Synthesis and Characterization of ZnO Nanoparticles by using gelatin as co-template

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Abstract. The purpose of the structure of these nanoparticles is characterized by Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy, nitrogen adsorption techniques and scanning electron microscopy. The method of this research is to analyze the elements on the surface monitored by EDAX showing that pure particles are produced by steps first produced by self-assembly routes. The results of this process are influenced by the infiltration of block copolymers into zinc precursors that make bulk formation of Zn. In another approach, the use of gelatin as a template has a large effect on morphology and structure on nanoparticles. The structure of nanoparticles synthesized by gelatin involves showing significantly improved texture morphology than zinc oxide without gelatin. The application is expected to prepare the future of nanoparticles using gelatin as a co template to become a new candidate for green material in the future. The results show that gelatin can be a new biotemplate for the synthesis of zinc oxide nanoparticles.

Keywords. zinc oxide, material, gelatin, soft template

1. Introduction

Today, zinc oxide nanoparticle has attracted great attention in the world due to the highly ordered structure and properties as optic, catalyst, sensor, semiconductor, and energy storage[1]. The method for zinc oxide synthesis is evaporation, laser ablation, templating and colloidal system. Laser ablation has higher performance for zinc oxide synthesis [2]. However, laser ablation is a high cost due to the energy consumed. The favorable method is the colloidal system due to the several reasons such as very simple, fast, efficient and environmentally-friendly.

The colloidal system was known as soft template technique which is colloidal particle act as pore directing agent of material during synthesis. The non-toxic and low cost of colloidal particle required not only by environmental but also an economic reason. The synthetic common colloidal particle as soft template which usually use for material synthesis such as triblock copolymer comprising poly(ethylene oxide)-(PEO)andpoly(propylene-oxide)(PPO)-P123,Poly(ethylene-glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-Poloxamer 407, Poloxamer 188, Pluronic L-81, Poloxalene, Poloxamer Tergitol XH, Pluronic F68, Pluronic L44, Poloxamer 407, Pluronic F 38 have minimized for using due to the high cost and less biodegradable [3-5]. The solution of this problem is using the natural source which has similar properties with the synthetic colloidal particle. One of the natural colloidal
particles that has great utility is gelatin. The powder of gelatin has been used in wide application such as medicinal field, food industry, separation, and adsorption. Gelatin has been applied for modifying poly (dl-lactic-co-glycolic acid) (PDLLGA) microsphere, cell delivery carrier, cell adhesion and proliferation, grafting agent, crosslinker and engineering applications due to the long chain of gelatin[5]. The hydrophobicity and hydrophilicity group of gelatin have good properties as pore director agent when interacting with other substances [6]. The previous work was successfully using gelatin during synthesis worm hole-like carbon and carbon foam [6]. However, the special character of gelatin has been rarely investigated for zinc oxide nanoparticle research.

Zinc oxide nanoparticle as semiconductor, electrodes, and energy storage material have been interesting material in the last decade due to the large surface area, high stability and high hydrophilicity. The textural and structural properties can be controlled by the appropriate surface active agent, hydrothermal condition and growth processes [7,8]. The surface active agent was the presence of hydroxyl and carbonyl groups could further increase the surface area of the material during growth process [9,10]. In this work, zinc oxide nanoparticle was synthesized using a simple hydrothermal process which is involving the gelatin as the novel surface active agent. The resulting sample morphology of zinc oxide nanoparticle has characterized by SEM, FTIR, and XRD. The purpose of the structure of these nanoparticles is characterized by Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy, nitrogen adsorption techniques and scanning electron microscopy. The method of this research is to analyze the elements on the surface monitored by EDAX showing that pure particles are produced by steps first produced by self-assembly routes.

2. Method

Material

Gelatin powders (Type B gelatin from Bovine skin, Sigma-UK), poly(ethylene glycol)-block-poly(propylene-glycol)-block-poly(ethylene-glycol)-poloxamer 127 from Sigma Aldrich (99.99%) and deionized water, sulfuric acid and zinc nitrate from Sigma Aldrich (99.99%).

Synthesis of Zinc Oxide nanoparticle (ZOnP)

Zinc Oxide nanoparticle ZOnP was prepared firstly by mixing gelatin in deionized water under stirring 60 min. Then the colloidal solution was prepared by adding a gelatin solution into poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-poloxamer solution under stirring 60 min. The colloidal of zinc oxide was prepared by added zinc nitrate and sulfuric acid solution drop by drop to the mixture of gelatin and poloxamer solution. Mass ratio of gelatin: poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-poloxamer:H₂O:H₂SO₄:Zn(NO₃)₂=0.011:0:175:5.000:0.002:0.120) %w/w. After constant stirring, the solution was carried out at the hydrothermal reactor at 100 °C for 24 h. The grey-white powder was obtained after the filtration and evaporating process. After that, the powder was calcinated in a furnace reactor using aluminosilicate as a sample holder at 600 °C overnight then labeled as ZOnP.

Characterization of Zinc Oxide nanoparticle (ZOnP)
Surface morphologies of ZOnP microstructures were characterized by JEOL JSM-6301 F scanning electron microscope (FESEM, Japan) working at 20 kV. The Fourier transform infrared (FT-IR) spectra of the ZOnP powders were measured by the KBr pellet method with a Shimadzu infrared spectrometer. Crystalline properties of the ZOnP samples were characterized by powder X-ray diffractometry (D/max-2200, Rigaku, Japan).

3. Result And Discussion

The facile preparation of zinc Oxide nanoparticle (ZOnP) was obtained from the cleavage of various zinc-polymer formed from gelatin and zinc nitrate solution. The ZOnP was characterized using XRD, SEM, and FTIR analyses. Fig 1 shows the spectra of zinc oxide nanoparticle which is synthesized using gelatin as a soft template. Figure 1 we can see that be no significant peak change in of ZOnP sample with the common zinc oxide in the previous report. We were expected that the carboxyl groups of the gelatin can interact with zinc element to form gelatin-zinc bonding during mix until the hydrothermal process. The general peak of zinc oxide observed at 1700–1750 cm−1 and 1650–1590 cm−1 as Zn-OH stretching and coordinated Zn-O-Zn that the zinc hydroxyl groups have a high degree of anionic characteristic. Nothing carbonyl group was observed in the sample indicating that gelatin and block copolymer that involve in synthesis has been fully removed from the sample in the decomposition process at high temperature.

![Figure 1](image_url)

**Figure 1.** Spectra FTIR zinc Oxide nanoparticle (ZOnP) sample synthesized using gelatin

Figure 1 shows zinc Oxide nanoparticle have only zinc ion and oxygen with high frequencies which is suggest that all of gelatin part and poly (ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-poloxamer chain totally removed after calcination. However, the main phase of the zinc Oxide nanoparticle sample is an crystalline phase corresponding to crystalline of ZnO. This information has been confirmed by the XRD.
Figure 2 shows the XRD patterns of zinc oxide nanoparticle (ZnOnP). The XRD pattern of the ZnOnP peaks indicate the and identical to the hexagonal phase with Wurtzite structure. The character of ZnOnP peaks obtained at angles 2θ around 31°, 35°, 37°, 48°, 56°, 62°, 68°, and 69° which corresponds to the reflection from 100, 002, 101, 102, 110, 103, 200 to 112 crystal planes. This result has no significant character with the general zinc oxide report in previous research. The zinc oxide crystal in ZnOnP structure seemed unchanged after calcination at high temperatures which is consistent with FTIR result. From Figure 3 it is observed that after the calcination process, gelatin and long chain of block copolymer fully decomposed to the air and have obtained only ZnOnP phase with Wurtzite structure of ZnOnP is connoted that gelatin and block copolymer act as colloidal crystal which plays the role at pore director during the structural formation at growth particle step. zinc particle fabricated only at the hydrothermal process which is the conjugates of gelatin and block copolymer helped the particle growth. In our prediction, zinc particle has been growth massively at colloidal system then condensed to the less particle size after decomposition at high temperature. The nanoparticle morphology of zinc oxide have been observed by SEM.
As seen in Figure 3, the shape of zinc oxide nanoparticle from gelatin observed as slight glass-like structures with almost single small piece have the size range 1-2 µm which is dominated by uniform distribution piece in the surface. From SEM image we can see that sample surface has tiny zinc oxide cluster without slight glass-like structures which are indicating that zinc growth as well as catalyzation work from acid. However, the damage structure was observed up to 25% due to the driving force at particle growth which is indicating acid not fully infiltrated onto zinc ion because of steric effect of the long chain of gelatin. Gelatin and block copolymer have a hydrophobic and hydrophilic site which is act as biotemplate for zinc ion at the hydrothermal process. In our prediction, the structural formation of zinc oxide has been driven by the high affinity of zinc ion site and hydrophobic site of gelatin. The hydrophilic sites of block copolymer act as an anchor chain to stabilize deposition zinc ion. In addition, gelatin not only acts as biotemplate but also pore template because of the pore or new space of zinc oxide fabricated by decomposition of gelatin element such as carbon, hydrogen, and oxygen. The procedure of zinc oxide nanoparticle formation can be seen in Figure 4.

Figure 3. SEM image of ZOnP sample

Figure 4. Scheme of zinc oxide nanoparticle synthesis using gelatin as co-template
Figure 4 shows illustration zinc oxide nanoparticle synthesis. The particle of zinc oxide formation was started from the mixing process between gelatin powder and water molecule with sulfuric acid added as a catalyst. The gelatin solution has been stirred continuously for not only reduce the viscosity of gelatin but also opened the carbonyl chain for exo-templatation initiation. After dissolution, the core of the soft templating process has been ready for used as the core of the pore directing process. The main pore director of zinc oxide has been generated by the rearrangement process between the long chain of gelatin and block copolymer F127. This step obtained by gelatin-F127 which is an gelatin solution carried out at buret apparatus and mixed into F127 solution drop by drop. The solution which is act as soft templating have been ready added into zinc oxide precursor. zinc particle shape has been formatted by gelatin-framework which is Zn-gelatin and Zn-F127 bond produced simultaneously. Hydrophobic and hydro The mixing result tapped into the hydrothermal reactor up to 150 ⁰C for 24 h. The solid was separated from filtrate then the solid part evaporated at 100C overnight. The pale powder then calcined at 500 °C for 5 h. The white resulting powder then labeled as zinc oxide nanoparticle (ZnP).

4. Conclusions

Zinc oxide nanoparticle has been successfully fabricated by a hydrothermal process using gelatin and block copolymer as template. The hydrothermal method was utilized to grow zinc ion to be zinc cluster nanoparticle. The homogenous slight glass-like structure of zinc oxide with size 1-2µm have been generated by the synergy of gelatin and block copolymer substrates of the growth solution. zinc oxide nanoparticle not only has had the uniform shape but also have rich of hydroxyl functional group which is good for many application such as catalysis and separation term. The soft templating system have been generated by hydrophobic and hydrophilic site between gelatin, block copolymer and zinc ion. The results demonstrate that the gelatin could be new biotemplate for zinc oxide nanoparticle synthesis.

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