Synthesis of immobilized nanostructured ZnO grown on glass and its photocatalytic activity for cyanide degradation

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Abstract. Nanostructured ZnO has been synthesized by using two simple steps, i.e. ultrasonic spray pyrolysis (USP) and chemical bath deposition (CBD) methods on glass substrates. The crystal structure, morphology, photoluminescence (PL) emission, and photocatalytic activity for cyanide degradation were studied. From the X-ray diffraction (XRD) examination, it was observed that the ZnO had the hexagonal wurtzite structure with the preferred orientation of (100). The field emission scanning electron microscopy (FESEM) image displayed that the ZnO had grass-like and bush-like nanostructures. The PL spectrum exhibited the near band-edge (NBE) peak at ~380 nm. The photocatalytic activity of the nanostructured ZnO for cyanide degradation in aqueous solution was evaluated under warm-white lamp (color temperature of 2700 K) and cool-daylight lamp (color temperature of 6500 K) irradiations, resulting enhanced cyanide degradation rates in presence of the nanostructured ZnO.

1. Introduction
Zinc oxide (ZnO) is a versatile semiconductor material that nowadays attracts much attention. With its wide band gap of ~3.37 eV, high exciton binding energy of ~60 meV, and native crystal defect properties, ZnO has a potential application as photocatalysts for degrading various hazardous chemicals, such as acetaldehyde [1], nitrophenols [2], organic dyes [3–8], and cyanide [8–12].

The photocatalytic activity of ZnO nanoparticles, which are considered highly mobile once immersed in non-stagnant aqueous solutions, has been reported in many scientific articles [1,2,8–12]. Other articles have also reported studies concerning the photocatalytic activity of immobilized ZnO grown on and adhered to fixed surfaces, such as silicon [13], indium tin oxide [7], sapphire [14], and glass [3–5]. However, none of those articles have discussed the use of immobilized ZnO adhered to fixed surfaces for cyanide photodegradation under daylight irradiation.

Some methods have been developed to produce ZnO nanostructures, such as pulsed laser ablation [10], pulsed laser deposition [14], metalorganic vapor-phase epitaxy [15], sol-gel [3,5,11], ultrasonic spray pyrolysis (USP) [4,7,16], sonochemical impregnation [12], combustion [17], chemical bath deposition (CBD) [18,19], and hydrothermal [3–7,16,20]. Among these methods, USP and CBD were chosen to be conducted in this study as they offer simplicity and efficiency in chemical use, and can be carried out at relatively low temperature [4,7,18,19].
In this report, we demonstrate the synthesis of immobilized nanostructured ZnO grown on glass substrates using two simple steps, i.e. USP and CBD methods, and its photocatalytic activity in degrading cyanide ions under warm-white lamp and cool-daylight lamp irradiations.

2. Experimental Details

2.1. Synthesis of Nanostructured ZnO
The first step was the USP method to seed glass substrates with ZnO seed layers before the nanostructured ZnO could be grown on the substrates. Prior to the process, the substrates were cleaned in acetone, ethanol, and distilled water, respectively. Zinc nitrate tetrahydrate (Zn(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O, 99.99%, Merck Millipore) dissolved in distilled water with the concentration of 0.2 M was placed into an ultrasonic nebulizer to be vaporized by ultrasonic vibration (1.65 MHz) at room temperature. The vapor then flew through a tube (flow rate set at 1.5 ml/min) and exposed the glass substrates placed on a hotplate at the set temperature of 500°C for 30 minutes without any vacuum system. The seeded substrates were then annealed at 400°C for an hour on the hotplate.

In the next step, nanostructured ZnO was grown on the seeded glass substrates using the CBD method similar to the growth method in the aqueous solution developed by Vayssieres [21] with some modifications. Growth solution was prepared by dissolving Zn(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O and hexamethylenetetramine (C\textsubscript{6}H\textsubscript{12}N\textsubscript{4}, 99.99%, Merck Millipore) in distilled water with the equimolar concentration of 0.05 M. The growth process was performed by immersing the seeded glass substrates into the growth solution in an uncovered glass beaker on a hotplate at ~85°C for 3 hours. After the growth process, samples were rinsed in distilled water and dried out on a hotplate set at 170°C for 10 minutes.

2.2. Characterization
The crystal structure was investigated using Rigaku MiniFlex 600 X-ray diffractometer with CuK\textalpha radiation (1.5406 Å). The morphology of the sample was observed using JOEL JIB-4610F Multi-Beam System field emission scanning electron microscope (FESEM). The photoluminescence (PL) emission was examined using Maya Ocean Optics detector under the emitting laser’s wavelength of 325 nm, measured at room temperature.

2.3. Photocatalytic activity evaluation
The photocatalytic activity for cyanide degradation was evaluated through exposing the cyanide solution in basic condition to the light from warm-white lamps (color temperature of 2700 K, intensity ~4800 lux) and cool-daylight lamps (color temperature of 6500 K, intensity ~4800 lux). The cyanide solution (200 ppm) was prepared by dissolving sodium cyanide (NaCN, 99%, technical grade) in distilled water, in which sodium hydroxide (NaOH, technical grade) had been added to raise pH until it reached 12.5 beforehand. Afterward the cyanide solution was irradiated with warm-white lamps and cool-daylight lamps, separately, in the presence and absence of the nanostructured ZnO grown on glass substrates with a total surface area of 12 square inches. The concentration of residual cyanide ions ([CN\textsuperscript{-}]) was determined every 15 minutes until two hours using the argentometric titration method with a few drops of 5-(4-dimethylaminobenzylidene)-rhodanine (≥98%, Merck Millipore) dissolved in acetone as the indicator and silver nitrate (AgNO\textsubscript{3}, 99.99%, Merck Millipore) dissolved in distilled water as the titrant.

3. Results and discussion
Figure 1 shows the X-ray diffraction (XRD) pattern of the nanostructured ZnO grown on the glass substrate. The pattern represents diffraction peaks attributed to (100), (002), (101), (102), (110), (103), and (112) planes, corresponding to the hexagonal wurtzite crystal structure of ZnO (ICDS 98-016-5002), and no phase other than ZnO was detected from the pattern. Since spray pyrolysis methods in general characteristically produce rough surfaces [20], the ZnO seed layer produced by the USP was quite rough and had many orientations, then affected the growth orientation of the nanostructured ZnO. The preferred orientation of the ZnO crystals was (100), determined by the extremely prominent peak at 20
of 31.78°. This result, thus, suggests that most of the ZnO nanorods had the lateral growth orientation along the a-axis (parallel to the substrate’s surface).

![Figure 1. XRD pattern of the nanostructured ZnO grown on glass.](image)

![Figure 2. FESEM images of the nanostructured ZnO grown on glass.](image)
Figure 2 displays the FESEM images taken from some points on the sample’s surface. The images represented the typical morphology of ZnO nanostructures grown on the seed layer fabricated using spray pyrolysis methods, which was comprised of numerous disarrayed ZnO nanorods grown along with many directions [20]. This morphology might benefit the photocatalytic activity since it obviously increases the surface area. Most of the nanorods were oriented parallel to the substrate, rendering the predominant grass-like nanostructure, and some of the nanorods randomly tilted and were perpendicular with respect to the substrate, rendering the flower-like nanostructure. This also confirms the result from XRD examination that the nanostructured ZnO had some plane orientations and the preferred orientation was along the a-axis.

Figure 3 shows the PL emission of the nanostructured ZnO grown on glass substrates in logarithmic scale. The near band-edge emission (NBE) of the ZnO, which attributes the excitonic recombination [4,7], is exhibited ranging from ~360 nm to ~420 nm with its peak in the ultraviolet region at ~380 nm. The bandgap obtained from the peak, determined by the equation $E = h\nu$, is ~3.26 eV. A deep level emission (DLE) generated by defects appeared extremely weak in the visible region, inferring that the ZnO crystals had very low defect density and excellent crystal quality [15,22].

Figure 3. PL emission of the nanostructured ZnO grown on glass in logarithmic scale.

Figure 4. Cyanide degradation under (a) warm-white lamp (color temperature of 2700 K) and (b) cool-day light lamp (color temperature of 6500 K) irradiations.
The evaluation of photocatalytic activity for cyanide degradation is presented by figure 4. It is shown that the cyanide degradation rates were slightly enhanced in presence of the nanostructured ZnO grown on glass substrates. Without the nanostructured ZnO immersed in the cyanide solution, the warm-white irradiation for two hours seemed to have a negligible effect on cyanide degradation. With the nanostructured ZnO, the warm-white lamp irradiation for two hours could degrade 8.79% of cyanide ions as shown in figure 4(a). On the other hand, the cool-daylight exposure seemed to render tenuous cyanide degradation up to 0.52% in absence of the nanostructured ZnO. However, with the nanostructured ZnO, the degraded cyanide ions reached 12.44% in two hours of cool-daylight lamp irradiation as shown in figure 4(b).

The mechanism behind the photocatalytic degradation of cyanide by ZnO can be explained as follows. When ZnO is irradiated by photons possessing enough energy, the electrons excite from the valence state to the conduction state generating free electrons (e\(^-\)) and holes (h\(^+\)). The electron–hole pairs (excitons) then react with oxygen and water, producing hydroxyl radicals (OH\(^•\)). In general, the mechanism for the photocatalytic degradation of cyanide by ZnO can be described as follows [8–11]:

\[
\text{ZnO} + \hbox{hv} \rightarrow \text{ZnO}(e^- + h^+) \quad (1)\\
\text{e}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}^* \quad (2)\\
\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^* \quad (3)\\
\text{CN}^- + 2\text{OH}^* \rightarrow \text{OCN}^- + \text{H}_2\text{O} \quad (4)
\]

In the case when ZnO has a fairly high amount of crystal defects, the above mechanism not only depends on the interband excitation. The existence of crystal defects in ZnO also plays an important role in photocatalytic degradation, as reported by some authors [4,5,8,11]. The defects provide some deep level energy states between the valence and conduction bands that can be occupied by electrons and allows photons lower than the bandgap to excite electrons and generate excitons [8,11]. Moreover, the defects can act as traps for electrons and holes, hence inhibiting recombination and improving the photocatalytic activity [4,5]. In this study, however, it can be inferred that the above photocatalytic degradation mechanism depends thoroughly on the interband excitation and does not quite rely on the deep level states since the PL emission (figure 3) indicated that the nanostructured ZnO contained a very slight quantity of crystal defects [10,12].

4. Conclusions

Nanostructured ZnO has been successfully synthesized using two simple steps, i.e. USP and CBD methods, immobilized on glass substrates. It was investigated that the nanostructured ZnO had the hexagonal wurtzite structure with the preferred orientation of (100), suggesting that most of the ZnO crystals had the lateral growth orientation along the a-axis. The nanostructure of the ZnO was made up of grass-like and bush-like formations of ZnO nanorods. From PL examination, a very strong NBE was exhibited at ~380 nm (~3.26 eV) and an extremely weak DLE appeared in the visible region, indicating that the ZnO crystals had very low defect density. The photocatalytic activity evaluation showed the enhancement of degraded cyanide from negligible decrease (without the nanostructured ZnO) to 8.79% (with the nanostructured ZnO) under warm-white lamp irradiation for two hours and from 0.52% (without the nanostructured ZnO) to 12.44% (with the nanostructured ZnO) under cool-daylight lamp irradiation for two hours. It is inferred that the photocatalytic degradation mechanism depends thoroughly on the interband excitation as the PL examination indicates that the nanostructured ZnO contained only a slight quantity of crystal defects.
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