Synthesis of iron-doped zinc oxide (Fe-ZnO) nanoparticles by using several stabilizers

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Abstract. Studies on the effect of the stabilizer of chitosan, citric acid and urea for preparation Fe-doped ZnO have been conducted. Both ZnO and Fe were prepared from each salt precursor solution. The Zn²⁺ was added first and subsequently Fe²⁺ by dropwise method into each stabilizer solution before converted into the hydroxide compounds before annealing. All metal ion solutions precipitated out after 7 minutes of NaOH addition except in urea stabilizer, where the solution remained in the colloidal form for more than 30 minutes. The hydroxyl ions are required for ZnO formation, but it weakens chitosan and citric acid stabilizing capacity, which instigated ZnO particles to be highly agglomerated. Each stabilizer generated a smaller ZnO crystallite size compared to the control sample. Fe-ZnO crystallite size prepared using chitosan, citric acid and urea as the stabilizer was 14.75, 23.29 and 22.51 nm, respectively. The crystallite size of Fe-ZnO that was prepared without stabilizer (control) was 32.89 nm.

1. Introduction

Zinc oxide (ZnO) is an interesting nanomaterial that has been known as a multipurpose material because of the wide application in various fields as like medicine[1], antibacterial[2], sunscreen[3], photocatalyst[4], sensor[5], optoelectronic[6], spintronic[7], etc. Reducing the particle size usually increases the activity due to the quickly penetrating the membrane and serving a wide surface area. Doping ZnO with other elements usually alters the original bandgap and the rate of recombination[8]. ZnO nanoparticles have been fabrication with several methods, both top-down and bottom-up approaches in the classification method. The top-down process is carried out through sieving and grinding the bulk particles into nanoparticles. The bottom-up carried out through collecting atom or ion into small particles with a growth controller or stabilizer. The bottom-up technique is usually conducted in a solution with the addition of a precipitated agent (usually base, e.g., NaOH, NH₃) and such a stabilizer for controlling the nucleation process[9][10].

The stabilizer used in the preparation process is usually the molecule with good interaction with the solvent and the metal ion (Zn²⁺) through their functional group. Chitosan[11-12], citric acid[13] and urea[14] were known stabilizers and had widespread use as a stabilizer for the ZnO nanoparticle
preparation. The stabilizer has an essential function during the nucleation process, where their functional group bonds to metal ions and is expected to prevent particle aggregation. In this research, we prepared the Fe-ZnO by the co-precipitation method using NaOH as a precipitated agent and various stabilizers that were chitosan, citric acid and urea. The iron ions were the dopant to improve the photocatalytic activity of ZnO. The stabilizer effect was studied by using several techniques before and after annealing.

2. Material and Method

2.1 Material

The precursors used in the preparation process were zinc nitrate hexahydrate, Zn(NO$_3$)$_2$, 6H$_2$O and iron nitrate nonahydrate, Fe(NO$_3$)$_3$, 9H$_2$O, which were from Sigma Aldrich. The precipitated agent was sodium hydroxide (NaOH), which produce from Merck. The stabilizer was a medium molecular weight of chitosan (D-glucosamine) was from Sigma Aldrich and urea (CO(NH$_2$)$_2$) and citric acid monohydrate (C$_6$H$_5$O$_7$·H$_2$O) produce by Merck. The weak acid for dilute the chitosan was acetic acid (CH$_3$COOH) produce by Merck. Distilled water (H$_2$O) was used as the solvent in the preparation process.

2.2 Method

2.2.1 Material. The Zn$^{2+}$ ion was prepared by diluting 23.8 g of Zn(NO$_3$)$_2$, 6H$_2$O into 80 ml distilled water and the Fe$^{3+}$ ion was prepared through diluted 0.032 g of Fe(NO$_3$)$_3$. 9H$_2$O into 8 ml of distilled water in a separate Erlenmeyer, which gives a concentration of 1 and 0.01 M, respectively. Chitosan 1% was prepared with diluted 0.2 g chitosan into 20 ml of 1.5% CH$_3$COOH. About 4.2 g of C$_6$H$_5$O$_7$·H$_2$O was dissolved into 20 ml of distilled water. Urea (CO(NH$_2$)$_2$ 1.2 g) was dissolved into 20 ml of distilled water to make CO(NH$_2$)$_2$ 1 M. The precipitate agent prepared by diluting 8 g of NaOH into 100 ml distilled water to prepare NaOH 2M.

2.2.2 Procedure. Each stabilizer solution (20 ml) was filled into different Erlenmeyer and the control was 20 ml of distilled water. While stirring, 20 ml of the Zn$^{2+}$ precursor solution was dropped wisely and followed with an additional 1 ml of Fe$^{3+}$ solution and kept stirred for 20 minutes before 20 ml NaOH (2 M) was dropped from a burette with a rate of 1 drop per second. For the citric acid stabilizer, 40 ml NaOH was required to precipitate the metal ions.

After the precipitation process, the sample was washed using distilled water until neutral, then following with drying at 150°C for 48 h. The samples were annealed at 500°C for two hours. The particle growth was observed by a light microscope. XRD was used to confirm the existence and measure the crystallite size of Fe-ZnO after annealing.

3. Result and Discussion

Without a stabilizer (control), the Zn$^{2+}$ ions settle down immediately in the presence of hydroxyl ion. The stabilizer prevented to form bigger particle and remain in colloidal solution[15]. Without a stabilizer, both Zn and Fe ions were ultimately settling down immediately after NaOH addition, as shown in Figure 1(a). Figure 1(b) shows colloidal aggregation in the presence of chitosan. Eventually, the colloidal solution precipitated since chitosan was also sedimented in basic solution, due to no longer the stabilizing function [16].

The chitosan, citric acid and urea have a functional group that might bond to Zinc ions before formation Zn(OH)$_2$. The backbone structure of those compounds is presented in Figure 2. The chitosan has long polymer chains with the lone pair in their functional group to act as Lewis base [17]. The citric acid has a less complicated structure than chitosan and urea chemical structure was the simplest backbone. Unlike chitosan, which only dissolves in acetic acid solution [18], citric acid and urea are water-soluble.
Figure 1. Zn and Fe ions in (a) Precipitated out of the Zn$^{2+}$ and Fe$^{3+}$ ions without the presence of stabilizer (control) (left) and with the presence of chitosan as a stabilizer (right).

Figure 2. Backbone structure of chitosan (left), citric acid (middle) and urea (right).

Theoretically, chitosan should have a better stabilizing function due to its stable structure. In fact, urea prevents Zn(OH)$_2$ from immediate precipitation and makes it longer in colloidal form than the other stabilizers. The Zn(OH)$_2$ in chitosan and citric acid precipitated out after 7 minutes, but it remains colloidal for more than 30 minutes in the urea. However, it was only 7 minutes, which is not ideal for nanoparticle characteristics. The comparison of this solution is presented in Figure 3. This finding contradicted with other reports proving that both chitosan and citric acid were effectively stabilizing agents [16]. The key difference, in this case, was on the basic condition that reduces the solubility of chitosan and citric acid and then subsequently lost their stabilizing function.

When the stabilization is failed, particle agglomeration occurs. This theory is confirmed by the microscope images of the ZnO particles, as shown in Figure 4. The imaging was taken using a light microscope at 1000x magnification and shows Zn(OH)$_2$ was highly agglomerated in chitosan (Figure 4a). The agglomeration was less in citric acid and urea (Figure 4b & 4c).

After annealing, the Fe(OH)$_3$-Zn(OH)$_2$ was converted to Fe-ZnO as confirmed by x-ray diffraction (XRD) diffractogram. The diffractogram was matched with the ZnO standard peak as in the card of the Joint Committee on Powder Diffraction Standards (JCPDS) 036-1451[19]. The Fe-ZnO sample contained several pollutants since some of the weak foreign peaks were also detected. The diffractogram comparison of the Fe-ZnO prepared with different stabilizers are presented in Figure 5.
Figure 3. The Zn(OH)$_2$ after precipitate out with different stabilizer right after shaken (left) and after keep out after 7 minutes (right).

Figure 4. The Zn(OH)$_2$ light microscope images at 1000x magnification. Zn(OH)$_2$ was prepared with and without stabilizer; (a) chitosan, (b) citric acid, (c) urea, (d) without stabilizer (control).

The Fe-ZnO that is prepared without stabilizer shows the highest crystallinity, the intensity over the 23,000 points. That condition provided an insight that the crystal growth's lattice arranged closely to each other and with a similar angle. That condition is relevant to the Debye-Scherer formula, increasing the crystallite affected by the decreasing of Full Width of Half Maximum (FWHM) of the diffractogram. Compared to other preparation, the chitosan stabilizer regulated the smallest Fe-ZnO crystallite size. It might indicate an arbitrary crystallite arrangement. In the citric acid and urea preparation, Fe-ZnO has a moderate crystallite size with a nearly similar crystallinity degree.

The Fe-ZnO crystal was dispersed in water and then the time of settle down was compared. After 30 and 60 minutes, suspend consistently that the Fe-ZnO without stabilizer remained in suspension longer than the others, as shown in Figure 6. Theoretically, the bigger particles (Figure 5d) shall precipitate faster than the smaller ones, but a reverse trend occurred [19]. Rationally, the phenomenon related to trace-stabilizer ashes trapped inside clusters. During annealing, the organic stabilizers were burning out and produced ashes trapped in the particle clusters. The ashes become heavier when getting wet that caused particles precipitate faster in water.
**Figure 5.** Diffractograms of Fe-ZnO prepared with and without stabilizers; (a) without stabilizer, (b) chitosan, (c) citric acid, (d) urea.

**Conclusion**
In basic solution, either chitosan and citric acid show a weaker stabilizing function than urea in preparation of Fe-ZnO with the co-precipitation method. In the basic condition, chitosan and citric acid were neutralized, which reduced the solubility in water and lost the stabilizing function. Although in weak stabilizing properties, the formation of crystalline Fe-ZnO nanoparticles was confirmed from XRD data and chitosan gave the smallest Fe-ZnO particles but more particle aggregated than by citric and urea stabilizers. Trace stabilizer ashes that were trapped in Fe-ZnO during the annealing process possibly caused Fe-ZnO particles to precipitate faster in water if the Fe-ZnO was suspended within the water.

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