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NANOCOMPOSITE OF POLYANILINE AND MAGNETIC ALLOYS (Ag-Fe, g-Co, Ag-Ni) THIN FILMS BASED AMPEROMETRIC SENSOR SYNTHESIZED BY LOW HEAT TREATMENT (300^{O}C) FOR *E. COLI* DETECTION

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ABSTRACT

The use of magnetic metals in sensor application has been widely attracted. The combination of one of the three main magnetic metals (Fe, Ni, Co) with antibacterial material, Ag and conducting polymer, PANI will produce a better characteristic of thin film for microbial sensor application. PANI-Ag-Fe, PANI-Ag-Ni and PANI-Ag-Co nanocomposite thin films were synthesized via sol-gel method with annealing at 300^{o}C. The films were characterized by XRD, AFM and UV-Vis to study the crystallite structure, surface morphology and internal structural property. Amperometric sensor performance was conducted by *I–V* measurement with and without incubated in *E. coli*. XRD analysis confirm the face-centered cubic of Ag, Fe, Co and Ni crystal with the crystallite size around 8 – 11 nm. AFM images show the surface of PANI-Ag-Ni thin film has the highest roughness but smallest grain size than PANI-Ag-Fe and PANI-Ag-Co. UV-Vis absorbance band show the maximum absorption peak is around 420 – 500 nm. The sensor performance from *I – V* measurements show that PANI-Ag-Ni thin film sensor produce the highest sensitivity towards *E. coli* followed by PANI-Ag-Co and PANI-Ag-Fe.

Keywords: Magnetic metals; polyaniline; alloys; nanocomposite; amperometric sensor; E. coli sensor.

INTRODUCTION

The performance of polymer and metal nanocomposite in bacterial detection application has been reported in our previous study [1-3]. Bimetallic nanomaterials consist of magnetic metals and noble metals have attracted much interest for their promising potentials. Noble metals and magnetic metals are two groups of the most prominent metal materials. Noble metals such as Ag mainly contain 4d metals whereas magnetic metal such as Fe, Co and Ni contain two 4s outermost electrons and unsaturated 3d electron shell [4]. Bimetallic silver nanoparticles are accordingly emerging as exciting candidates for the development of biosensors. Silver-based magnetic alloys with solute magnetic elements Fe, Co and Ni, can exhibit enhanced magnetic anisotropy and chemical stability in contrast to monometallic Fe, Co and Ni nanoparticles, furthermore, the catalytic activity of silver alloys (Ag-Fe, Ag-Co and Ag-Ni) could enhance the detection limits of biosensors. Magnetic materials are widely studied and applied in field such as magnetic sensors [5-7], catalysts [8-9], optical detection [10] and biomedical applications [11-14]. Nanosized magnetic nanoparticles show different magnetic behaviors compared to its bulk material due to the reduced number of magnetic domains leading to so called superparamagnetic behavior [15]. The synthesis of magnetic nanoparticles in biological sensor application needs a balance condition between high sensor properties and low biological toxicity. Although magnetic alloys can offer high saturation magnetization and resistance to oxidation, control of composition, size and shape are required in order to achieve optimal properties [16]. In this present work, we report for the nanocomposite of PANI and magnetic alloys (Ag-Fe, Ag-Co and Ag-Ni) for amperometric *E. coli* sensor. PANI-magnetic alloys were heated with low temperature (300^{o}C) to control the structure and the size of particle. The sensitivity performance was conducted using *I-V* measurement to detect the presence of *E. coli* in water.

EXPERIMENTAL DETAILS

The nanocomposite of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni was synthesized by sol-gel method. Aniline, polyvinyl alcohol (PVA), silver nitrate ($AgNO_3$), iron (III) nitrate ($Fe(NO_3)_3$, cobalt nitrate ($Co(NO_3)_2$ and nickel nitrate ($Ni(NO_3)_2$ were purchased from Sigma-Aldrich and R&M Chemicals. All chemicals were diluted in deionized water. 2.5 g of PVA was diluted in deionized water by stirring and heating the mixture at 80 – 90 ^{o}C. 0.5 g of the mixture of silver nitrate and iron (III) nitrate, or silver nitrate and cobalt nitrate, or silver nitrate and nickel nitrate, were added to the PVA solution drop by drop. Aniline was added to the solution followed by 1.0 M of nitric acid. PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni were produced with polymerization process by oxidation of aniline in the presence of metal compounds. The nanocomposite solutions were deposited onto glass substrates using spin coating technique. The substrates were spinned at 2000 rpm for 15 s. The prepared thin films were annealed in a tube furnace with maximum temperature of 300 ^{o}C for 1 day. A 100 nm layer of comb-structure silver electrode was sputtered on the nanocomposite thin films using magnetron sputtering. Copper wires were soldered to the silver electrodes as a connection to the

measuring equipment. The nanocomposite thin films of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni were characterized by X-ray diffraction (XRD), UV-vis spectroscopy and atomic force microscopy (AFM) to study the crystallite, particles and surface morphology. The sensor performance was tested on the sensor device using *I–V* measurement with dipping the device into *E. coli* solution and deionized water.

RESULTS AND DISCUSSIONS

X-Ray Diffraction (XRD)

Figure 1 shows the XRD patterns of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni nanocomposite thin films. The prominent peaks located at (1 1 1) and 2θ = 39.2° represent the crystal of Ag whereas the unclear peaks at (2 0 0) and 2θ = 45.6° represent (a) Ag-Co, (b) Ag-Fe and (c) Ag-Ni alloys. All the crystals are face-centered cubic structure. The crystallite sizes have been calculated using Scherrer equation [17]:

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \qquad (1)$$

where D is crystallite size, κ is the Scherrer constant (0.9), λ is the X-ray wavelength (1.5406 Å), β is full width at half maximum (FHWM) and θ is the Bragg's angle. The high degree of crystallinity is shown by PANI-Ag-Co with the high crystallite size which is 11.03 nm, then followed by the crystallite size of PANI-Ag-Ni (10.04 nm) and PANI-Ag-Fe (8.40 nm). The crystallite size values have been summarized in Table 1.

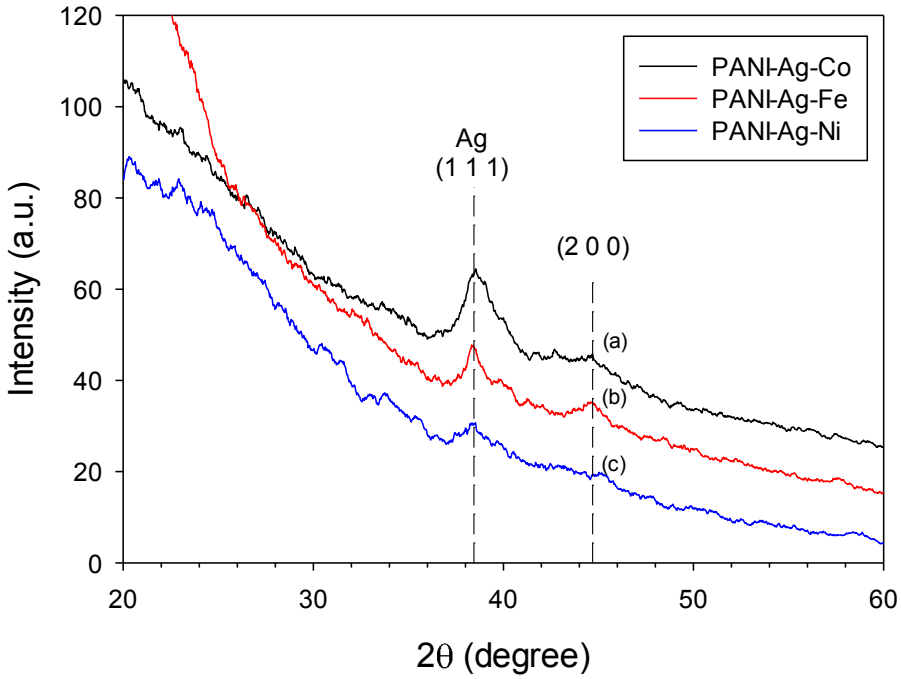

Figure 1: XRD patterns of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni nanocomposite thin films

Table 1: Crystallite size calculated from XRD analysis

Sample	Crystallite size (nm)
(a) PANI-Ag-Co	11.03
(b) PANI-Ag-Fe	8.40
(c) PANI-Ag-Ni	10.04

UV-Visible Spectroscopy

The absorbance spectra of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni nanocomposite thin films in Figure 2 are obtained from UV-visible spectroscopy. The appearance of single peak at each band indicates that present Ag-Fe, Ag-Co and Ag-Ni bimetallic particles are in alloy form rather than being a mixture of individual metal particles. Those spectra contain maximum absorption band at wavelength 422 nm for PANI-Ag-Fe, 430 nm for PANI-Ag-Co and 497 nm for PANI-Ag-Ni nanocomposite thin films. The maximum absorption band for Ag nanoparticle has been known located at 400 – 450 nm [18]. With the addition of magnetic metal Fe, Co and Ni, the absorbance peaks shift to the longer wavelength. From PANI-Ag-Fe, PANI-Ag-Co to PANI-Ag-NI, the absorbance peaks shift to longer wavelength which indicates the size particles become larger. This is because larger particles require less energy and hence longer wavelength [19].

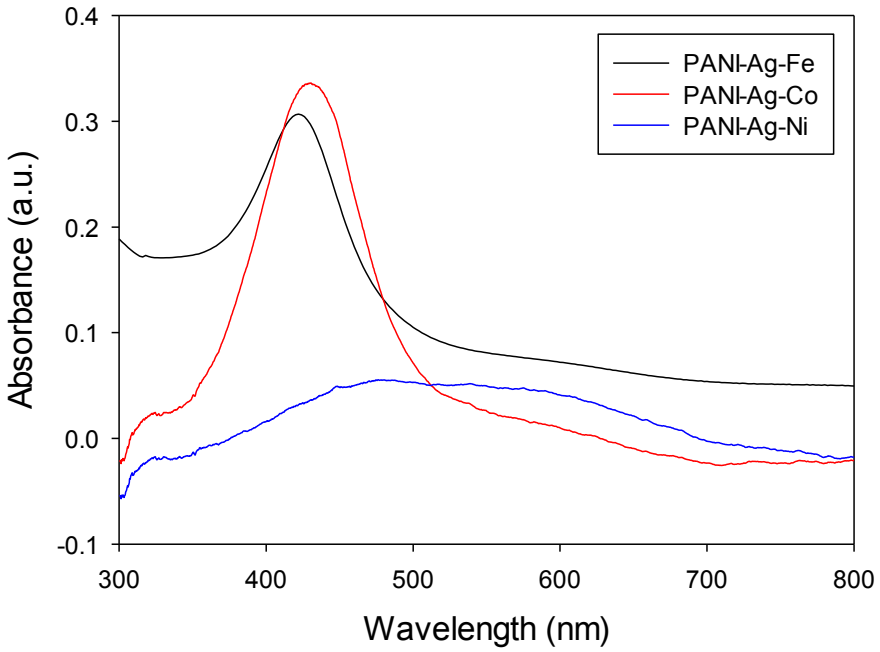

Figure 2: UV-Vis absorption spectra of (a) PANI-Ag-Fe, (b) PANI-Ag-Co and (c) PANI-Ag-Ni nanocomposite thin films

Atomic Force Microscopy (AFM)

AFM analysis of PANI-magnetic alloys nanocomposite thin films can determine the surface roughness and grain size of the samples. To evaluate the surface roughness as well as the grain size of the films, an area of 1µm x 1µm was scanned in tapping mode. Figure 3 shows the 3D morphology of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni nanocomposite thin films surface. The average surface roughness and grain size were being listed in Table 2. The lowest value of roughness is from sample PANI-Ag-Fe, but the lowest value of grain size is from PANI-Ag-Ni.

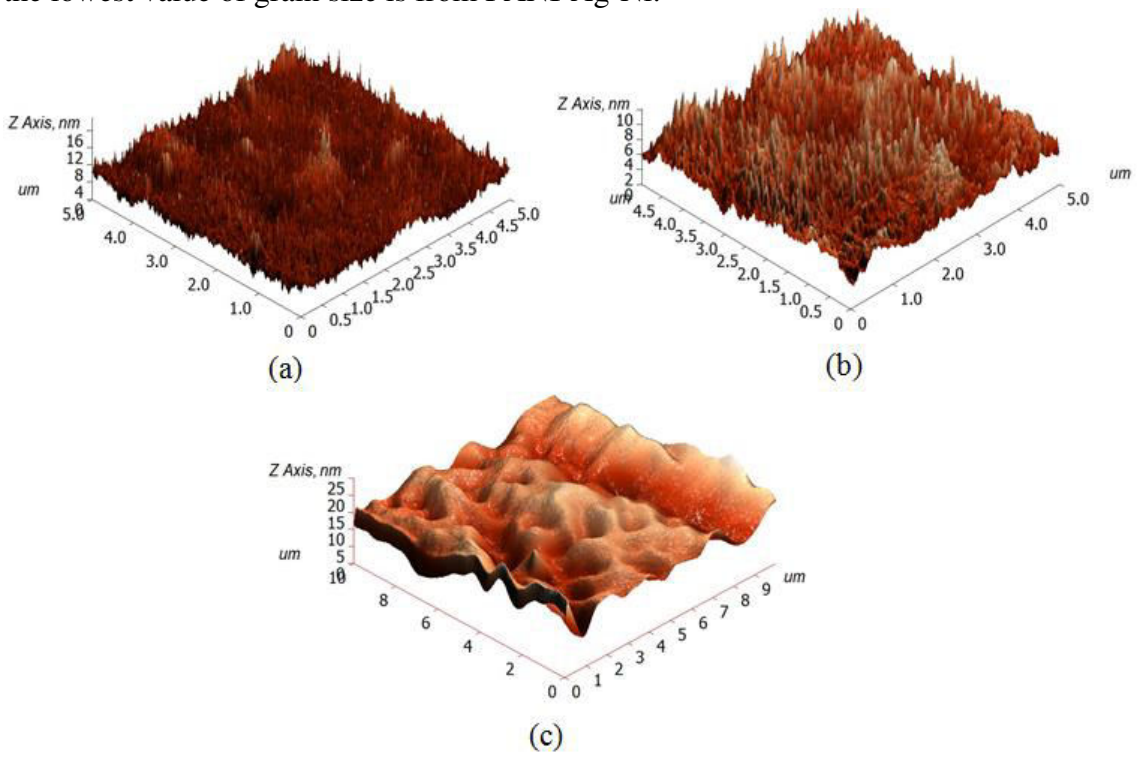

Figure 3: AFM images of (a) PANI-Ag-Co, (b) PANI-Ag-Fe and (c) PANI-Ag-Ni nanocomposite thin films

Table 2: Average roughness and grain size from AFM analysis

Sample	Average roughness (nm)	Grain size (nm)
(a) PANI-Ag-Fe	0.791	54.3
(b) PANI-Ag-Co	1.187	36.8
(c) PANI-Ag-Ni	2.281	5.1

Sensor Performance

Amperometric sensors basically measure the current produced during the oxidation or reduction process of a reactant at a constant applied potential [20]. *I-V* measurement is used to supply current flow to the reactant sensor electrode in the bacteria solution at constant voltage of 4V to -4V. *I-V* curve produced from the reaction in bacteria solution

was compared to the reaction in water without *E. coli*. The current produced from both experiment was different. The reaction between *E. coli* bacteria cell wall with magnetic alloy nanoparticles cause the current flow increased. The sensitivity of the sensor is described as the ratio of the magnitude of response upon exposure to the *E. coli* (I_e) to that of without exposure to the *E. coli* (I_o). Table 3 shows the value of sensitivity (S) on *E. coli* which is calculated using the formula [21].

$$S = \frac{I_e - I_o}{I_o} \tag{2}$$

where S is the sensitivity of sensor electrode on *E. coli*, I_e is the current when the sensor electrode is exposed to *E. coli*, and I_o is the current when the sensor electrode is not exposed to *E. coli*. From Table 3, it shows that PANI-Ag-Ni nanocomposite thin film performed the highest sensitivity followed by PANI-Ag-Co and PANI-Ag-Fe.

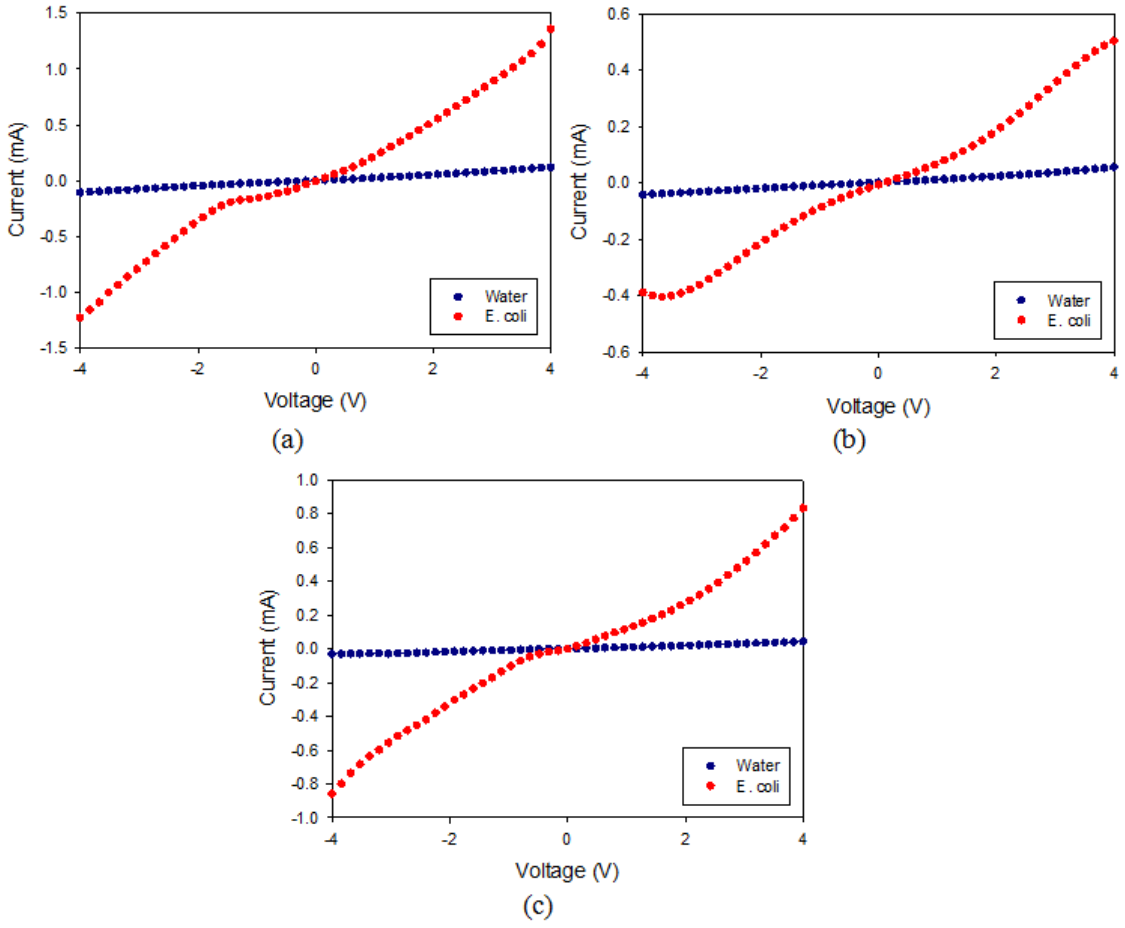

Figure 4: *I-V* characteristic of (a) PANI-Ag-Co, (b) PANI-Ag-Fe and (c) PANI-Ag-Ni nanocomposite thin films in clean water and *E. coli* bacteria solution

Table 3: Sensitivity (*S*) of PANI-magnetic alloy on *E. coli* bacteria

Sample	Sensitivity (*S*)
(a) PANI-Ag-Fe	7.679
(b) PANI-Ag-Co	8.556
(c) PANI-Ag-Ni	16.595

CONCLUSION

The nanocomposite thin films of PANI-Ag-Fe, PANI-Ag-Co and PANI-Ag-Ni were prepared using sol-gel method. The peaks in the XRD patterns show the crystals are oriented along (111) planes for Ag while (200) plane for Ag-Fe, Ag-Co and Ag-Ni. XRD analysis found out the crystallite size of those samples is 8 – 11 nm. From UV-visible spectroscopy, the single absorbance peak appears at 422 nm, 430 nm and 497 nm in each band indicating the Ag-Fe, Ag-Co and Ag-Ni alloy nanoparticles formed. AFM images indicate the PANI-Ag-Ni surface roughness is highest than others but the grain size is lowest. The films were fabricated to be applied as a prototype microbial sensor to detect *E. coli* in water. *I–V* characteristic shows the sample PANI-Ag-Ni performed the highest sensitivity on *E. coli*, followed by PANI-Ag-Co and PANI-Ag-Fe. It was concluded that all the samples of PANI-magnetic alloys have potential to be applied as amperometric based bacteria sensor for future study.

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