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Effect of ZnO Addition on Structural Properties of ZnO-PANi/Carbon Black Thin Films

(Kesan Penambahan ZnO ke Atas Sifat Struktur Filem Nipis Zno-PANi/Karbon Hitam)

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ABSTRACT

The aim of this project was to investigate the effect of ZnO addition on the structural properties of ZnO-PANi/carbon black thin films. The sol gel method was employed for the preparation of ZnO sol. The sol was dried for 24 h at 100°C and then annealed at 600°C for 5 h. XRD characterization of the ZnO powder showed the formation of wurtzite type ZnO crystals. The ZnO powder were mixed into PANi/carbon black solution which was dissolved into M-Pyrol, N-Methyl-2-Pyrrolidinone (NMP) to produce a composite solution of ZnO-PANi/carbon black. The weight ratio of ZnO were 4 wt%, 6 wt% and 8 wt%. The composite solutions were deposited onto glass substrates using a spin-coating technique to fabricate ZnO-PANi/carbon black thin films. AFM characterization showed the decreasing of average roughness from 7.98 nm to 2.23 nm with the increment of ZnO addition in PANi/carbon black films. The thickness of the films also decreased from 59.5 nm to 28.3 nm. FESEM image revealed that ZnO-PANi/carbon black thin films have changed into agglomerated surface morphology resulting in the increment of porosity of the films.

Keywords: Sol gel method; spin coating technique; structural properties; ZnO thin film

ABSTRAK

Tujuan kertas ini dijalankan adalah untuk mengkaji kesan penambahan ZnO ke atas sifat dan struktur filem nipis ZnO-PANi/karbon hitam. Serbuk ZnO disediakan melalui kaedah sol gel dengan sol tersebut telah dikeringkan selama 24 jam pada suhu 100°C dan diikuti dengan proses sepuh lindap pada suhu 600°C selama 5 jam. Pencirian XRD terhadap serbuk ZnO menunjukkan pembentukan hablur ZnO jenis wurzite. Kemudian, serbuk ZnO tersebut dicampur dengan larutan PANi/karbon hitam yang telah dilarutkkan di dalam M-Pyrol, N-Methyl-2-Pyrrolidinone (NMP) bagi menghasilkan larutan komposit ZnO-PANi/karbon hitam. Tiga amaun serbuk ZnO yang diuji ialah 4wt%, 6wt% dan 8wt%. Seterusnya larutan komposit dimendapkan ke atas substrat kaca menggunakan teknik salutan titisan bagi menghasilkan filem nipis ZnO-PANi/karbon hitam. Pencirian AFM menunjukkan pengurangan purata kekasaran daripada 7.98 nm kepada 2.23 nm dengan penambahan ZnO dalam filem nipis PANi/karbon hitam. Ketebalan filem nipis tersebut juga berkurang daripada 59.5 nm kepada 28.3 nm. Manakala imej FESEM menunjukkan bahawa morfologi permukaan filem nipis ZnO-PANi/karbon hitam berubah menjadi semakin bergumpal dengan pertambahan amaun ZnO dan memberi kesan terhadap keporosan filem nipis tersebut.

Kata kunci: Filem nipis Zn; kaedah sol gel; sifat struktur; teknik salutan titisan

INTRODUCTION

In recent years, nanomaterials like metal (gold, silver), carbon and polymers (especially conducting polymers) have received great attention because of their unique optical, electronic, chemical and mechanical properties (Dutta & De 2007; Tai et al. 2007). Conducting polymers belong to a class of organic materials which can be synthesized by chemical and electrochemical methods and exhibit highly reversible redox behaviour with a distinguishable chemical memory and hence have been considered as a prominent new material for the fabrication of chemical and biological sensors (Lange et al. 2008; Rajesh et al. 2009).

Among all conducting polymers, polyaniline (PANi) received great attention because of its unique conduction mechanism and environmental stability (Lange et al. 2008; Rajesh et al. 2009: Sharma et al. 2009). PANi is soluble in common organic solvents from which free standing films can be cast. It is also considered to be one of the most technologically promising conducting polymers because of its easy preparation, low cost and relatively stable electrical conductivity in air (Sharma et al. 2009; Wang et al. 2006). It has been used as a sensing material for different vapours like ethanol, methanol, acetone, ammonia and benzene (Wang et al. 2006). Selected functionality introduced into the polyaniline structure by appropriate counter-ions leads to substantial changes in the chemical and biological sensing. Conducting polymers lead to a new stage of detecting gas. However, they have several disadvantages which need to be improved, such as long-time instability, irreversibility and have low selectivity where a single sensor cannot distinguish different analytes and the response is easy to be influenced by the presence of other gases (Sharma et al. 2009; Wang et al. 2006).

Recently the study of organic-inorganic hybrid materials for gas sensor application has proved that hybridization improved the sensing properties of pure organic and inorganic materials. In general, the synthesis of hybrid of polymer/inorganic material has the goal of obtaining a new composite material having synergetic or complementary behaviours between the polymer and inorganic material (Sharma et al. 2009). There are a few reports on the synthesis, morphological, electrical and optical studies of PANi-ZnO composite (Dimitrov et al. 2008; He 2004; Sharma et al. 2009). The morphology of the sensing films is an important characteristic for gas detection. A porous surface with small grain size is recommended for better gas sensitivity (Dimitrov et al. 2008). In addition, a strong adhesion of a polymer layer to a support is an important requirement to sensor construction, maintaining the long-term performance and its large-scale production. The adhesion depends on many factors: the nature of the polymer and support, procedure of synthesis, solvent and counter ions (Lange et al. 2008).

In this work, a ZnO-PANi/carbon black hybrid thin film was prepared and characterized by X-ray powder diffraction (XRD), FESEM and AFM. The effect of ZnO additions into PANi/carbon black on structural properties at room temperature was observed and discussed.

Experimental Method

Preparation for ZnO-PANi/Carbon Black Composite Solution

ZnO solution was prepared by dissolving zinc acetate dehydrate [$Zn(CH_3COO_2).2H_2O$] in ethanol (Fluka 99.8%). Then diethanolamine (DEA) was added and the solution was stirred for 30 min at 60°C to produce clear and homogeneous solution. Subsequently, the solution was dried at 100°C for 24 h followed by annealing at 600°C for 5 h. The resultant powder was characterized using XRD.

PANi/carbon black solution was prepared by dissolving 0.01 g PANi powder (Emeraldine Salt, 20 wt% on carbon black) into 20 mL M-Pyrol, N-Methyl-2-Pyrrolidinone (NMP) and stirred in sonicator for 1 hours. Then the solution was stirred continuously on magnetic stirrer for 3 h. A composite solution of ZnO-PANi/carbon black was produced by mixing 3 different amounts of ZnO powder with weight ratio of 4 wt%, 6 wt% and 8 wt% into 3 mL PANi/carbon black solution each. Then, these composite solutions were stirred vigorously for 18 h to produce homogenous solution.

Fabrication of ZnO-PANi/Carbon Black Thin Films

The composite solutions were deposited onto glass substrate using a spin-coating technique to fabricate ZnO-PANi/carbon black thin films with 1,500 rpm for 30 s. The same process was repeated until 3 layers of films each was produced.

Microstructural Characterization

ZnO powder was characterized using X-ray diffractometer (Bruker model D8 Advance). Surface morphology of the films were determined using scanning electron microscope (Zeiss Gemini FESEM) and atomic force microscope (Veeco Model CPII).

Results and Discussions

The XRD patterns of annealed ZnO powder showed the (101) peak was the highest peak and the existence of sharp peaks indicating that the powder was crystalline and showing single phase ZnO. The peaks have been indexed to the hexagonally wurzite structured ZnO consistent with the standard values for ZnO given in JCPD files (01-080-074).

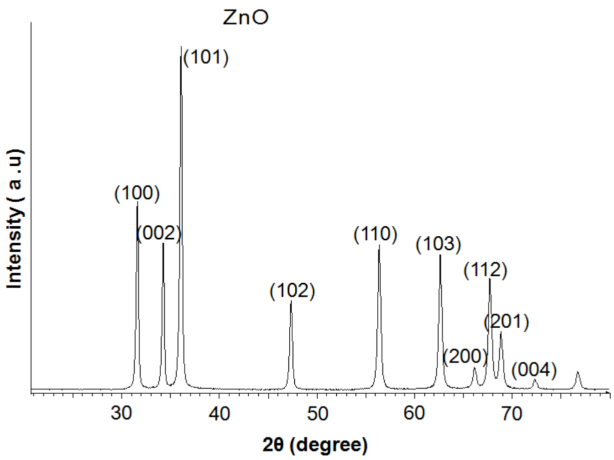

FIGURE 1. XRD result for ZnO powder

The 3D AFM image of ZnO-PANi/carbon black thin films deposited on glass substrate (Figure 2) shows porous, well-packed layer with almost complete coverage and crack free film morphology of ZnO-PANi/carbon black. The grain size decreased when ZnO ratio was increased. Addition of ZnO decreased the average roughness of the film from 7.98 nm to 2.23 nm. The thicknesses of the ZnO-PANi/carbon black film also decrease from 59.5 nm to 28.3 nm with the additions of ZnO (Figure 3).

Figure 4 shows the FESEM image of the ZnO-PANi/carbon black thin films with weight ratio of 0 wt%, 4 wt%, 6 wt% and 8 wt%. The morphology revealed a fibrous structure with many pores among the fibres. PANi/carbon black film with 0 wt% content of ZnO (Figure 4(a)) tends to agglomerate in a huge cluster. It can be observed that the surface morphology of the films is dependent on the ratio of ZnO (Figure 4(b) - 4(d)). The additions of ZnO decreased the agglomeration and the films become smoother. These FESEM results were consistent with AFM results. Composition of 4 wt% ZnO showed surface morphology with smaller grains with grain size around ~30 nm to ~40 nm. The addition of 6 wt% and 8 wt% ZnO into PANi/carbon black (Figure 4(c) and 4(d)) made the surface to become more packed and the

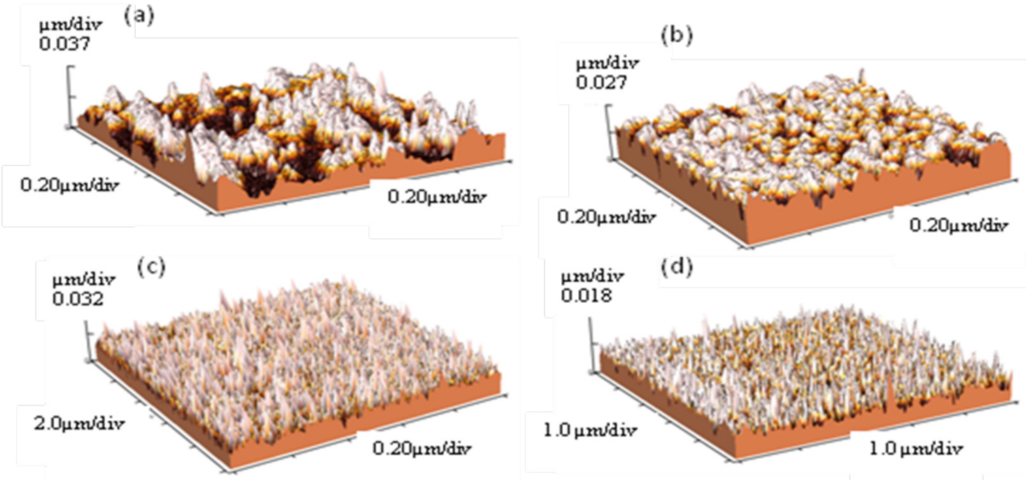

FIGURE 2. 3-D AFM image of ZnO-PANi/carbon black thin films with different weight ratio of ZnO (a) 0 wt%, (b) 4 wt%, (c) 6 wt% and (d) 8 wt%

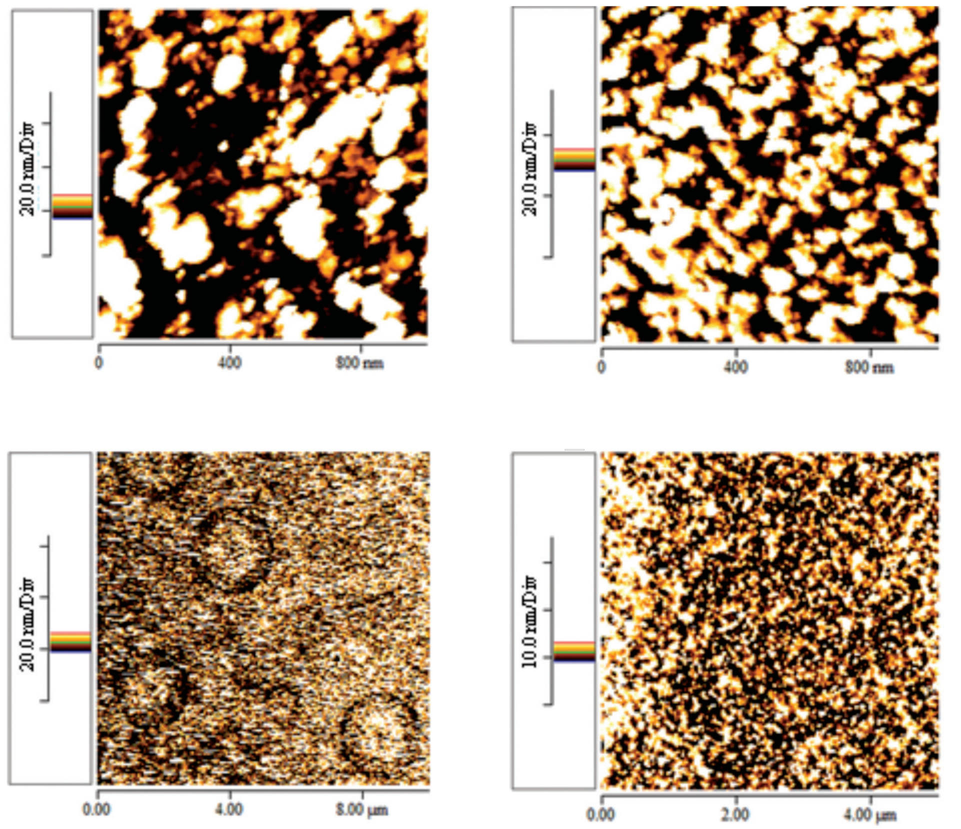

FIGURE 3. AFM morphology for ZnO-PANi/carbon black thin films with different weight ratio of ZnO (a) 0 wt%, (b) 4 wt%, (c) 6 wt% and (d) 8 wt%

pore size become bigger where the diameter of porous size (Figure 4(c)) are around 12 nm to 20 nm while for 8 wt% of ZnO (Figure 4(d)) are in the range of 18 nm to 35 nm. In gas sensing application, the porous structures will trap gas molecules and this will make the reaction between gas molecules and the film to occur easily. Excellent sensitivity results in gas sensing are expected because the sensitivity strongly depends on the porosity of the material (Dimitrov et al. 2008; Lupan et al. 2008).

Conclusion

ZnO-PANi/carbon black thin films were fabricated using spin-coating technique. The increase of ZnO amount

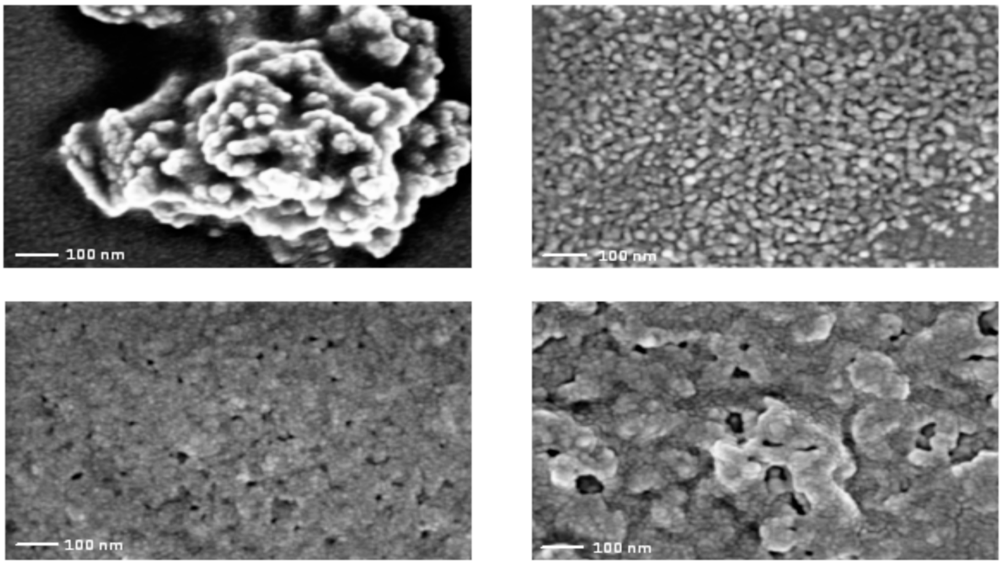

FIGURE 4. FE-SEM micrographs of ZnO-PANi/carbon black composite films for (a) 0 wt%, (b) 4 wt%, (c) 6 wt% and (d) 8 wt%

decreased the roughness and thickness of the as-deposited ZnO-PANi/carbon black thin films, thus tend to change the films into agglomerated surface morphology accompanied by the increment of porosity of the films. Further study will be conducted to obtain the best ratio of ZnO into ZnO-PANi/carbon black thin films for gas sensing.

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REFERENCES

Dimitrov, A.O. Dikovska, Atanasov P.A., Stoyanchov, T.R. & Vasilev, T. 2008. Al doped ZnO thin films for gas sensor application. *Journal of Physics: Conference Series* 113: 012044.

Dutta & De. S.K. 2007. Optical and nonlinear electrical properties of SnO_2-polyaniline nanocomposites. *Materials Letters* 61: 4967-4971.

He. 2004. Preparation of polyaniline/nano-ZnO composites via a novel Pickering emulsion route. *Powder Technology* 147: 59-63.

Lupan, S. Shishiyanu, Chow, L. & Shishiyanu, T. 2008. Nanostructured zinc oxide gas sensors by successive ionic layer adsorption and reaction method and rapid photothermal processing. *Thin Solid Films* 516: 3338-3345.

Lange, Roznyatovskaya N.V. & Mirsky V.M. 2008. Review article: Conducting polymers in chemical sensors and arrays. *Analytica Chimica Acta* 614: 1-26.

Rajesh, T. Ajuha, D. Kumar. 2009. Review: Recent progress in the development of nano-stuctured conducting polymers/nanocomposites for sensor applications. *Sensors and Actuators B* 136: 275-286.

Sharma, A.K., Gupta, N., Khare, S.K., Dhawan, H.C. & Gupta. 2009. Synthesis and characterization of polyaniline-ZnO composite and its dielectric behaviour. *Synthetic Metals* 159: 391-395.

Sharma, M.V.S., Suryanarayana, A.K. Nigam, A.S., Chauhan, L.N.S. & Tomar. 2009. [PANi/ZnO] composite: Catalyst for solvent-free selective oxidation of sulfides. *Catalysis Communications* 10: 905-912.

Tai, Y. Jiang, G. Xie, J. Yu X. Chen. 2007. Fabrication and gas sensitivity of polyaniline-titanium dioxide nanocomposite thin film. *Sensors and Actuators B* 125: 644-650.

Wang, I. Matsubara, N. Murayama, S. Woosuck, N. Izu. 2006. The preparation of polyaniline intercalated MoO_3 thin film and its sensitivity to volatile organic compounds. *Thin Solid Films* 514: 329-333.

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