/L MB dye solution. Prior to the irradiation, the mixture was stirred in the dark for 30 minutes to establish an adsorption/ desorption equilibrium. The solution then was irradiated under ultraviolet (UV) light (main wavelength: 254 nm). After irradiating for 10, 20, 30, 40, 50 and 60 minutes, a certain amount of solutions was collected and the concentration of residual MB was determined by the absorption of the reaction solution at the characteristic absorption wavelength 664 nm using UV–visible spectrophotometer.

Results and Discussion

Figure 1 shows the FESEM images of (a) pure ZnO, (b) 0.05 M AgNPs decorated microstructures ZnO, (c) 0.1 M AgNPs decorated microstructures ZnO and (d) the EDS spectra of selected area of all samples. The images clearly revealed that all samples composed of rod-like and cubic-like particles with average size about 100 - 500 nm. In addition, the morphology and size of the photocatalyst do not show significant changes when Ag was introduced.

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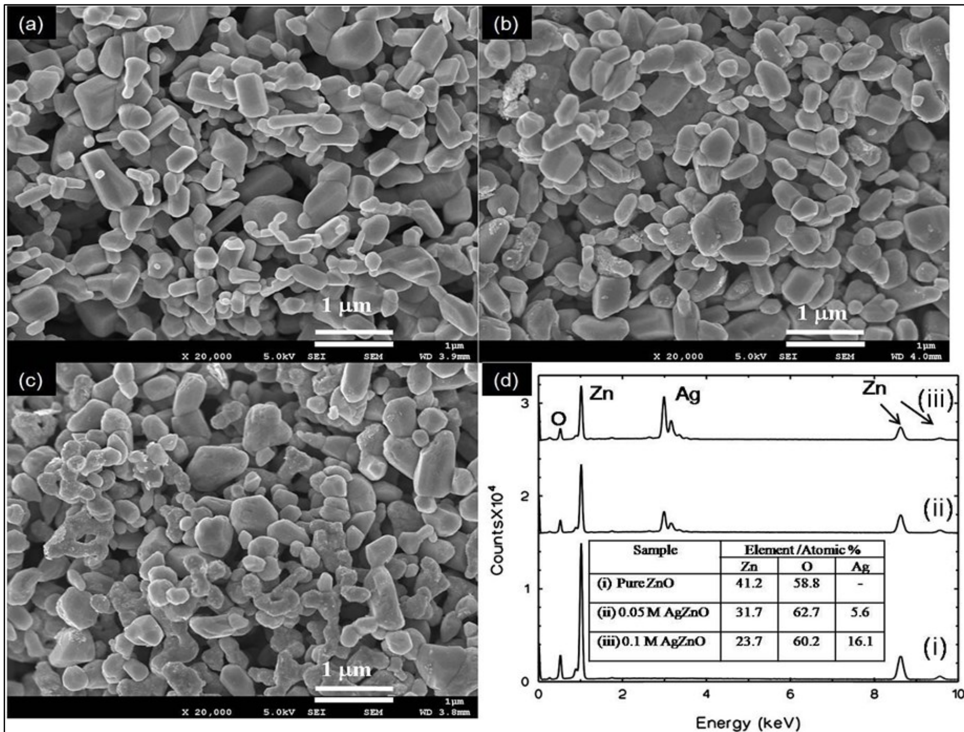

Figure 1. FESEM images of (a) pure ZnO, (b) 0.05M AgNPs decorated microstructures ZnO, (c) 0.1M AgNPs decorated microstructures ZnO and (d) the corresponding EDS analysis

However, from the EDS analysis confirmed that Ag element was detected in sample AgNPs decorated microstructures ZnO, shown in Figure 1 (b) and (c), respectively. As can be seen from the EDS graph, Ag was incorporated in the samples and the atomic percentage of Ag increased as higher concentration was applied with value of 5.6 at.% and 16.1 at.% for sample 0.05 M and 0.1 M AgNPs decorated microstructures ZnO. Besides, there was no other impurities was detected as EDS analysis of the sample only composed the element of Zn, O, and Ag.

Figure 2 shows the normalized XRD patterns for (a) pure ZnO, (b) 0.05 M AgNPs decorated microstructures ZnO and (c) 0.1 M AgNPs decorated microstructures ZnO. All the diffraction peaks are corresponding to the hexagonal wurtzite ZnO and cubic metallic Ag crystal structure (labelled as * in the graph) respectively. No other peak was detected and there was no significant shift for all diffraction peaks indicating that the silver did not substitutes for Zn^{2+} or interstitial atom [9] and suggested that the silver just decorated on the surface [10].

The photocatalytic degradation of the pure ZnO and AgNPs decorated microstructures ZnO in MB dye solution is shown in Figure 3 (a) – (d). From the time dependent absorbance spectra, the absorbance peak at 664 nm was reduced significantly, indicating the degradation of the dye molecule. It can be seen from Figure 3, AgNPs decorated microstructures ZnO showed a remarkable enhancement of photocatalytic activity compared with pure ZnO particles. Moreover, 0.1 M AgNPs decorated microstructures ZnO show the highest catalytic activity compared to 0.05 M AgNPs decorated microstructures ZnO and pure ZnO particles. The photocatalytic degradation of MB can be described to a linear pattern using pseudo-first kinetics model as stated in Equation (1):

$$\ln(C/C_0) = -kt \tag{1}$$

where k is the degradation rate constant, C_0 and C are the MB initial concentration and the concentration of solution after the degradation time of t, respectively.

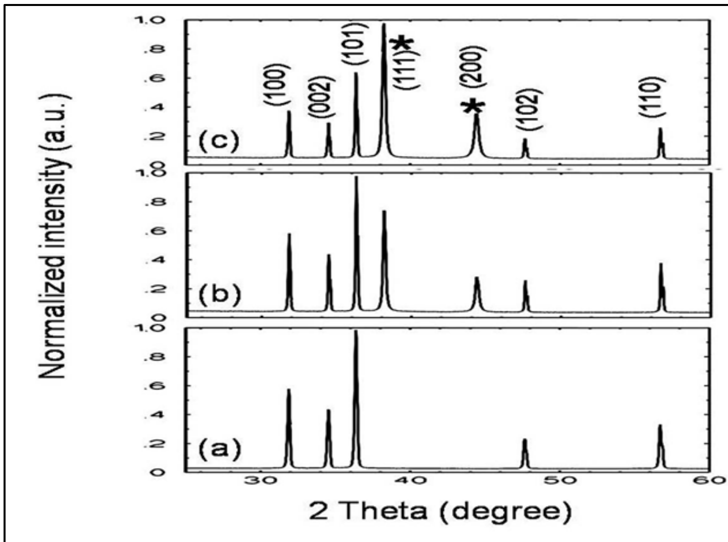

Figure 2. Normalized XRD patterns of the (a) pure ZnO, (b) 0.05M AgNPs decorated microstructures ZnO and (c) 0.1M AgNPs decorated microstructures ZnO, (Ag labelled as * in the graph)

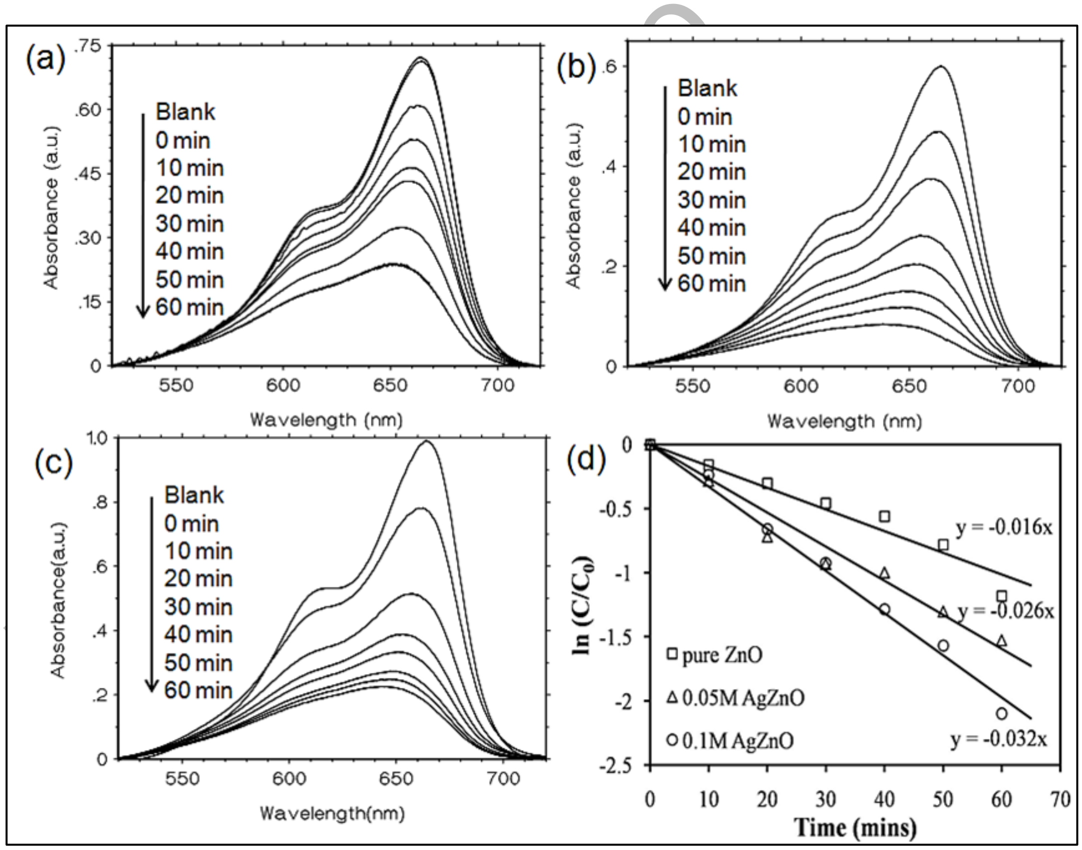

Figure 3. UV-Vis absorption spectral changes of MB under UV light irradiation by (a) pure ZnO, (b) 0.05M AgNPs decorated microstructures ZnO, (c) 0.1 M AgNPs decorated microstructures ZnO and (d) MB photodegradation curves of ln C/C_0 versus time for all photocatalyst

The obtained results are shown in Figure 3(d) where the photodegradation rate constant, *k* of different photocatalyst were 0.016, 0.026 and 0.032 min^{-1} for pure ZnO, 0.05 M and 0.1 M AgNPs decorated microstructures ZnO, respectively. Therefore, it can be seen that the photocatalytic activities efficiency of MB molecules increases in the following order: pure ZnO < 0.05 M AgNPs decorated microstructures ZnO < 0.1 M AgNPs decorated microstructures ZnO. In addition, the results showed that MB solution greatly degrade in the presence of AgNPs decorated microstructures ZnO and the rate constant is much higher using 0.1M AgNPs decorated microstructures ZnO. This significant effect of AgNPs decorated microstructures ZnO is possibly due to the efficient charge electron-hole separation of Ag and ZnO [11 – 13].

Generally, on semiconductor surface Ag having a characteristic like an electron sinks, which provide sites for the accumulation of photogenerated electrons, and then improve the separation of photogenerated electrons and holes [13, 14]. In addition, the electron pairs lifetime can be prolong and thus can enhance the photocatalytic activity of AgZnO photocatalyst [11]. Other than that, higher dispersity of Ag particles on the ZnO surfaces also gives higher photocatalytic activity of AgNPs decorated microstructures ZnO. Ag particles have a higher Fermi energy level compared to ZnO, caused a movement of electrons from Ag to the conduction band (CB) of ZnO in order to achieve Fermi energy level equilibrium (E_f).

Conclusion

The AgNPs decorated microstructures ZnO were successfully prepared by sol-gel method. After comparison with pure ZnO particles, AgNPs decorated microstructures ZnO exhibited better photocatalytic activity with photodegradation rate constant, *k* value of 0.016, 0.026 and 0.032 min^{-1} for pure ZnO, 0.05 M and 0.1M AgNPs decorated microstructures ZnO, respectively. The enhance performance of AgNPs decorated microstructures ZnO shows that it can be used as an alternative photocatalyst for remediation of environmental problem.

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