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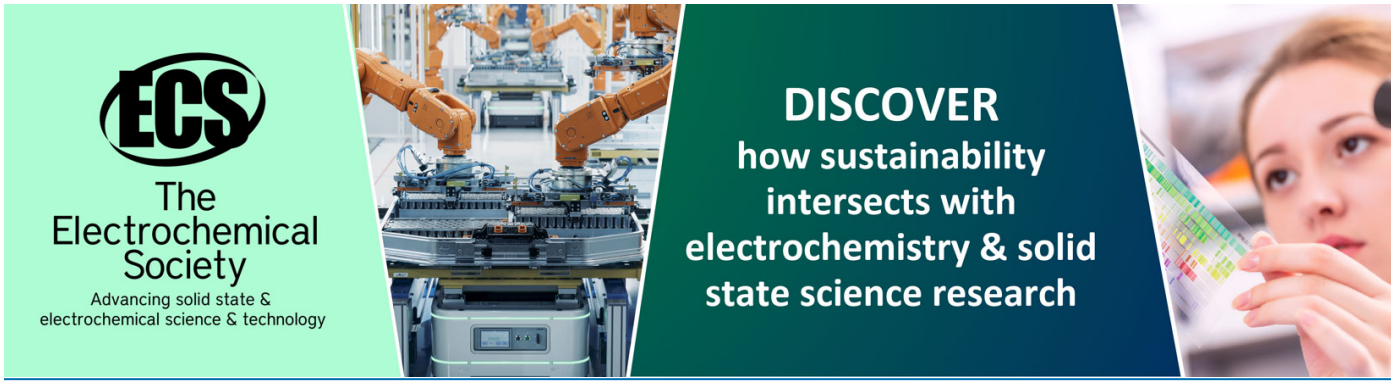

IOP Conf. Series: Journal of Physics: Conf. Series **829** (2017) 012014 doi:10.1088/1742-6596/829/1/012014

Green Synthesis of ZnO Nanoparticles by an Alginate Mediated Ion-Exchange Process and a case study for Photocatalysis of Methylene Blue Dye

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Abstract. In this study, zinc oxide (ZnO) was prepared via extrusion-dripping method through an ion exchange mediated process using sodium alginate. The samples were synthesized at 500 ˚C and 600 ˚C to study the effect of calcination temperature. The morphology, microstructure and optical activity of the calcined ZnO nanoparticles were analyzed by TGA, FESEM and XRD. It was found that ZnO nanoparticles synthesized at 600 ˚C was of higher purity with high crystallinity. To enhance the photocatalytic efficiency of zinc oxide, ZnO/NCC films were synthesized at varying ZnO loading fractions of 10 wt%, 15 wt%, 20 wt% and 25 wt% and were evaluated by photodegradation of Methylene blue dye and the highest dye percentage removal is found to be 96% which is obtained at ZnO loadings of 25 wt%. The usage of ion-exchange process has shown promising results in producing ZnO of desirable characteristics.

1. Introduction

Over the past decades, water pollution has become one of the major issues as it contains heavy ions and reactive dyes from industries. The huge discharge amount of waste water has driven researchers to solve this environmental problem. Conventional methods such as precipitation, air stripping, adsorption, reverse osmosis and ultra-filtration are non-destructive techniques as they only transfer the non-biodegradable matter into sludge [1] where only phase change occurs. This leads to pollution and the need for further treatment arises which leads to additional costs.

Zinc Oxide (ZnO) is an n-type semiconductor notable for its wide band gap (3.2 eV), large binding energy (60 meV), non-toxic nature and similar photodegradation mechanism to TiO_2 [2] which allows it to be a potential alternate photocatalyst. Many techniques have been employed to synthesis nanosized ZnO, namely sol-gel processing [3], co-precipitation [4], hydrothermal growth [5] and thermal decomposition [6]. Despite the importance of emphasizing on the geometry, size and chemical homogeneity, the overall feasibility and simplicity of the ZnO synthesis processes are also greatly considered to improve the efficiency of the fabrication process. Most of these synthesizing techniques are usually associated with energy consuming and multi-step time methods which are not environmentally friendly [7].

Extrusion dripping is a novel technique which mainly comprises of the extruding of desired solution through a narrow passageway and dripping it into a gelation bath. Mono-dispersed spherical particles are formed when the liquid drop enters the gelation bath due to effect of viscous-surface tension forces and impact-drag forces which preserves the drop shape [8]. Previous study on the preparation of spherical Ca-Alginate beads encapsulated with oil was successfully performed through extrusion dripping by Chan [9] where a stable alginate-oil emulsion was obtained. Furthermore, spherical chitosan-HNT beads were successfully produced through extrusion dripping which shows a high tendency of crosslinking copper ions [10]. Various modifications have been extensively researched in the recent years on synthesis of ZnO nanoparticles as its properties provide promising application for photocatalysis. Although ZnO finds a wider application in terms of availability, low cost and favorable gap energy, it possesses certain drawbacks as a semiconductor photocatalyst, namely the difficulty in the separation of ZnO powder after the degradation reaction, formation of aggregation at high loading and difficulty in application to continuous flow systems [11].

Cellulose, the most abundant biopolymer, is a potential alternative support for fabricating nanocomposites with semiconductors due to its thermal stability and insolubility in ordinary solvents [12]. As a renewable biomass material, cellulose is degradable, environmental friendly and cost effective. Cellulose is a linear polysaccharide with long chains which consists of β-D-glucopyranose units joined with β-1,4 glycosidic links. The repeating chains of cellulose contain methylol and hydroxyl groups as its functional group. The high amount of active sites present in the structure of cellulose and high cation-exchange capacity of its functional groups enables the coordination of metal ions on cellulose [13].

The improved thermal, mechanical stability and solvent resistibility of the hybrid in the presence of cellulose leads to a recyclable photocatalyst. However, the incorporation of support to obtained porous inorganic metal oxides is difficult due to the high reactivity of transition metal which complicates the synthesis process [14]. In this study, zinc oxide nanoparticles will be synthesized via an extrusion dripped ion-exchange mediated process and templated on nanocrystalline cellulose (NCC) as a new polymerizable support. The application of NCC as a green material allows a more eco-friendly approach to the conventional synthesizing method. The effects of calcination temperature on the characteristics of the synthesized zinc oxide were studied before subjected to application tests by analyzing its photocatalytic activity in removing Methylene Blue dye in aqueous solution.

2. Materials and Methods

2.1. Materials

Zinc nitrate tetrahydrate (Zn(NO3)2.4H2O) with molecular weight of 261.44 g/mol and sodium alginate were purchased from Merck and Sigma-Aldrich respectively. Furthermore, nanocrystalline cellulose with sulphur content of 0.89 wt% was obtained from University of Maine. All the chemicals used in the study were of Analytical Grade.

2.2. Preparation of ZnO nanoparticle

2.0 wt.% sodium alginate solution was prepared by mixing with deionised water under a digital mechanical stirrer (IKA-RW 20, IKA® Works, Malaysia). Similarly, stoichiometric amount of zinc nitrate solution was prepared by dissolving zinc nitrate tetrahydrate in deionised water. ZnO nanoparticles were then synthesized by extrusion dripping by drop wise addition of 10 mL alginate solution, controlled using syringe pump to 6.25 mL of zinc nitrate solution under magnetic stirring at 200rpm. The suspension was then stirred slowly for 15 hours to ensure the ion-exchange process and stabilize the nanoparticles formed. The nanoparticles were then separated from the solution through a sieve and washed with deionised water. Then, the nanoparticles were collected and oven-dried at 40°C for 24 hours prior to calcinations in furnace at temperature 500°C and 600 °C for 4 hours with a heating rate of 1°C/min. The morphology of the prepared ZnO powder is then analysed through FE-SEM (Hitachi Ultra-high resolution SU8010) by subjecting to a platinum coater (Quarum Q150R S).

Furthermore, the crystal structure of the powder specimens was observed by using X-ray Diffraction (Bruker D8 Discover) at room temperature by subjecting to Cu-Kα radiation.

2.3. Preparation of ZnO/Nanocrystalline(NCC) microfilm

The synthesized ZnO nanopowders were used to fabricate a polymeric NCC microfilm containing dispersed ZnO nanopowders. 2g of NCC was dispersed in 20 mL deionised water under an ultrasonic probe (QSONICA, 700 W, USA) where the process time was set as 6 minutes with 3 seconds pulse whereas the ultrasound amplitude is fixed at 70% under constant frequency. Different amount of ZnO nanopowders were then calculated and added based on various ZnO loading fractions of 10wt%, 15wt%, 20wt% and 25wt% before undergoing ultrasound for another 5 minutes to obtain the mixed slurry. The mixed product was then spread out on a glass plate to make a thin layer (10mL) before polymerizing in an oven at 90^{o}C overnight. The ZnO/NCC microfilm is obtained after pulverizing the dried product into small pieces by a kitchen blender.

2.4. Photocatalytic study of ZnO/NCC microfilm

The degradation studies of the microfilm were conducted in a reactor fitted with a 5W lamp as an ultraviolet light source. 0.15g of ZnO/NCC microfilm with various ZnO loading fractions was added to 30 ml of 100 ppm Methylene Blue solution and left to be magnetically stirred during the photodegradation. The concentration of MB was then analysed at given intervals by monitoring the absorption peak at 665 nm using a UV-vis spectrophotometer.

3. Results and Discussion

3.1. Microstructural Analysis

The FESEM images shown in Figure 1A and 1B reveals the surface morphology of the nanoparticles and the effect of calcination temperature. It is evident that ZnO nanoparticles obtained from this study were spherical shaped and relatively uniform in size. However, nanoparticles synthesized at 500^{o}C exhibits moderate agglomeration with lesser spherical particles. This is due to the low hydrolysis rate of precursor at low calcination temperature which leads to the formation of agglomerates due to a large difference in growth times between the non-aggregated nuclei and aggregated nuclei. The growth times between nuclei decreases as the calcination temperature is increased which leads to less agglomerates at 600 ^{o}C [15]. Furthermore, Figure 1C shows the FESEM image of the surface of the ZnO/NCC film after overnight oven drying. It was observed that the obtained film possesses a considerably smooth surface with little agglomerations.

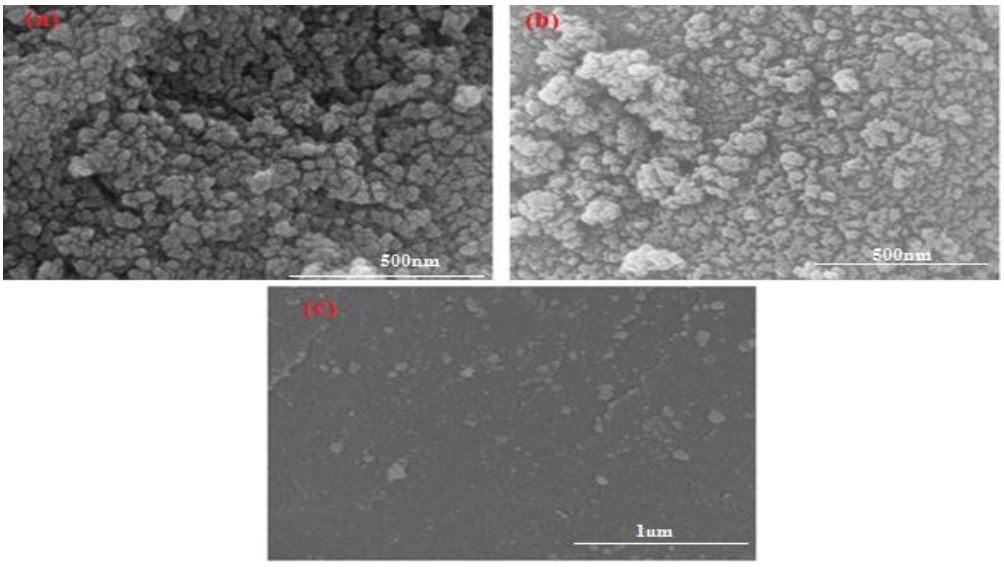

Figure 1: FE-SEM images of ZnO nanoparticles calcinated at (a) 600°C, (b) 500°C and (c) ZnO/NCC microfilm (25wt%)

3.2. X-ray Diffractogram Analysis

Figure 2 shows the XRD peaks obtained for zinc oxide nanoparticles calcined at 500 °C and 600 °C. It was observed that the product shows Bragg reflections of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) at 31.5°, 34°, 36°, 47°, 56.1°, 61.77°, 67.48° and 68.15° which indicates the formation of ZnO with wurtzite hexagonal phase [16]. As seen from Figure 2, it is evident that the peaks become more intense and sharper at higher calcination temperatures. The presence of high and narrow shaped peaks highlight that ZnO nanoparticles possess high crystallinity and low surface defects [17]. Furthermore, no diffraction peaks from other impurities were observed in the XRD diffractograms which indicates that the ZnO product obtained after the calcination were of ultrapure phase.

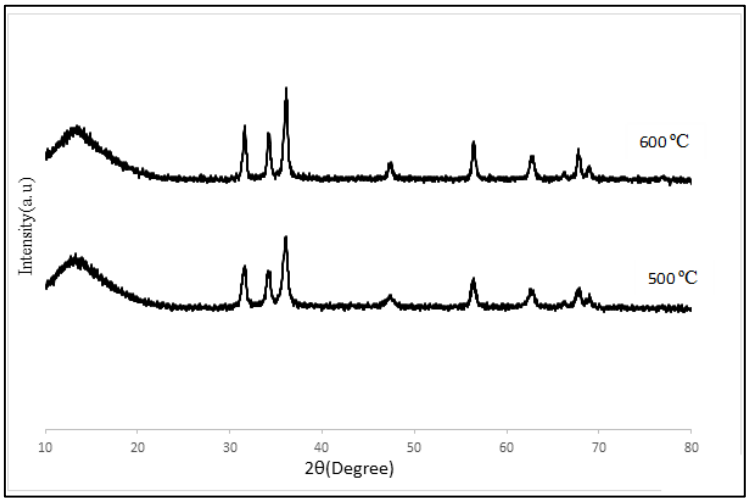

Figure 2: Comparison of XRD results for zinc oxide samples synthesized at (a) 600°C and (b) 500°C

3.3. Thermalgravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on the bead samples prior to calcination to determine the suitable starting temperature for the calcination process. Figure 3 shows the relationship between percentage weight change and temperature for the sample before calcination. By analysing the graph, it is evident that there are two major degradation steps involved. The first drop in weight loss takes place at 170 ºC, which could be the loosely bond water or moisture entrapped within the sample. The second drop demonstrates a major weight loss at 390ºC, and this could be attributed to the near complete decomposition of sodium alginate, which is the precursor used in this study. At 445 ºC, the change in weight loss has become insignificant, and most of the sodium alginate present has been converted to carbonaceous products, leaving behind pure metal oxide as residue [18]. It is evident that the organic compound has completely decomposed after 450ºC, therefore 500 ºC was selected as the lower limit of calcination temperature of the extrusion dripped beads.

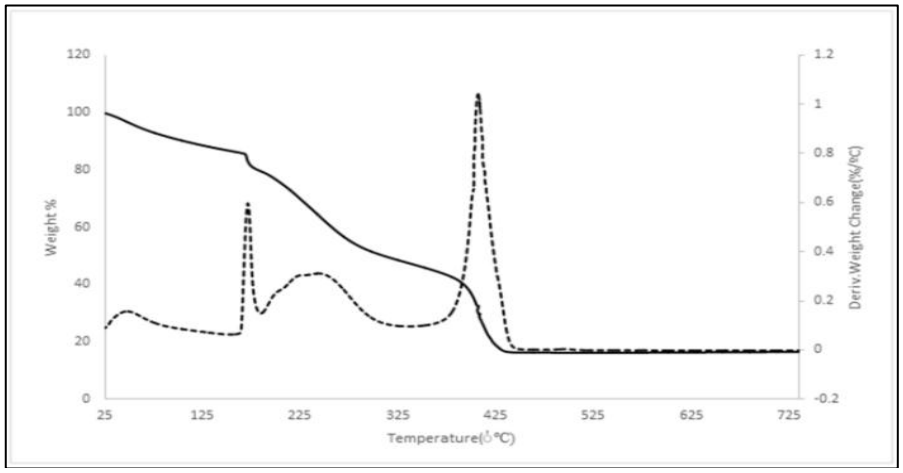

Figure 3: TGA results of Sodium Alginate-Zinc Nitrate beads

3.4. Photocatalytic Application

Figure 4 shows the degradation behaviour of methylene blue in ZnO/NCC microfilm loaded with 15wt%, 20wt% and 25wt% ZnO loadings. The percentage removal of methylene blue dye was calculated using the following equation:

$$\text{Percentage Removal} = \frac{C_o - C_T}{C_o} \times 100 \quad (1)$$

where C_o is the initial concentration of dye (mg/L) and C_T is the concentration of dye (mg/L) at different contact times. It is very evident from the trend of the graph that the percentage removal of dye is increased with increasing weight loadings of ZnO where the highest percentage dye removal were found to be 96% using 25wt% ZnO loading. As seen in Figure 1C, it is clear that the ZnO particles are densely residing on the outer surfaces of the film where it plays a major role in the photodegradation process as they accept photons and generate electron- holes for the oxidative decomposition of methylene blue. The enhancement in photodegradation activity which is observed at high ZnO loading could be attributed to the increased in total surface area and total number of active sites on the catalyst surface. This leads to the increase in the number of hydroxyl and superoxide radicals in the catalyst material which facilitates the overall degradation of methylene blue dye [19].

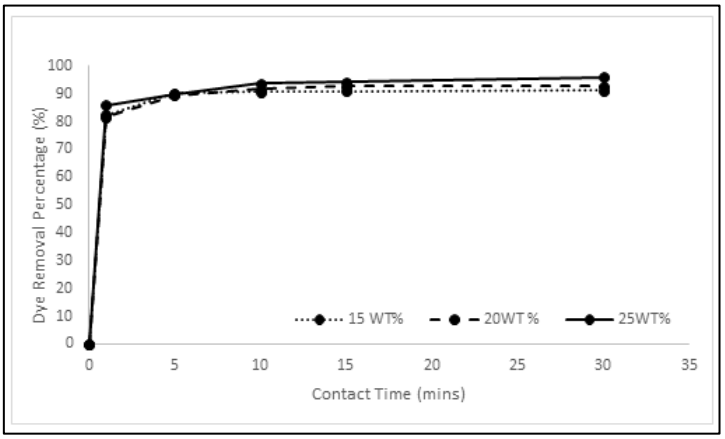

Figure 4: Percentage Removal of Methylene Blue by ZnO/NCC microfilm loaded with (a) 15wt%, (b) 20wt% (c) 25wt% loading fraction

4. Conclusion

Successful synthesis of the ZnO nanoparticles was achieved using an alginate mediated ion-exchange process for the preparation of a ZnO/NCC microfilm where the photodegradation studies of methylene

blue dye is conducted as a case study. The nanoparticles formed at the calcination temperature of 600°C were found to provide the most desirable characteristics as shown from the results obtained from FE-SEM and XRD. Furthermore, the microfilm with 25wt% ZnO loading showed the highest methylene dye removal where the percentage removal is found to be 96%. The application of green materials provides a more eco-friendly approach to the current technologies in wastewater treatment.

Acknowledgement
The authors would like to acknowledge Ministry of Education Malaysia (MOE) for providing research funding under the FRGS scheme number FRGS/2/2014 TK05/MUSM/02/1. Furthermore, the authors would like to thank Monash University Malaysia for all the analytical support provided. Besides that, Ms Indi Chandra Harrisa is also highly appreciated for her assistance throughout the project.

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