

Polyaniline/Zinc Oxide Nanocomposite as a Remarkable Antimicrobial Agent in Contrast with PANI and ZnO

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ABSTRACT

Zinc oxide (ZnO) nanostructures were synthesized by microwave assisted hydrothermal route. Polyaniline (PANI) based nanocomposite filled with ZnO nanoparticles were prepared by in situ chemical oxidative polymerization method of aniline in an acid medium with ammonium peroxydisulfate as an oxidant. The composition, morphology, and structure of the polymer and the composite were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction, scanning electron microscopy, and ultraviolet-visible spectroscopy. The flaky shaped structure of PANI/ZnO nanocomposite confirms the smooth PANI layer on the surface of ZnO nanoparticles and formation of a core-shell structure. Furthermore, the PANI/ZnO nanocomposite possess high antimicrobial activity against the model microbes *Escherichia coli* (Gram-negative) and *Staphylococcus* (Gram-positive). It is expected that the PANI/ZnO nanocomposite is the promising material for the application in the biomedical field.

Key words: Nanocomposites, Polyaniline/zinc oxide nanocomposites, Microwave-assisted method, Antibacterial activity.

1. INTRODUCTION

In recent years, developments of inorganic-organic hybrid materials on nanometer scale have been receiving significant attention due to a wide range of potential applications and high absorption in the visible part of the spectrum and high mobility of the charge carriers. Polymer-metal oxide nanocomposite has excellent antimicrobial properties and potential applications in public health care and biomedical field [1]. Polyaniline (PANI) is the most attractive conducting polymer because of the presence of the reactive NH group in the polymer chain [2-4] and used in the broad applications such as batteries, sensors, electronic devices, supercapacitors and corrosion protection in the organic coatings due to its physical and chemical properties, good electrical conductivity, high environmental stability, low cost, light weight, flexibility, facile fabrication, and possibility of both chemical and electrochemical synthesis [5]. Metal and semiconducting nanostructure materials are used as stabilizers or capping agents of these conducting polymers [6]. In recent decades, several reports have been published on the synthesis of the PANI nanocomposite with the inorganic nanoscale such as TiO₂, CdS [7-10], silica [11,12] CeO₂ [13], Fe₃O₄ [14], and MnO₂ [15]. This nanocomposite exhibits many new characters such as electrical, optical, antibacterial, catalytic and mechanical properties that the single material does not have. Most recently, PANI/TiO₂ composite was synthesized and studied as well, but about PANI/zinc oxide (ZnO) nanocomposite especially filler with nanoparticles, there is less attention. The synthesis of the antimicrobial polymer-metallic nanocomposite including polyester/clay silver nanocomposites [16] and polymer/silver bromide composite films [17] has been tried. Maneerung *et al.* [18] succeeded in impregnating silver nanoparticles into bacterial cellulose with strong antibacterial activity for antimicrobial wound dressing. Recently, Suresh Kumar [19] reported the synthesis of magnetic antimicrobial nanocomposite based on bacterial cellulose and silver nanoparticles by high-speed blending using polydopamine as reducing reagent.

Various methods have been widely used for the synthesis of the nanocomposite of PANI with inorganic nanoparticles such as TiO₂, ZnO, CdS, Pd, and Au. Since the conducting PANI and inorganic semiconducting material ZnO in nanoform both are having a wide range of technological applications, we got motivated to make a composite of PANI and ZnO and believed to get novel properties resulting from the molecular level interaction of these two dissimilar chemical components. Various physical and chemical methods have been reported for the preparation of these composite. Here, we used simple chemical oxidation polymerization methods for the preparation of PANI/ZnO nanocomposite (Figure 1).

In this paper, deals to explore the synthesis of nanostructure ZnO by simple microwave-assisted hydrothermal process and PANI/ZnO nanocomposite was fabricated by *in situ* polymerization of aniline monomer with ammonium peroxydisulfate (APS) as an oxidant in acidic medium. The product was characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet (UV)-visible spectroscopy. The interaction between PANI and ZnO nanoparticles was investigated, and the results show the doping effect of ZnO on the PANI matrix. Moreover, the inhibition zone experiment was applied to evaluate the antimicrobial activity of PANI/ZnO nanocomposite using the model microbes *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive), respectively.

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ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2018.602002

Received: 05th October 2017;

Revised: 22nd March 2018;

Accepted: 26th March 2018

2. EXPERIMENTAL

2.1. Materials

The aniline AR grade (MERCK) was distilled twice under reduced pressure. APS [(NH₄)₂S₂O₈] (analytical reagent, RANBAXY fine chemicals Limited India), hydrochloric acid AR grade (MERCK), zinc nitrate (Zn(NO₃)₂·4H₂O) AR grade (MERCK), and sodium hydroxide (NaOH) AR grade (MERCK) were used to prepare the nanocomposite of this study.

2.2. Synthesis of ZnO Nanoparticles

Nanostructure ZnO was prepared by microwave assisted hydrothermal routes. 0.5 g of Zn(NO₃)₂·4H₂O was put into 100 mL de-ionized water under continuous stirring. After 30 min stirring, 10 mL of 2M NaOH aqueous solution was introduced dropwise into the solution under stirring, resulting in a white aqueous solution which was then transferred into Teflon-line stainless steel autoclave. The autoclave was put into silica carbide chamber introduced in microwave irradiation system. The microwave is having 2.45 GHz frequency multimode source and deliverable power 700 W. The reaction product in the form of a precipitate was filtered and washed with distilled water and ethanol to remove the ions possibly remaining in the final products. Finally, the products were dried in hot air oven at 80°C. The final white products were collected for characterization and preparations of nanocomposites in PANI matrix.

2.3. Synthesis of PANI

PANI was synthesized by polymerization of aniline in the presence of hydrochloric acid as do pent and APS as an oxidant by the chemical oxidative polymerization method. For the synthesis, 50 mL, 1M HCl, and 2 mL of aniline were added together in a 250 mL beaker with constant stirring at 0°C, 4.99 g of APS in 50 mL and 1 M HCl was suddenly added into the above solution. The temperature was maintained at 0°C for 5 h to complete the polymerization reaction. The precipitate obtained after the polymerization reaction was washed repeatedly with water and acetone afterward dried at 60°C for 24 h under vacuum to obtain a fine dark green powder.

2.4. Synthesis of PANI/ZnO Nanocomposite

ZnO nanoparticles (1 g) were dispersed in 100 mL of 1M HCl aqueous solution containing 2 mL of aniline under ultrasonic vibration to reduce the aggregation of ZnO nanoparticles. The solution was mechanically stirred for 1 h to obtain a uniform suspension containing ZnO particles, in an ice bath. 50 mL of a pre-cooled 1M HCl containing 4.9 g of APS was added dropwise into the solution containing aniline monomer under stirring. The mixture was allowed to polymerize under stirring for 5 h at 20°C. The precipitated dark green colored PANI-ZnO nanocomposite powder was filtered and washed with a large amount of de-ionized water, methanol and acetone. Finally, the product was dried at 80°C till the constant mass was reached.

2.5. Antimicrobial Activity Studies

The antimicrobial activities of PANI/ZnO nanocomposites have been investigated against *E. coli* as the model Gram-negative bacteria and *S. aureus* as the model Gram-positive bacteria by the disc diffusion method. In the inhibition zone experiment, nutrient agar was poured into disposable sterilized Petri dishes. This was done for both the bacterial strains. The PANI/ZnO nanocomposite was cut into a disc shape with 2 cm diameter, sterilized by autoclaving at 120°C for 20 min, and was placed on *E. coli*-cultured and *S. aureus*-cultured agar plates, which were then incubated at 37°C for 24 h. Finally, the inhibition zone was monitored.

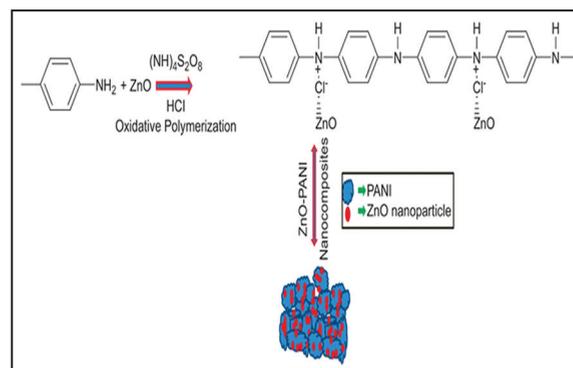


Figure 1 Schematic illustration of PANI/ZnO nanocomposite synthesis

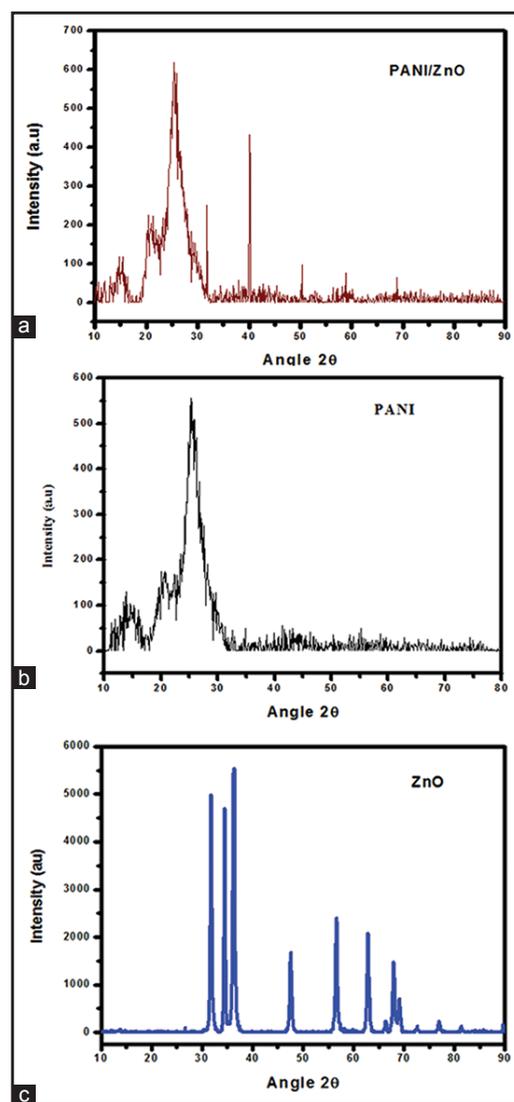


Figure 2: (a-c) The X-ray diffraction pattern of HCl doped PANI, nano zinc oxide, PANI/ZnO nanocomposite.

2.6. Characterization Techniques

The sample was characterized by SEM using Holland Philips XL30 microscope. XRD patterns of the sample were recorded in ambient air using a Holland Philips X-ray powder diffraction (Cu K α , $\lambda = 1.5406 \text{ \AA}$), at scanning speed of 2°/min from 20 to 80°.

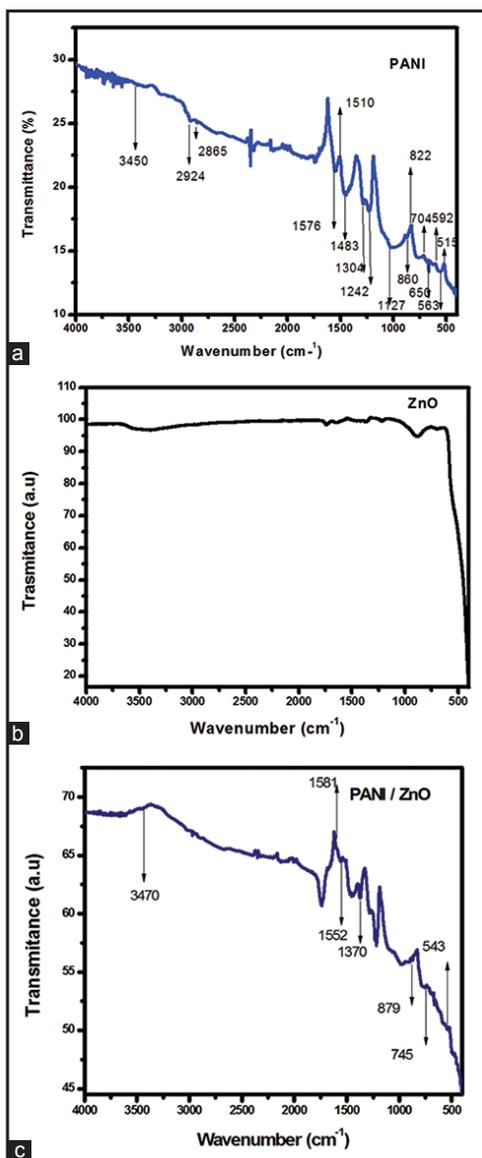


Figure 3: (a-c) Fourier transform infrared spectrum of HCl doped polyaniline (PANI), zinc oxide (ZnO) nanoparticles, PANI/ZnO nanocomposite.

was prepared by Shimadzu analytical equipment (UV-2100). The FTIR was studied using a Bruker IR spectrometer of 4 cm^{-1} resolution in the $400\text{--}4000\text{ cm}^{-1}$ range.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

XRD analysis was used to examine the structure of the PANI, ZnO, and PANI/ZnO nanocomposite and investigate the effect of the ZnO nanoparticles on the PANI structure. Figure 2 shows the typical XRD patterns of PANI, ZnO, and PANI/ZnO nanocomposites. As is evident in PANI and its nanocomposite, Figure 2a indicate broad diffraction peaks occur between 11° and 32° due to the parallel and perpendicular periodicity of the polymer (PANI) chain. The PANI peak diffracted at an angle of $2\theta = 11.76^\circ$, $2\theta = 15.13^\circ$, and $2\theta = 25.37^\circ$ with a d spacing 7.516 \AA , 5.850 \AA , and 3.506 \AA , respectively, in the XRD pattern which shows low crystallinity of the conductive polymers due to the repetition of benzenoid and quinoid rings in the PANI

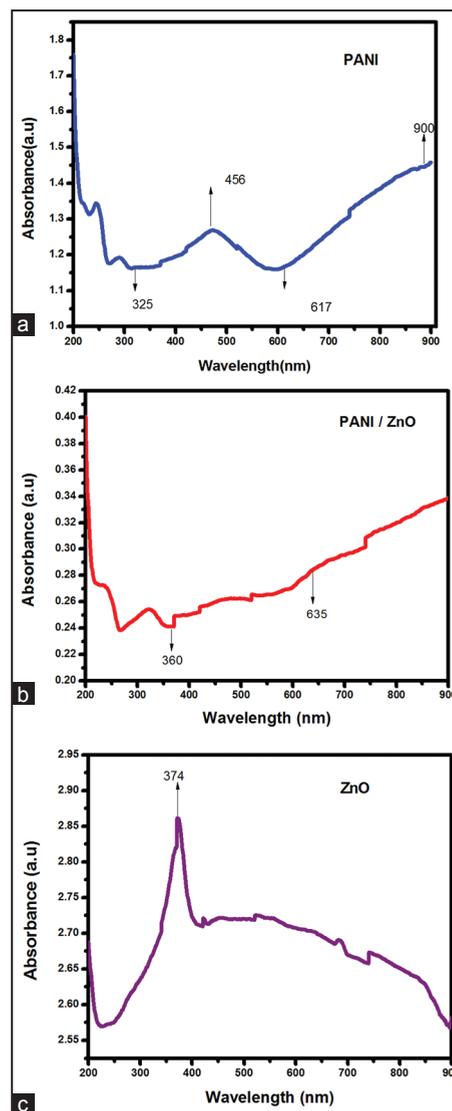


Figure 4: (a-c) Ultraviolet-visible spectra of polyaniline (PANI), zinc oxide (ZnO), PANI/ZnO.

chains [9,10]; moreover, PANI crystal size is 8 nm which was calculated by Scherrer's equation [13]. The presence of ZnO nanoparticles, crystal size of nanocomposite increased from 8 nm to 11 nm. Figure 2b is XRD patterns of ZnO nanoparticles have characteristic peaks of ZnO with the crystalline structure of wurtzite. It can be seen that Figure 2c is the XRD patterns of PANI/ZnO nanocomposite are similar to that of PANI, but the intensity of the peak was increased by addition of ZnO nanoparticles which means that there is an interaction of ZnO and PANI by formation of hydrogen bonding between H-N and oxygen of ZnO [6].

3.2. FTIR Analysis

PANI, ZnO and PANI/ZnO nanocomposite were characterized using the FTIR technique. Figure 3 shows the FTIR pattern of PANI, ZnO nanoparticles and PANI/ZnO nanocomposite. The characteristic absorption band of PANI Figure 3a is 515 cm^{-1} (C-N- C bonding mode of aromatic ring), 592 cm^{-1} and 704 cm^{-1} (C-C, C-H bonding mode of aromatic ring), 822 cm^{-1} (C-H out of plane bonding in benzenoid ring), 1304 cm^{-1} and 1510 cm^{-1} (C-N stretching of benzenoid ring), and 1576 cm^{-1} (C=N stretching of quinoid ring). The PANI/ZnO nanocomposite Figure 3c shows the same characteristic

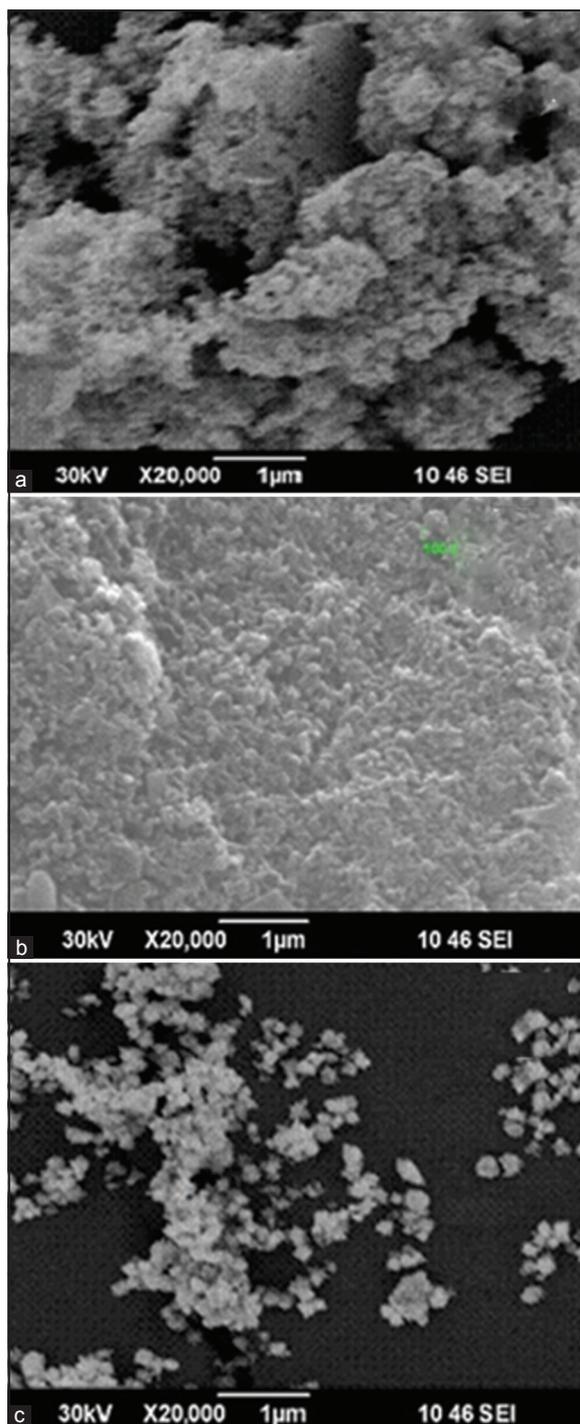


Figure 5: The scanning electron microscopy images of (a) HCl doped polyaniline (PANI), (b) zinc oxide (ZnO) nanoparticles, (c) PANI/ZnO nanocomposite.

peaks. However, there is an evidence of peak displacement when ZnO nanoparticles are added to the PANI. These shifts include $1576\text{-}1581\text{ cm}^{-1}$, $1510\text{-}1552\text{ cm}^{-1}$, $822\text{-}879\text{ cm}^{-1}$, and $515\text{-}543\text{ cm}^{-1}$, $1304\text{-}1370\text{ cm}^{-1}$, and $1510\text{-}1552\text{ cm}^{-1}$. Furthermore, in PANI/ZnO nanocomposite, a broad peak appeared in 3470 cm^{-1} which can be associated to the interaction between ZnO nanoparticles and PANI by formation of hydrogen bonding between H-N and oxygen of ZnO, so the peak displacement which was observed in FTIR spectra may be ascribed to the formation of hydrogen bonding between ZnO and the N-H group of PANI on the surface of the

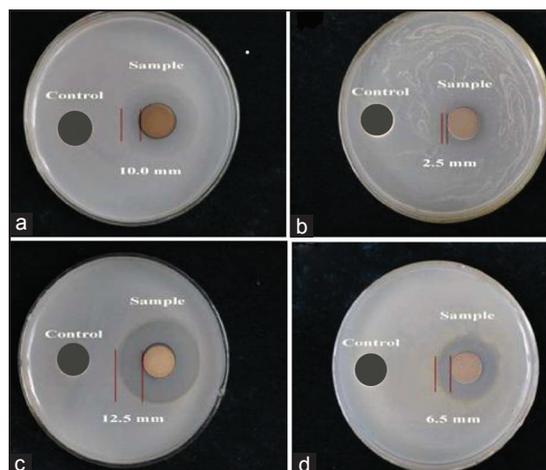


Figure 6: Antimicrobial activity of PANI/ZnO nanocomposites: (a and c) *Escherichia coli* and (b and d) *Staphylococcus aureus*.

ZnO nanoparticles [20,21]. Figure 3b shows the FTIR spectrum of ZnO nanoparticles in which the characteristic peaks at 430 cm^{-1} and 496 cm^{-1} is related to the Zn-O stretching mode [6]. According to the patterns, absorption intensity is increased by adding ZnO nanoparticles in the case of nanocomposites due to the uniform distribution of ZnO nanoparticles in nanocomposite matrix and elimination of agglomeration.

3.3. UV-visible Analysis

The absorption properties of PANI, ZnO, and PANI/ZnO nanocomposites are presented in Figure 4a. The PANI shows sharp and broader bands at 325 and 617 nm which are ascribed to $\pi\text{-}\pi^*$ transitions of the benzenoid groups and $n\text{-}\pi^*$ transitions due to polaron formation into the conducting PANI, respectively [22]. A considerable large redshift at 360 nm from 325 nm and 635 nm from 617 nm has been observed for PANI/ZnO nanocomposites Figure 4c. This prominent redshift might occur due to the interaction between the hydroxyl groups of ZnO and the quinoid ring of emeraldine salt which facilitates the charge transfer from highly reactive imine groups at quinoid unit of emeraldine salt to ZnO nanomaterials through partial hydrogen bonding. Figure 4b exhibits a strong narrow absorption peak in the UV region at 378 nm which is characteristic band of ZnO nanomaterials, i.e., typical wurtzite hexagonal structure. This prominent single peak reveals that the prepared ZnO nanomaterials do not contain impurities [23]. In addition, the relative intensity of the peaks increases in PANI/ZnO nanocomposite by adding ZnO nanomaterials. This increased intensities of the peaks might attribute to the enhanced hydrogen bonding in the form of NH-(PANI)...O—Z [24].

3.4. SEM Analysis

Figure 5 shows surface images of PANI, ZnO nanoparticles, and PANI/ZnO nanocomposite. Figure 5a indicates the SEM image of PANI; it has various structures such as granules, nanofibers, nanotubes, nanospheres, and microsphere. The diameter of PANI is approximately 100nm, and they have an irregular road-like morphology. The morphology of PANI has changed by the introduction of ZnO nanoparticles, as depicted in Figure 5c it can be concluded that a thin layer of PANI molecules was adsorbed on the surface of ZnO nanoparticles, and a core-shell structure of ZnO/PANI nanocomposite with the core of ZnO inorganic nanoparticle and the shell of monolayer PANI chains has been formed [25]. The ZnO nanoparticles have a crystalline spherical structure Figure 5b.

3.5. Antimicrobial Activity of the PANI/ZnO Nanocomposite

The antibacterial activity of the PANI/ZnO nanocomposite with low concentration was obtained using 0.100 g of PANI/ZnO nanocomposite while using 0.500 g of PANI/ZnO nanocomposite, the antibacterial activity of the PANI/ZnO nanocomposite with high concentration was obtained. Pure microcrystalline PANI was used as a control. The antibacterial activity of PANI/ZnO nanocomposite against *E. coli* and *S. aureus* was measured. *E. coli* and *S. aureus* are general bacteria that are found on the contaminated wound. From Figure 6, it was found that the PANI/ZnO nanocomposite exhibited an inhibition zone. The inhibition zones of the PANI/ZnO nanocomposite with low concentration for *E. coli* and *S. aureus* were 10 mm and 2.5 mm, respectively, while inhibition zone of the PANI/ZnO nanocomposite with high concentration for *E. coli* and *S. aureus* was 12.5 mm and 6.5 mm, respectively, the result clearly demonstrated that the PANI/ZnO nanocomposite had good antibacterial activity against both *E. coli* and *S. aureus*, and the antimicrobial activity against *E. coli* is higher than that against *S. aureus*, probably due to the difference in cell wall between Gram-negative and Gram-positive bacteria.

As the concentration of PANI/ZnO nanocomposite increased from 0.100 g to 0.500 g, the inhibition zone against *S. aureus* was dramatically increased. From the images, no inhibition zone was observed for the microcrystalline PANI as control (Figure 6), implying that the microcrystalline PANI do not have any antibacterial properties. These result clearly indicate that the antibacterial activity is only due to the ZnO nanoparticles which were impregnated inside PANI and not due to the microcrystalline PANI.

4. CONCLUSION

In summary, the PANI/ZnO nanocomposites with excellent antimicrobial properties have been successfully synthesized by sol-gel assisted method. The result of spectroscopic method such as XRD, FTIR, UV-visible, and SEM measurement indicates that PANI/ZnO nanocomposite is successfully prepared. The diffraction spectra of the nanocomposite show that the crystal structure of ZnO nanomaterials has not modified due to the presence of PANI. The structural and absorption studies demonstrate shifting and the changes in the intensity of peaks which confirm the effective interaction between PANI and ZnO nanomaterials through the hydrogen bonding between imine(-NH) of PANI and hydroxyl (-OH) group of ZnO nanomaterials. UV-visible results confirm that NH group was adsorbed on the surface of ZnO nanoparticles. The PANI/ZnO nanocomposite exhibited a strong antibacterial activity against both *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria).

5. REFERENCES

- J. W. Rhim, P. K. W. Ng, (2007) Natural biopolymer-based nanocomposite films for packing applications, *Critical Reviews in Food Science and Nutrition*, **47**: 411-415.
- S. Ameen, M. S. Akhtar, S. G. Ansari, O. Yang, H. S. Shin, (2009) Electrophoretically deposited polyaniline/ZnO nanoparticles for p-n heterostructure diodes, *Superlattices and Microstructures*, **46**: 872-875.
- S. Sathiyaranan, S. S. Azim, G. Venkatachari, (2007) Preparation of polyaniline-TiO₂ composite and its comparative corrosion protection performance with polyaniline, *Synthetic Metals*, **157**: 205-209.
- J. Stejskal, I. Sapurina, M. Trchova, (2010) Polyaniline nanostructures and the role of aniline oligomers in their formation, *Progress in Polymer Science*, **35**: 1420-1425.
- G. K. Prasad, T. Takei, Y. Yonesaki, N. Kumada, N. Kinomura, (2006) Hybrid nanocomposite based on NbWO₆ nanosheet and polyaniline, *Material Letters*, **60**: 3727-3731.
- B. K. Sharma, A. K. Gupta, N. Kharea, S. K. Dhawan, H. C. Gupta, (2009) Synthesis and characterization of polyaniline-ZnO composite and its dielectrical behavior, *Synthetic Metals*, **159**: 391-395.
- R. C. Pattil, S. Radhakrishnan, (2006) Conducting polymer based hybrid nanocomposite for enhanced corrosion protective coatings, *Progress in Organic Coatings*, **57**: 332-337.
- J. C. Xu, W. M. Lu, H. L. Li, (2005) Titanium dioxide doped polyaniline, *Material Science and Engineering*, **25**: 444-449.
- T. C. Mo, H. W. Wang, S. Y. Chen, Y. C. Yeh, (2008) Synthesis and dielectric properties of polyaniline/titanium dioxide nanocomposite, *Ceramic International*, **34**: 176710-176715.
- L. Shi, X. Wang, L. Lu, X. Yang, X. Wu, (2009) Preparation of TiO₂ polyaniline nanocomposite from allotropic liquid crystalline solution, *Synthetic Metals*, **159**: 2525-2529.
- W. Jia, E. Segal, D. Kornemandel, Y. Lamhot, M. Narkis, A. Siegmann, (2002) Polyaniline-DBSA/organophilic clay nanocomposite synthesis and characterization, *Synthetic Metals*, **28**: 115-119.
- P. Liu, (2008) Preparation and characterization of conducting polyaniline/silica nano sheet composite, *Current Opinion in solid state and Material Science*, **12**: 9-14.
- Y. He, (2005) Synthesis of polyaniline/CeO₂ composite microspheres via-stabilized emulsion route, *Material Chemistry and Physics*, **92**: 134-138.
- W. Xue, K. Fang, H. Qiu, J. Li, W. Mao, (2006) Electrical and magnetic properties of the Fe₃O₄-Polyaniline nanocomposite pellets containing DBSA-doped polyaniline and HCl -doped polyaniline with Fe₃O₄ nanoparticles, *Synthesis Metals*, **156**: 506-511.
- X. Zhang, L. Li, S. Zhang, W. Yang W, (2001) Synthesis of a novel polyaniline intercalated layered manganese dioxide nanocomposite as electrode material for electro chemical capacitors, *Journal of Power Sources*, **173**: 1017-1023.
- U. Konwar, N. Karak, M. Mandal, (2010) Vegetable oil based highly branched polyester/clay silver nanocomposites as antimicrobial surface coating materials. *Progress in Organic Coatings*, **68**: 265-269.
- V. Sambhy, M. M. MacBride, B. R. Peterson, (2006) Silver bromide nanoparticle/polymer composite: Dual action tunable antimicrobial materials, *Journal of the American Chemical Society*, **128**: 979.
- T. Maneerung, S. Tokura, R. Rujiravanit, (2008) Impregnation of silver nanoparticles in to bacterial cellulose for antimicrobial wound dressing, *Carbohydrate Polymers*, **72**: 43-49.
- M. Sureshkumar, D. Y. Siswanto, C. K. Lee, (2010), Magnetic antimicrobial nanocomposite based on bacterial cellulose and silver nanoparticles, *Journal of Material Chemistry*, **20**: 6948-6954.
- B. K. Sharma, N. Khare, S. K. Dhawan, H. C. Gupta, (2009) Dielectric properties of nano ZnO-polyaniline composite in the microwave frequency range, *Journal of Alloys and Compounds*, **477**: 370-376.
- H. He, (2004) Preparation of polyaniline/nanoZnO composite via a novel pickering emulsion route, *Powder Technology*, **147**: 59.
- W. Pan, S. L. Yang, G. Li, J. M. Jiang, (2005) Electrical and



- structural analysis of conductive polyaniline/polyacrylonitrile composite, *European Polymer Journal*, **41**: 2127-2130.
23. N. Lu, X. Jin, X. Lu X, (2007) Preparation and characterization of UV-curable ZnO/polymer nanocomposite films, *Polymer International*, **56**: 138-141.
24. Y. He, (2004) Preparation of polyaniline/nano-ZnO composite via a novel pickering emulsion route, *Powder Technology*, **147**: 59-62.
25. Y. He, (2005) A novel emulsion route to sub-micrometer polyaniline/nano-ZnO composite fibers, *Applied Surface Science*, **249**: 1-4.

*Bibliographical Sketch



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