THE PHILIPPINE-AMERICAN Academy of Science & Engineering

Surface Modification of Ceramic through HCl treatment and its effect on the Growth of Spray-Pyrolized ZnO

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ABSTRACT

We investigated the effects of hydrochloric acid (HCl) treatment of ceramic and determine the effect of molarity of precursor solution on the morphology of zinc oxide (ZnO) grown on the ceramic substrate. We hypothesize that the acidic treatment of the ceramic surface leaves charges that act as a seeding layer for the growth of ZnO. We were able to verify our hypothesis by synthesizing ZnO nanostructures via spray pyrolysis under different molarities of zinc chloride solution. The growth was confirmed using energy-dispersive x-ray spectroscopy (EDX) and scanning electron microscopy.

KEYWORDS: Surface Modification; Ceramic; Spray Pyrolysis; Zinc Oxide

1 INTRODUCTION

Zinc oxide, a hexagonal wurtzite crystal in ambient conditions, is known for its versatility for various applications due to its electrical, gas sensing and for its anti-bacterial properties (Cuevas et. al, 2013). This material can be easily manufactured due to its low cost. Synthesis of this material, via Modified Spray Pyrolysis Deposition Technique, can be used to coat the substrate for enhancing its properties.

In this study, a kaolinite ceramic was used as a substrate. Recent work has led to the development of kaolinite ceramics as water filters with submicron pores. The antibacterial property of ZnO can be added as a surface coating for the ceramic to improve its effectiveness (Wahab, et al., 2012). In order to achieve this, surface modification of the ceramic by immersion in acid was required.

2 METHODOLOGY

2.1 Substrate Preparation

The idea in the surface modification involves the use of an acid to charge the surface of the kaolinite ceramic, producing hydroxide bonds its surface, effectively making the surface positively charged. The kaolinite ceramic was submerged in a 37% hydrochloric acid solution to modify its surface. After 16 hours of submersion, the substrate was then rinsed in deionized water. The prepared substrate was heated to 197.3±6.52^{o}C and was placed inside a soda can to create a thermal equilibrium environment.

2.2 Precursor Preparation

A $ZnCl_2$ solution was used as the precursor of the zinc oxide growth. $ZnCl_2$ powder was dissolved in deionized water to produce different molarities of $ZnCl_2$ solutions. 1M of HCl solution was added until

the $ZnCl_2$ solutions has a pH of 6.5. The solution was ultrasonicated for ten minutes to ensure a uniform dispersion of the salt in the solution.

2.3 Modified Spray Pyrolysis Setup

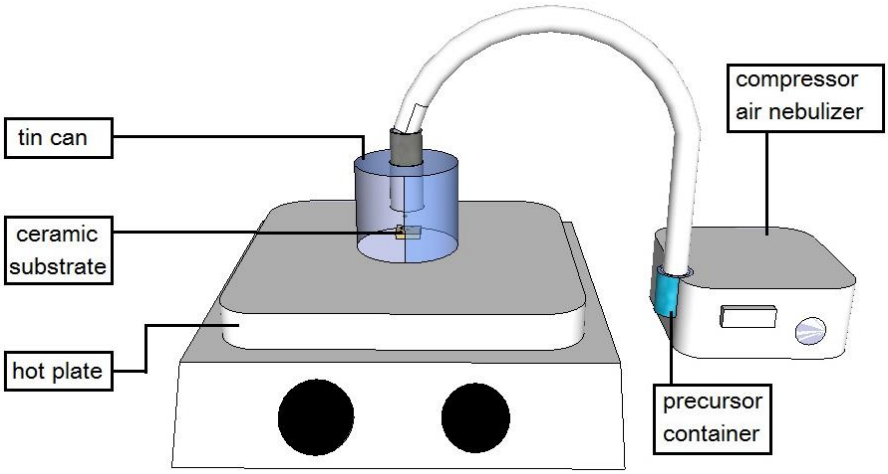

Figure 1: Schematic of Modified Spray Pyrolysis Setup using a Nebulizer

This experiment used an Omron compressor air nebulizer, as an atomizer, for the spray pyrolysis setup. This nebulizer compresses ambient air and vibrates at high frequency to turn and atomize the solution into mist. The mist was directed through a tube wherein the prepared ceramic substrate was placed directly below. A tube of 30 mm in diameter was chosen to minimize the cooling effect of the carrier gas as it transports the mist to the heated substrate. Also, a 30 mm substrate-nozzle distance was set.

2.4 Synthesis of ZnO nanostructures

The hot plate, with a prepared substrate, was heated to 197.3±6.52^{o}C prior to spraying. The prepared $ZnCl_2$ precursor solution was poured into the nebulizer container, subsequently, turning on the nebulizer to start deposition. After 6 hours of deposition, samples grown using 0.01M, 0.05M, and 0.10M of $ZnCl_2$ precursor solution was obtained. This deposition time was chosen due to the low flow rate of the nebulizer, 0.13ml/min. Samples were immediately stored in a pillbox upon removal from the hot plate after the desired deposition time for sample characterization. The growth was examined using Energy-dispersive X-ray Spectroscopy (EDX) and Scanning Electron Microscopy.

3 RESULTS AND DISCUSSION

A hypothesis was proposed wherein kaolinite ceramic was positively charged through acidic treatment. A possible deposition mechanism occurs when the atomized droplet reaches the heated ceramic substrate. Higher temperature causes a fairly stable zinc hydroxide to form within the droplet (Beverskog & Puigdomenech, 1997). As more hydroxide bonds to the zinc hydroxide, it will decompose to form a negatively charged droplet with zinc oxide nuclei. The droplet will move towards positively charged sites that serve as a seeding layer for the zinc oxide nanoparticles to form as shown in Figure 2.

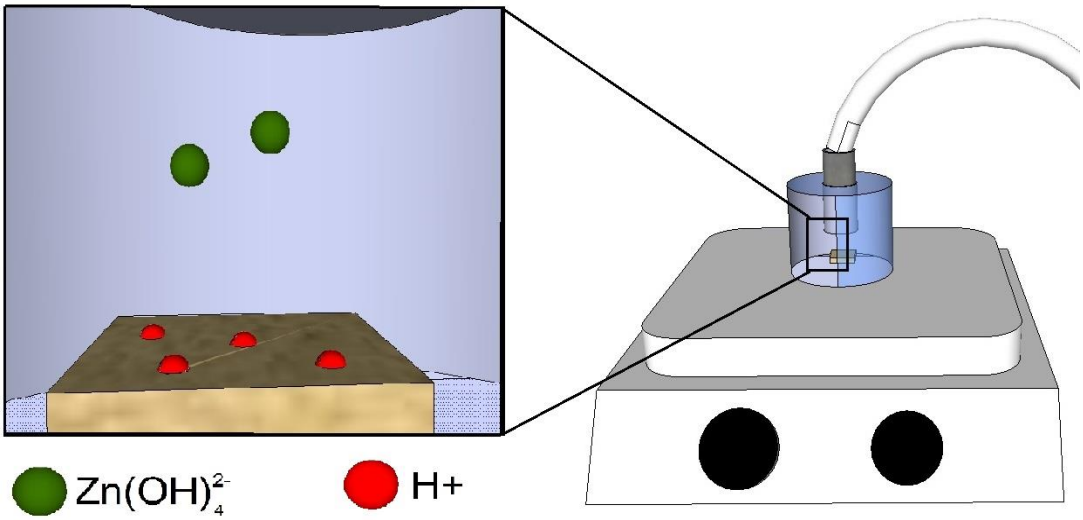

Figure 2: Proposed Deposition of ZnO via Attraction of $Zn(OH)_4^{2-}$ droplets to the H^+ seeding layer

The formation of ZnO can be represented through the following chemical reactions:

$$ZnCl_2 + H_2O \rightarrow Zn(OH)_2 + 2HCl \quad (1)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (2)$$

$$Zn(OH)_4^{-2} + H^+ \rightarrow ZnO + 2H_2O \quad (3)$$

Equations (1)-(2) above happens inside the droplet. The HCl acid produced in (1) turned into a vapour when it was exposed to the heated environment inside the can. In equation (2), the hydroxyl came from the dissociation of water from the solution.

In Equation (3), the combination reaction of the $Zn(OH)_4^{2-}$ and H^+ will yield zinc oxide and water as a by-product. The remaining water will be evaporated due to the surface temperature of the ceramic.

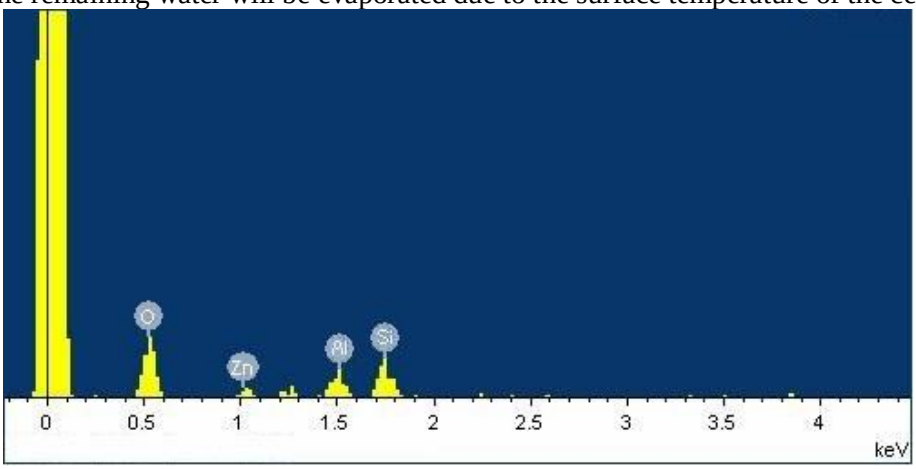

Figure 3: EDX spectra of 0.1M $ZnCl_2$ Solution deposited on treated ceramic

Figure 3 shows an EDX measurement of a sample grown using 0.1M $ZnCl_2$ solution. The measurement verifies the presence of zinc and oxygen, possibly from the formed zinc oxide particles successfully deposited on the kaolinite ceramic substrate. The identified aluminum and silicon peaks on EDX measurement are inherently found on kaolinite.

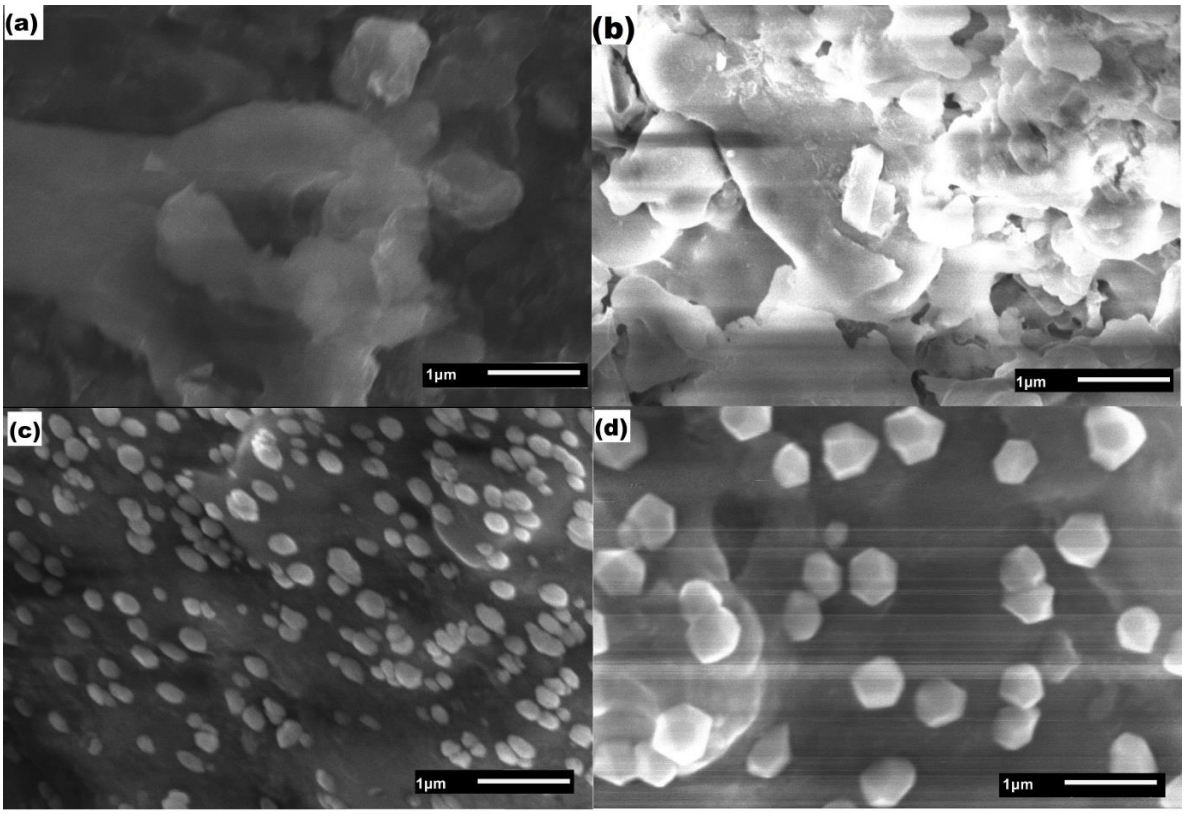

Figure 4: SEM images of ZnO nanoparticles in (a) untreated, and treated ceramic with molarities (b) 0.01M, (c) 0.05M and (d) 0.10M.

The SEM images in Figure 4 show the deposited ZnO nanostructures in untreated and treated ceramic. The untreated ceramic shows no sign of ZnO deposition for all molarities used. Growth of ZnO was observed on a treated ceramic when the precursor molarity was 0.05M and 0.10M. A hexagonal structure with sizes, 0.54±0.09µm, was observed at 0.10M with densities of 0.38 particles per square microns. For 0.05M, nanoparticles of 0.21±0.07µm in size were observed with a particle density of 2.18 per square microns. The 0.01M did not yield any ZnO nanoparticles, probably due to the diluteness of the concentration used.

4 CONCLUSION

The theory is that the acidic treatment of the ceramic surface leaves charges that act as a seeding layer for the growth of ZnO. We have demonstrated that the theory works and that the synthesis of ZnO nanostructures via spray pyrolysis is possible. Future studies should include optimization, where the ZnO nanoparticles are conformally grown on the ceramic surface.

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