

Growth Mechanisms of Silica-Modified Polyaniline and Zinc Oxide Nanostructures on Glass Substrates

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Abstract—Silica-modified polyaniline (SM-PANI) thin films were prepared on glass substrates by oxidative polymerization. Zinc oxide (ZnO) nanostructures were grown on top of SM-PANI thin films by chemical bath deposition using zinc sulphate and varying concentrations of ammonium hydroxide. SM-PANI and ZnO nanostructures were characterized by scanning electron microscopy (SEM). SEM images revealed surface morphology of the nanostructures: SM-PANI forming rod-like nanostructures, and ZnO forming sea-urchin-like nanostructures grown on top of SM-PANI. Characterization results also revealed that ammonium hydroxide concentration can modify ZnO nanostructures grown on top of SM-PANI. For 1M concentration, hexagonal rod-like SM-PANI and sea-urchin-like ZnO nanostructures were present; for 3M concentration, flake-like ZnO nanostructures were grown with deformed rod-like SM-PANI. This mechanism can be explained via competition between growth of SM-PANI and ZnO nanostructures, and etching process during the chemical bath deposition of ZnO at different concentrations of ammonium hydroxide.

Index Terms—Ammonium hydroxide, nanostructures, silica-modified polyaniline, zinc oxide.

I. INTRODUCTION

In the last few decades, since the rise of nanotechnology initiative, nanostructures have been widely developed as a leading edge in science and technology. Reducing the size of the materials in their nanometer scale provides opportunities to further study their novel electrical, mechanical, chemical and optical properties [1]. The synthesis of nanostructures is a growing field of research for various important applications with emphasis on developing nanostructures via low cost processes [2]. Among the nanostructures that have been studied intensively, ZnO has become the most active area of research and is dubbed to be the most important nanomaterial after the carbon tubes [3]. This is due to the unique properties of ZnO such as a wideband gap of 3.37 eV suitable for short wavelength optoelectronic applications, and high exciton

energy of 60 meV that can ensure efficient excitonic emission at room temperature [1]. Furthermore, ZnO can easily form a diverse group of growth morphologies such as nanocombs, nanorings, nanobelts, nanowires among others, which have the potential for catalysis or solar cell applications due to their high specific surface area and reactivity [4].

Recently, hybrid nanocomposites have been developed to enhance the advantages of conducting organic polymers (COPs) by combining it to an inorganic material (such as ZnO). The multifunctionality observed from hybrid nanocomposite materials empowers their application in a wide variety of energy-related devices particularly solar cells [5]. The key factor behind the operation of hybrid nanocomposites is the close contact between the inorganic material and COPs [6].

For COPs, polyaniline (PANI) is the most promising owing to its high conductivity, environmental stability and ease to prepare [7]. Mechanisms of the formation of PANI nanostructures have recently been reviewed and assessed for various applications as COP [8]. PANI has three individual forms – leucoemeraldine, emeraldine, and pernigraniline. The protonated emeraldine is obtained as a product of polymerization. Its conversion to an emeraldine base after treatment with alkali is one of the most famous reactions of PANI: the reduction of emeraldine to leucoemeraldine and the oxidation to pernigraniline [9]. Of the three forms, PANI in its emeraldine form is the most fabricated because it has the most conductive state with its environmental stability, and straightforward fabrication.

Furthermore, PANI is incorporated with silica, which acts as limiting director for growth of PANI nanostructures on the substrate. Study shows that silica enhances the agglomeration of polyaniline on the substrate [10], [11]. The addition of colloidal silica into the polymerization mixture of aniline has been explored by Stejskal, et al. [12] to prevent the occurrence of macroscopic agglomeration that led to formation of thinner PANI films (see Fig. 1.). When PANI is deposited in the presence of silica, the resulting PANI and silica nanocomposite possessed higher surface areas, larger redox charge capacities, and higher doping levels, thus enhancing its optical properties [10], [12].

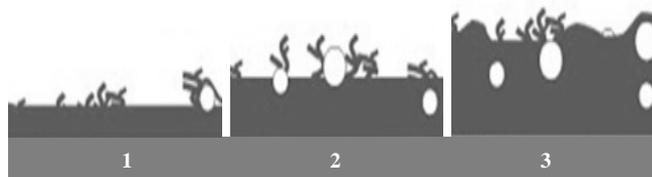


Fig. 1. Growth mechanism of PANI modified with colloidal silica.

Manuscript received January 12, 2013; revised March 18, 2013. This work was supported in part by the Department of Science and Technology Accelerated Science and Technology Human Resource Development Program and the Commission on Higher Education - Philippine Higher Education Network in the Philippines.

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In this study, hybrid nanocomposites have been fabricated by combining SM-PANI and ZnO. Oxidative polymerization of aniline with ammonium peroxodisulphate (APS) as an oxidizing agent was carried out to synthesize SM-PANI nanostructures. On the other hand, chemical bath deposition was employed to synthesize ZnO nanostructures on top of SM-PANI using zinc sulphate and varying concentrations of ammonium hydroxide.

II. EXPERIMENTAL PROCEDURES

A. Preparation of Glass Substrates

SM-PANI and ZnO nanostructures were grown on rectangular glass slides with dimension 26mm × 76mm × 1mm. Glass slides which serve as substrates were washed with acetone, ethanol, 1M hydrochloric acid, and distilled water. Acetone removes oils and inorganic substances present in the substrate, while the ethanol and 1M hydrochloric acid remove the residues of acetone and the oxides in the substrates, respectively. The substrates are then dried at room temperature after cleaning.

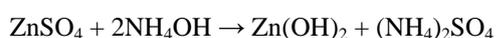
B. Synthesis of Silica-Modified Polyaniline Nanostructures

Synthesis of silica-modified PANI nanostructures is carried out by the oxidative aniline polymerization and incorporation of silica extracted from rice husks ash. To obtain the best result of PANI, a stoichiometric peroxodisulphate/aniline ratio of 1.25 is maintained. This minimizes the presence of residual aniline. To achieve the stoichiometric ratio, of pure liquid aniline and 12M HCl is dissolved in distilled water. Upon achieving homogeneity between aniline and 12M HCl, silica powder from rice husks is added to the solution.

Another solution is prepared by dissolving APS in distilled water. Both solutions are left for an hour at room temperature. The solutions are then rapidly mixed inside the beaker. The substrates are placed inside the beaker as reaction vessel where polymerization is carried out for five hours. When the post-polymerization is achieved, indicated by the rapid decrease of temperature after hitting the highest temperature, the substrates are immediately removed and washed with 0.2M hydrochloric acid and ethanol to remove the residual monomer, oxidants and its decomposition products; and to remove low-molecular-weight organic intermediates and oligomers, respectively [13]. The samples are then dried at room temperature.

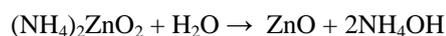
C. Synthesis of Zinc Oxide Nanostructures

Chemical bath deposition is carried out to synthesize ZnO nanostructures. The ammonium zincate bath, used for deposition of ZnO is prepared by adding ammonium hydroxide (25% ammonia solution) to an aqueous solution of zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) which will react to the chemical equation:



where a white precipitate is formed. The ammonium zincate bath used for the deposition contains ammonium sulphate. It

appears that while zincate precipitates as ZnO in presence of high concentration of water when dipped with hot bath, the sulphate goes into the solution to its high solubility in water as in the chemical equation:



The substrates are then synthesized at different concentrations of ammonium hydroxide for comparison (1M and 3M). Ammonium hydroxide is added to distilled water. Another solution is prepared by mixing zinc sulphate powder with distilled water. The two solutions are then stirred in a beaker, placed in the bath, using a magnetic stirrer having a 360 rpm. After 30 minutes, the bath is heated, maintaining the temperature to 70°C for 5 hours. The procedure is carried out following the standard chemical bath deposition method [14]. After 5 hours, the substrates are then dried at room temperature.

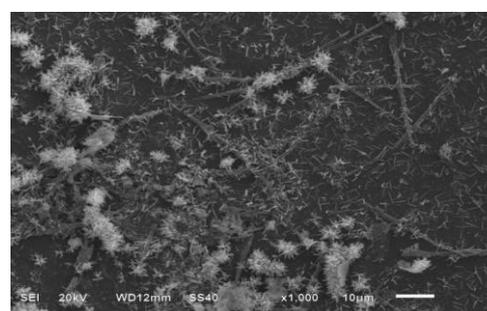
D. Characterization of SM-PANI and ZnO Nanocomposite

The fabricated nanocomposites were characterized with SEM (JEOL Model JSM-6510LA) for its surface morphology and elemental analysis.

III. RESULTS AND DISCUSSION

A. Morphology of SM-PANI and ZnO Nanocomposites

The morphologies of the nanocomposites produced from the oxidative polymerization of SM-PANI and chemical bath deposition of ZnO are shown in Fig. 2 and Fig. 3.



(a)

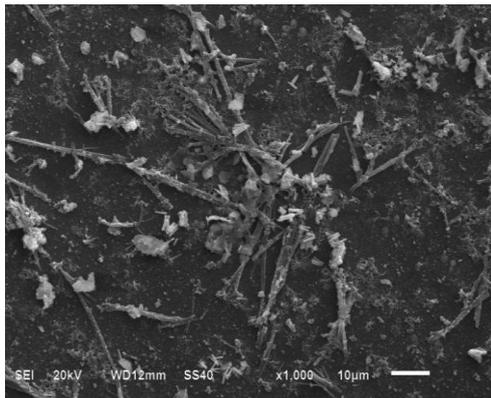


(b)

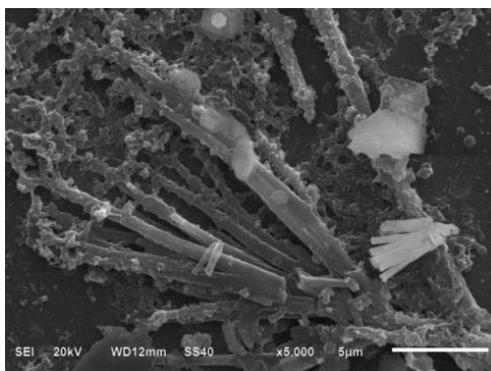
Fig. 2. SEM micrographs of SM-PANI and ZnO nanocomposites with 1M concentration of ammonium hydroxide at (a) higher magnification (1000x) and (b) lower magnification (5000x).

Fig. 2 shows the morphology of the nanocomposites at 1M

concentration of ammonium hydroxide. SEM image reveals the presence of rod-like SM-PANI nanostructures and sea-urchin-like ZnO nanostructures.



(a)



(b)

Fig. 3. SEM micrographs of SM-PANI and ZnO nanocomposites with 3M concentration of ammonium hydroxide at (a) higher magnification (1000x) and (b) lower magnification (5000x).

1) Morphology of SM-PANI and ZnO nanostructures in 1M ammonium hydroxide

Instead of the formation of PANI precipitates on the substrates that usually leads to the formation of non-uniform agglomerates [15], the presence of dispersed silica produces PANI nanostructures. Furthermore, the morphology of SM-PANI indicates that there is an increase of surface area when silica particles are present in the polymerization of aniline which served as small adsorbing substrates initiating the growth of uniform particles in bulk polymerization. In the presence of ZnO nanostructures with 1M concentration of ammonium hydroxide, the morphology of SM-PANI indicates presence of rod-like nanostructures. The formation of SM-PANI rod-like nanostructures in the nanocomposite shows uniform agglomeration due to aniline oligomers which initiated the growth of PANI with silica.

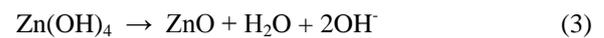
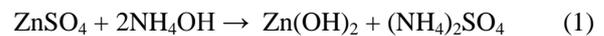
On the other hand, ZnO nanostructures with 1M concentration of ammonium hydroxide are accumulated at the center (seed nuclei) and are grown on different direction forming sea-urchin-like nanostructure. Previous work reported that this sea-urchin-like structure is attributed to the $Zn(OH)_2$ formed after mixing the $ZnSO_4$ and NH_4OH which served as the seed nuclei on the substrate [16], [17].

2) Morphology of SM-PANI and ZnO nanostructures in 3M ammonium hydroxide

Fig. 3 shows the morphology of SM-PANI and ZnO nanocomposites with 3M concentration of ammonium hydroxide. Instead of producing uniform rod-like nanostructures of SM-PANI, the nanostructures are deformed. There is uneven agglomeration of structures on the substrates. On the other hand, ZnO nanostructures apparently became flake-like which can be attributed to the etching effect of ammonium hydroxide. With 3M concentration of ammonium hydroxide, the surface of the substrates is covered with flake-like structures which grow randomly in different directions.

B. Etching Process of Ammonium Hydroxide on SM-PANI and ZnO Nanocomposites

The diameter of nanostructures increases 1 μm as the concentration of ammonium hydroxide increases [18]. The nanostructures composing the sea-urchin-like ZnO is attributed to the increase of ammonium hydroxide concentration which can be explained in the following chemical reaction:



The ZnO will react to water producing $Zn(OH)_4$ with zinc ion which supply free Zn^{2+} ions to combine with O^{2-} to form ZnO as shown in Equation (3). As the amount of zinc hydroxide increases, the zinc complex $Zn(OH)_4$ with zinc ion also increases. This decreases the number of Zn^{2+} ions that will combine to O^{2-} to form nanostructures. At higher concentration, there is an excess of OH^- on the solution that attacks the nanostructures on the substrates.

IV. CONCLUSION

SM-PANI and ZnO nanostructures were successfully grown on glass substrates. SM-PANI nanostructures were synthesized via oxidative polymerization; ZnO nanocomposites via chemical bath deposition. SEM images revealed surface morphology of the nanostructures: SM-PANI forming rod-like nanostructures, and ZnO forming sea-urchin-like nanostructures grown on top of SM-PANI. Characterization results also revealed that ammonium hydroxide concentration can modify ZnO nanostructures grown on top of SM-PANI. For 1M concentration, hexagonal rod-like SM-PANI and sea-urchin-like ZnO nanostructures were present; for 3M concentration, flake-like ZnO nanostructures were grown with deformed rod-like SM-PANI. This mechanism can be explained via competition between growth of SM-PANI and ZnO nanostructures, and etching process during the chemical bath deposition of ZnO at different concentrations of ammonium hydroxide.

ACKNOWLEDGMENT

Authors would like to thank CHED-PherNet for partial support in this work. CALR would to acknowledge the Department of Science and Technology- Science Education Institute in the Philippines for the scholarship grant.

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