Manipulation of surface morphology of flower-like Ag/ZnO nanorods to enhance photocatalytic performance

Kasira U-thaipan and Karaked Tedsree

Faculty of Science, Department of Chemistry, Nanocatalysis Laboratory, Burapha University, Chonburi 20131, Thailand

E-mail: karaked@go.buu.ac.th

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Abstract

The surface morphology of flower-like Ag/ZnO nanorod can be manipulated by adopting different synthetic routes and also loading different levels of Ag in order to alter their surface structures to achieve the maximum photocatalytic efficiency. In a single-step preparation method Ag/ZnO was prepared by heating directly a mixture of Zn$^{2+}$ and Ag$^{+}$ precursors in an aqueous NaOH-ethylene glycol solution, while in the two-step preparation method an intermediate of flower-shaped ZnO nanorod was obtained by a hydrothermal process before depositing Ag particles on the ZnO surfaces by chemical reduction. The structure, morphology and optical properties of the synthesized samples were characterized using TEM, SEM, XRD, DRS and PL techniques. The sample prepared by single-step method are characterized with agglomeration of Ag atoms as clusters on the surface of ZnO, whereas in the sample prepared by two-step method Ag atoms are found uniformly dispersed and deposited as discrete Ag nanoparticles on the surface of ZnO. A significant enhancement in the adsorption of visible light was evident for Ag/ZnO samples prepared by two-step method especially with low Ag content (0.5 mol%). The flower-like Ag/ZnO nanorod prepared with 0.5 mol% Ag by two-step process was found to be the most efficient photocatalyst for the degradation of phenol, which can decompose 90% of phenol within 120 min.

Keywords: surface manipulation, flower-like Ag/ZnO nanorods, photocatalytic degradation

Classification numbers: 2.03, 4.06, 5.00, 5.07
metal/metal ions and surface modification with noble metals [17]. Among these methods, modification of ZnO nanostructure with noble metals such as Pd, Ag and Cu is a promising way to improve the overall quantum efficiency of the photocatalytic process [18, 19]. Different preparation methods of metal-modified ZnO have been reported such as photoreduction, co-precipitation, deposition-precipitation, sol-gel and solvothermal methods [12, 20–23]. These methods led to materials with different surface structures and compositions, affecting their resulting photocatalytic activities. Xie et al [24] synthesized Ag-modified ZnO (Ag/ZnO) photocatalyst with various amounts of Ag contents by photocatalytic reduction of Ag⁺ on ZnO in ethanol. They reported that loading an appropriate amount Ag on ZnO not only enhances its photocatalytic activity but also improves its photostability. Chamjangali et al [25] synthesized Ag/ZnO by using a two-step process, wherein ZnO with flower-like morphology was first prepared by precipitation method and Ag nanoparticles were then deposited on the surface via photoreduction of Ag⁺ by UV irradiation. The resulting Ag/ZnO displayed higher photocatalytic activity than pure ZnO. Chauhana et al [26] synthesized Ag-doped zinc oxide nanocrystals by co-precipitation method. The incorporation of Ag⁺ in the place of Zn²⁺ provoked an increase in the size of nanocrystals as compared to pure ZnO. This resulted in a red shift in the absorption band edge. Similarly, Zheng et al [27] successfully prepared Ag/ZnO nanorods with different Ag contents through solvothermal method without use of surfactants. In addition, they carried out detail investigation of the relationship between preparation methods and photocatalytic activity of Ag/ZnO nanocatalysts. In comparison with chemical reduction and photolysis reaction, deposition-precipitation was found to be a more efficient method for the synthesis of Ag/ZnO catalysts with a high dispersion of Ag clusters and/or nanoparticles [28].

Phenol and its derivatives are the most common organic pollutants encountered in industrial effluents that cause severe environmental problems. These pollutants may pose a major health hazard even in low concentration due to their mutagenicity and genotoxicity [29]. In recent years many studies have been focused on the photocatalytic degradation of phenol by metal modified TiO₂ and ZnO semiconductor particles [30–32]. However, the correlation between structure of the semiconductors and photocatalytic activity for the degradation of phenol has scarcely been reported. In this work Ag-modified flower-like ZnO nanorods were synthesized by two different methods and with different levels of Ag content to manipulate and optimize the surface structures so as to achieve the maximum photocatalytic performance towards degradation of phenol. The relationships between surface structure, surface composition, optical properties and photocatalytic activity can therefore be established.

2. Experimental

2.1. Synthesis of flower-like ZnO nanorod (Z1)

In a typical experiment 0.52 g of Zn(NO₃)₂·6H₂O was dissolved in 14.0 ml of distilled water. Then, 14 ml of an aqueous solution of 1.25 M NaOH was slowly added into the solution under stirring. The solution was then transferred to a teflon-lined stainless steel autoclave (50 ml capacity) and heated in an oven at 180 °C for 5 h. A white precipitate was separated from the solution by membrane filtration and washed with distilled water and ethanol. The precipitate was then dried at 120 °C for 2 h.

2.2. Single-step synthesis of Ag-modified flower-like ZnO nanorod (AZ1)

Single-step synthesis of Ag-modified flower-like ZnO nanorod (AZ1) was prepared by using 0.52 g of Zn(NO₃)₂·6H₂O dissolved in 14 ml of distilled water. 14 ml of an aqueous solution of 1.25 M NaOH was slowly added into the solution under stirring. The required quantity of AgNO₃ and 0.034 g of PVP in 10 ml of ethylene glycol were added to the mixed solution. The resulting mixture was then transferred to a teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 5 h. The yellow-orange precipitates were collected via membrane filtration, washed with distilled water and ethanol and dried under nitrogen atmosphere.

2.3. Two-step synthesis of Ag-modified flower-like ZnO nanorod (AZ2)

In this experiment 0.10 g of the synthesized Z1 was dispersed in 20 ml of ethylene glycol under an ultrasonic bath. The required quantity of AgNO₃ in 10 ml of ethylene glycol and 0.034 g of PVP stabilizer were added to above pre-dispersed Z1 and the resulting mixture was heated at 120 °C for 1 h. The yellow-brown precipitate was separated by membrane filtration and washed with ethanol and dried under nitrogen atmosphere.

2.4. Characterization

The x-ray diffraction (XRD) patterns were acquired on a Bruker AXS D8 advance x-ray diffractometer using Cu-Kα radiation as an x-ray source. Transmission electron microscopy (TEM) was conducted on a JEOL JEM2011 microscope operated at 200kV. Scanning electron microscopy (SEM) images were recorded on a LEO 1450 VP electron microscope (LEO). Energy-dispersive x-ray (EDX) spectrometer (INCA-Oxford) was connected to SEM for the elemental analysis. UV-Vis diffuse reflectance spectra were measured on UV-Vis-NIR Cary 5000 (Agilent Technologies). Photoluminescence spectra were recorded at room temperature using FP-6200 Modle (Jasco) with an excitation wavelength of 255 nm.

2.5. Photocatalytic reactivity

In a typical experiment, 0.1 g of the synthesized ZnO photocatalyst was suspended in 100 ml of an aqueous solution of phenol (25 ppm) at pH 7 in the presence of phosphate buffer. The colloidal suspension was continuously stirred for 30 min in the dark to reach an adsorption/desorption equilibrium on the catalyst surface. The colloidal suspension was then
transferred to 250 ml glass photo-reactor attached to water cooling jacket. The catalyst suspension was illuminated in the reactor for a specific time period by ultraviolet light (a 450 W medium pressure Hg lamp) with a major emission at 365 nm. After irradiation, the solution is separated by centrifuge and transferred to UV cell using membrane filter syringe (0.45 micron). The concentration of phenol was quantitatively determined by measuring its absorption with a UV-Vis spectrophotometer (Agilent technologies 8453) at wavelength 270 nm. A calibration curve was prepared by measuring absorptions of an aqueous solution of phenol at different concentrations.

3. Results and discussion

3.1. Morphology and crystal structure

The morphologies of three different types of photocatalysts, namely flower-like ZnO nanorod (Z1), Ag-modified flower-like ZnO nanorod prepared by single-step method (AZ1) and two-step method (AZ2) were studied by SEM and TEM. SEM images of Z1 reveal flower-like morphology, as shown in figure 1 with pencil-like hexagonal rods giving a diameter in the range of 250-350 nm and length between 1200 nm and 1700 nm. SEM and TEM images of AZ2 (containing 3 mol% Ag), were collected and are shown in figures 1(b) and 2(a), (b), respectively. The images clearly depict a uniform dispersion of metallic Ag particles of 50 nm on the surface of Z1 nanorods. The morphology of AZ1 (0.5 and 3 mol% Ag) is different from that of Z1 in such a way that the nanorods of AZ1 have no center of growth but combined to form clusters, as shown in figures 3(a) and (b). TEM images (figure 4(a)) of AZ1 with low Ag content (0.5 mol%) show the absence of distinct Ag particles on Z1 but in form of clusters of Ag atoms. The darker areas of Ag clusters located at the facet surface of ZnO crystallites tend to segregate as small islands. At higher %mole Ag contents (figure 4(b)) Ag nanoparticles are clearly attached onto ZnO. It seems likely that Ag atoms are grown as clusters on the surface and can accumulate as particles at increasing amount of Ag atoms.

Figure 1. SEM images of (a) flower-like ZnO nanorod (Z1), and (b) Ag/ZnO nanorod (AZ2).

Figure 2. TEM images of (a) AZ2 (with 3 mol% Ag), and (b) the AZ2 image showing Ag nanoparticle attached to the surface of ZnO nanorod.
The percentage of Ag contents was determined by EDX analysis. Elemental analysis of AZ1 samples is close to the value obtained by theoretical calculation while the analysis of AZ2 is 10%–15% lower than the corresponding theoretical value. It is possible that Ag particles which are weakly interacting or attached on the surface were lost during purification stage involving washing with water and alcohol.

Regarding the formation of flower-like ZnO, the concentration of Zn$^{2+}$ and OH$^-$ have played the key roles, since no template, organic additive, or surfactant existed in the reaction [33]. In strong basic medium, the hydroxyl groups bind to metal cations through coordination as Zn(OH)$_2$$^{2-}$, which upon dehydroxylation forms ZnO. Therefore the Zn(OH)$_2$$^{2-}$ intermediate plays an important role in determining the morphology of ZnO. ZnO is a polar crystal with hexagonal structure, which consists of a positive polar (0001) plane covered with Zn cations, a negative polar (0001) plane covered with O anions and a non-polar {10$ar{1}$1} plane. In general, their growth rate under solution follows: (0001) > {10$ar{1}$1} > (0001) and thus, one-dimensional (1 D) hexagonal nanorods can be obtained [34]. In single-step synthesis, both Ag$^{+}$ and Zn$^{2+}$ precursors were dissolved in a mixed solvent of water and ethylene glycol under basic condition. Initially Zn(OH)$_2$$^{2-}$ and Ag(OH)$_2$$^{2-}$ species were formed. Upon dehydroxylation, they were converted to Ag$_2$O/ZnO wherein ZnO and Ag$_2$O were connected through Zn–O–Ag interaction before Ag$^{+}$ get reduced to Ag particles through hydro/solvothermal route. When Ag$_2$O is reduced, Ag particle may either get into the grain boundaries of ZnO or into the lattice of ZnO [27]. In the two-step process, flower-like morphology ZnO was initially synthesized and then Ag$^{+}$ ions were reduced to Ag atoms and deposited on the surfaces of ZnO.Ethylene glycol (EG) and PVP polymer were used as reducing agent and stabilizer, respectively. The reaction mechanisms for both the methods are presented in scheme 1.

The crystal structure of the ZnO was determined by x-ray diffraction. XRD patterns in figure 5 confirm the presence of ZnO phase. The Ag-modified flower-like ZnO nanorods are crystallines with a hexagonal wurtzite structure. The high intensity of (10$ar{1}$1) crystal plane corresponds to the pyramidal plane at the tip of rod.

There is no significant difference in the XRD patterns of Z1 and AZ2 (0.5 and 3 mol% Ag) whereas small peaks at 2θ = 38.19° and 44.34° can be indexed according to the
face-centered-cubic (fcc) structure of metallic Ag for AZ1 especially at higher loading of Ag (3 mol%). It implies that the Ag particles in AZ2 (prepared by two-step method) are distributed as distinct and discrete particles on ZnO surface and in the case of AZ1 (prepared by single-step method) Ag particles are agglomerated as clusters/particles on ZnO surface due to uncontrolled synthesis. These results are in agreement with the findings by using microscopic techniques. In addition, there is no significant shift of diffraction peaks which indicates that Zn\textsubscript{1-x}Ag\textsubscript{x}O solid solution is not formed and the change of the lattice parameters of ZnO nanocrystals is negligible [24, 35]. It may be due to the ionic radius of silver (\(r_{\text{ion Ag}^+} = 1.26\ \text{Å}\)) is quite larger than one of zinc in ZnO (\(r_{\text{ion Zn}^{2+}} = 0.74\ \text{Å}\)). This can explain the segregation of Ag particles in the grain boundaries of ZnO crystallites rather than getting into the lattice of ZnO. A shift of diffraction peak position for the samples of Pd modified ZnO is reported in the literature, which indicates lattice expansion due to similar size between Pd\textsuperscript{2+} (0.08 nm) and Zn\textsuperscript{2+} ion. Thus, partial Pd is doped in the lattice of ZnO [35]. This is in contrast to the present study wherein Ag\textsuperscript{+} is much larger in size hence giving Ag clusters or agglomeration on ZnO nanorod surface during the single step synthesis, which remains in the crystallite grain boundaries.

3.2. Optical properties

The UV-Vis diffuse-reflectance spectra of Z1, AZ1 and AZ2 (0.5 mol% Ag loading on ZnO in AZ1 and AZ2) samples are shown in figure 6. All the three samples display excitonic absorption peaks at about 398 nm in the spectra. Samples AZ1 and AZ2 exhibit absorption bands in the visible region at about 400–550 nm, which is not observed for pure Z1 sample. Absorption band in the visible region is attributed to the characteristic absorption of surface plasmon resonance resulting from metallic Ag clusters on the surface of ZnO structure [36]. Sample AZ1 shows a broad plasmon band with higher intensity compared to AZ2 sample. This may be due to the fact that Ag atoms are segregated as small clusters on the surface of ZnO in the single-step process while in the two-step process distinct Ag nanoparticles of definite sizes are located on the surface. These results are in agreement with the observations made by our TEM images.
The diffuse reflectance (R%) data of all three different types of nanorods were converted to the absorption coefficient F(R) values according to the Kubelka-Munk equation [37]. After the treatment, the function $[F(R)h\nu]^2$ versus $\nu$ (eV) are shown as Tauc’s plots in figure 7. The optical band gap was determined by taking the intercept of the extrapolation to zero absorption with photon energy axis. According to the figure, energy band gaps of Z1, AZ1 and AZ2 are found to be 3.01, 3.12 and 3.08 eV, respectively, which are narrower than that of bulk ZnO (3.37 eV). Silver-modified samples (AZ1 and AZ2) exhibit an increased energy band gap compared neat Z1 nanorods. Doping Ag by the single-step method is found to be more effective for optical properties than that of the sample prepared by two-step process. However, this change may not significantly affect to their photocatalytic activity.

Photoluminescence (PL) spectroscopy was employed to investigate the relationship between structural properties and optical properties. PL spectra of Z1, AZ1, and AZ2 nanomaterials are shown in figure 8. Enhancement of UV-visible emission intensity was prominent for Ag/ZnO samples prepared either by single-step or two-step methods especially for samples modified with low Ag content (0.5 %mol). At higher concentrations (≥ 1 mol% Ag), the emission intensity sharply decreased and at 3 mol% Ag, the intensity was much lower than that of neat nano-ZnO. Moreover, the characteristics of the emission spectra of Ag/ZnO samples prepared by two methods were different. The intensity of blue emission at 419-465 nm of single step AZ1 sample was weak whereas the two-step AZ2 sample displayed a strong blue emission.

The emission intensity observed for each band of nanomaterials can be used to identify their surface properties. A shoulder with low intensity in UV region between 395-405 nm corresponds to the recombination of electrons from conduction band with the hole from valence band [38]. A number of hypotheses have been proposed in the literature to explain visible emissions of ZnO nanocrystals [39–42]. A broad band of visible emissions with peaks centered at 419, 445, 465 and 498 nm and a shoulder at 500-600 nm is due to charge transition of various defects. Blue emission band at 419–465 nm is attributed to an electron transition from deep donor level of zinc interstitials (Zni) to the valence band of ZnO [39], green emission peak at 498 nm due to transition between electron close to the conduction band and deeply trapped holes at oxygen vacancy [40] and the yellow emission band (550–600 nm) due to transition from shallow donor to deep acceptor level, zinc vacancy or interstitial oxygen defects [41, 42].

The enhancement of PL emission of ZnO after modification of its surface with Ag might be attributed to hot electron transfer from excited state to the conduction band edge due to surface plasmon resonance [43]. When the emitted visible light
photon energy of ZnO matches the surface plasmon resonance energy of Ag, the emitted photons produce the surface plasmon resonance through energy transfer, which promotes the electrons of Ag to an excited state by surface plasmon waves. The excited electrons will tunnel to the conduction band and defect level of ZnO. Thus, the visible emission intensity of the Ag-modified ZnO becomes much higher than ZnO. Such strong emission intensity in a green-yellow region of AZ1 illustrates that the reduction of Ag₂O on ZnO has a tendency to generate high oxygen vacancy on ZnO [39]. In the case of AZ2 sample, stronger emission intensity is found in the blue-green region, which indicates the role of interstitial zinc defects. Reduction of Ag⁺ followed by their deposition Ag atoms and grows as discrete nanoparticles at defect sites on the surface of ZnO causes high electron density on defect sites due to the transfer of electrons from the excited state of Ag to Zn interstitial defect level which close to conduction level [44]. At higher Ag loading (1 and 3 %mol) emission band is reduced substantially (quenched). High visible emission intensity of Ag modified ZnO samples containing lower levels of Ag content (0.5 mol%) may be attributed to a higher number of the remaining defect sites on ZnO surface, which are not blocked by Ag particles and contribute plasmon electrons. Higher loading of Ag not only decreases the defect sites but also blocks ZnO surfaces from light irradiation. In addition, the transferred electrons from the excited state of Ag are driving back to Ag causing a decrease in an electron density [27]. Thus, the method of preparation and % loading of Ag can alter the surface structure and the optical properties of Ag-modified ZnO samples.

### 3.3. Photocatalytic degradation of phenol

The photocatalytic activity of neat flower-like ZnO nanorod and Ag/ZnO containing different levels of Ag content on the degradation of phenol was investigated. A plot of irradiation time versus percentage degradation for different types of nanocatalysts is shown in figure 9.

Sample AZ2 exhibits higher catalytic activity towards degradation of phenol than the sample AZ1. Interestingly, the photocatalytic activity of both samples decreases with increasing Ag contents, as shown in figure 9. The maximum percentage degradation of phenol by Z1, AZ1 and AZ2 were found to be 50%, 60%, and 90%, respectively, for a specific period of 120 min. Among various loading levels of Ag, AZ1 and AZ2 samples with 0.5 mol% of Ag exhibited higher photocatalytic performance towards degradation of phenol than unmodified nano-ZnO. AZ2 showed the highest photocatalytic performance among all the catalysts investigated in this work. These results indicate the influence of nanocatalysts composition and surface morphology on photocatalytic degradation of phenol.

In a photocatalytic process, the separation and recombination of photoinduced electron and hole follow competitive pathways and the photocatalytic activity is more effective when the recombination is prevented [23]. Photocatalytic degradation of phenol starts when ZnO is irradiated by UV light with photon energy higher or equal to its band gap and the electrons (e⁻) in the valence band is either excites to the conduction band or transfer to defect level with simultaneous generation of the same amount of holes (h⁺) in the valence band. When Ag modified ZnO sample (AZ1 and AZ2) is irradiated with incident light having a wavelength larger than the particle sizes, the electrons form electron cloud and oscillate at the interface between Ag and ZnO. This leads to easy electron transfer from Ag nanoparticles to ZnO causing an increased electron density in the conduction band of ZnO and the partial photogenerated electrons could transfer to defect level on the surface of ZnO. Electrons at defect level are active to react with adsorbed oxygen to produce superoxide anion radical and hydroxyl radicals in the presence of water. Hydroxyl radicals are active species to further oxidize phenol [36]. High electron density at defect sites results in an enhanced photocatalytic activity. AZ2 (0.5 mol% Ag) with strong emission intensity in visible region of photoluminescence spectra exhibits high photocatalytic activity towards degradation of phenol, which indicates a relationship between emission intensity and concentration of electron on defect levels. AZ2 (0.5 mol% Ag) exhibits emission intensity in visible region
10 times stronger than Z1 and its photocatalytic activity is almost 2 times that of Z1. While for the samples prepared by the single-step method a little improvement in photocatalytic activity compared to neat ZnO is obtained. It is possible that zinc vacancy or interstitial oxygen defect level may not be the active site for the degradation of phenol. These results confirm that the surface structure and composition are the important parameters for photocatalytic degradation of phenol. In addition, the photocatalytic efficiency of Ag/ZnO catalyst is found to be related to a dispersion of metallic Ag. Among the two different preparation methods for Ag/ZnO, two-step method shows a high dispersion of Ag particles on the surface of ZnO, leading to higher photocatalytic activity. This is in agreement with Zheng et al who prepared Ag/ZnO nanocatalyst by different methods. They reported that deposition-precipitation is an efficient method to obtain highly dispersed metallic Ag on the surface of ZnO nanocrystals and they also showed that the photocatalytic activity depends on the dispersion of Ag clusters and/or nanoparticles in Ag/ZnO [27, 35].

Though preparation of nanocatalyst by single-step is a simple process compared two-step method, there are several advantages associated with two-step process: (i) the surface structure and dispersion of Ag can be well controlled by following two-step process, (ii) involving reduction and deposition of Ag particles at defect sites on the surface of ZnO by two-step method brings sufficient interaction for electron to transfer between ZnO and Ag at interface, (iii) the loading level can be precisely controlled in the two-step method by maintaining the desired level of photoactive sites of ZnO to achieve the maximum catalytic efficiency whereas the formation of Ag clusters on the surface defect of ZnO during single-step covers most of the photoactive sites.

4. Conclusions

The surface structure of flower-like Ag/ZnO can be tailored to enhance photocatalytic activity by loading different levels of Ag and also by using different preparation techniques. With uniformly dispersion and deposition as discrete Ag nanoparticles on the surface of ZnO nanorod, the Ag/ZnO (0.5 mol%) catalyst obtained by two-step process exhibits the best photocatalytic activity under identical reaction conditions than the catalyst obtained by single-step method.

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