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The character istics (compositions, morphological, and structure) of nanocomposites polyaniline (PANI)/ZnO

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Abstract. In recent years, development of inorganic-organic hybrid materials has been receiving significant attention due to wide range of potential applications and high absorption in visible spectrum. Polyaniline (PANI) and nanocomposite PANI/ZnO were prepared by interfacial polymerization method of two-phase organic/water. The characteristics (composition, morphology and structure) of the nanocomposites characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-Energy dispersive X-ray (SEM-EDX) and UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). The characteristic FT-IR peaks of PANI and nanocomposite (PANI)/ZnO due to formation H-Bonding. UV-Vis characterization showed the presence of electron transitions in PANI compound. The characterization by DRS showed the compound PANI, PANI/ZnO 5% and 10% have an energy value of ~ 2.0 eV band gap. SEM analysis with image-J software showed a decreasing of the particle size due to the increasing content of ZnO.

Key words: photocatalyst, PANI, nanocomposite polyaniline/ZnO

1. Introduction

The inorganic semiconductor materials such as TiO₂, ZnO and others as photocatalysts to degrade waste in water has been widely studied. The metal oxides have been known are the best activity and have high stability in photocatalytic reactions of organic and inorganic compounds. However, most of the inorganic semiconductors above have a wide band gap, so that it can only absorb energy from ultraviolet light ($\lambda < 400$ nm) to be able to do photoexcitation [1]. The silver orthophosphate (Ag₃PO₄) also had a great activity for photocatalysis [2-5], but the level of stability is less for repeated use. The metal oxides can be effective photocatalysts in visible light by making them into polyaniline/metal oxide nanocomposites [6].

In recent years, research on conductive polymers has been of great interest to researchers. One of the most interesting conductive polymers is polyaniline (PANI). Polyaniline is stable in the environment, cheap and easily synthesized, and can be transformed from one oxidation form to another due to oxidation and reduction as well as conductive properties to become isolative due to the acid-base reaction that occurs. Therefore polyaniline is widely used, among others, as sensors, transistors, battery, capacitors, and corrosive inhibitors [7].



Synthesis of polyaniline (PANI) was done by interfacial polymerization method of two phases system (organic/water). Interfacial polymerization performed to produce PANI with nanoseric morphology. The process of preparing polyaniline with interfacial polymerization is carried out by using a mixture of hydrochloric acid with ammonium peroxodisulphate (APS) as a water phase and a toluene solution mixture with aniline as an organic phase. The water phase used is a hydrochloric acid solution aims to protonation the emeraldine base (EB) and produce polyaniline in the form of emeraldine salt (ES). Based on the oxidation level, polyaniline can be synthesized in several isolative forms including fully reduced leucomeraldine base (LB), half oxidized emeraldine base (EB) and fully oxidized pernigraniline base (PB) [8]. The shape of the EB is the most stable form and is also the most widely studied because its conductivity can be adjusted from 10-10 S/cm to 100 S/cm through a doping process. The basic shape of the EB changes to ES (emeraldine salt) which is a conductive form through an oxidation reaction with protonic acids such as hydrochloric acid.

Development of inorganic-organic hybrid materials on nanometres scale have been receiving significant attention due to wide range of potential applications and high absorption in visible spectrum [9, 10]. In this paper, we report the synthesis of PANI and PANI/ZnO composites by interfacial polymerization method of two phases system (organic/water) and study of their composition, morphology and structure properties.

2. Materials and Methods

2.1. Materials

Commercially available aniline (99.5%), toluene, ammonium peroxodisulphate (98%), hydrochloric acid (35% GR), acetone and zinc oxide (ZnO) were purchased from Merck. Distillated water was employed as a medium for polymerization of aniline.

2.2. Synthesis of Polyaniline

The synthesis of polyaniline was carried out by the interfacial polymerization method of a two-phase organic/aqueous solutions. The first step, 50 mL toluene solution was added with 1 mL of monomer aniline as organic phase and 50 mL of HCl (1M) solution which was added by 0.6 grams of ammonium peroxodisulphate as aqueous phase. The two solutions were mixed into a beaker glass without stirring and separated because of different in phase, the toluene-aniline solution was on top and the solution of HCl-ammonium peroxodisulphate at the bottom. Shortly after mixing, the polymerization quickly starts at the interface of the organic and the water phase. This process left overnight with aluminium foil closed to give complete polymerization time. Polyaniline deposits were collected and purified by filtration, washed with HCl (0.2 M) and acetone then dried in an oven at 50°C for 5 hours.

2.3. Synthesis of ZnO-PANI composite

The PANI-ZnO nanocomposite was prepared by comparing the ZnO weight ratio, using 0.204 g (5% w/w) and 0.408 g (10% w/w) ZnO mixed with 4.080 g monomer aniline and 200 mL toluene in beaker glass. The mixture stirred with a magnetic stirrer at low temperature for 4 hours to form a suspension of the composite. Polymerization carried out such as the synthesis of pure polyaniline to obtain PANI/ZnO nanocomposites.

2.4. Characterization

The synthesized of PANI and PANI/ZnO nanocomposites were characterized by the following methods: *FTIR spectroscopy*, the FTIR spectra were recorded with a PerkinElmer Spectrum 100 spectrometer over the wave number range of 4000-500 cm^{-1} . The spectra of PANI and PANI/ZnO composites were taken using KBr disks. *Electron microscopy*, the scanning electron micrographs of PANI and PANI/ZnO composites were analysed using SEM-EDX (SEM JEOL JSM 6510 LA). *UV-vis DR Spectroscopy*, UV-vis diffuse reflectance spectra were recorded on T80+/PG instruments Ltd Spectrophotometer

3. Results and Discussions

3.1. Scanning Electron Microscopy (SEM)

Morphology of the PANI and PANI/ZnO nanocomposites with different concentration (5% and 10% w/w) are shown in Fig.1. All nanocomposites reveal flaky shaped structures, which the size of the flakes reduced with increasing percentage of ZnO. It can be seen that the size of ZnO crystals covered by PANI decreases with increasing ZnO due to agglomeration, and PANI particles has decreased. According to Mostafaei and Zolriasatein [11], differences in PANI and PANI/ZnO size were caused by PANI agglomeration in the presence of ZnO. Increasing the amount of ZnO can reduce PANI size. This agglomeration is caused by hydrogen bonds that occur due to the interaction between ZnO and N-H groups [6] or coordination bonds [12]. The SEM image helped us to concluded that the increasing of ZnO percentage has a big effect on the morphology of PANI, since PANI has various structure such as granules, nanofiber, nanotubes, nanosphere, microspheres and flake [13].

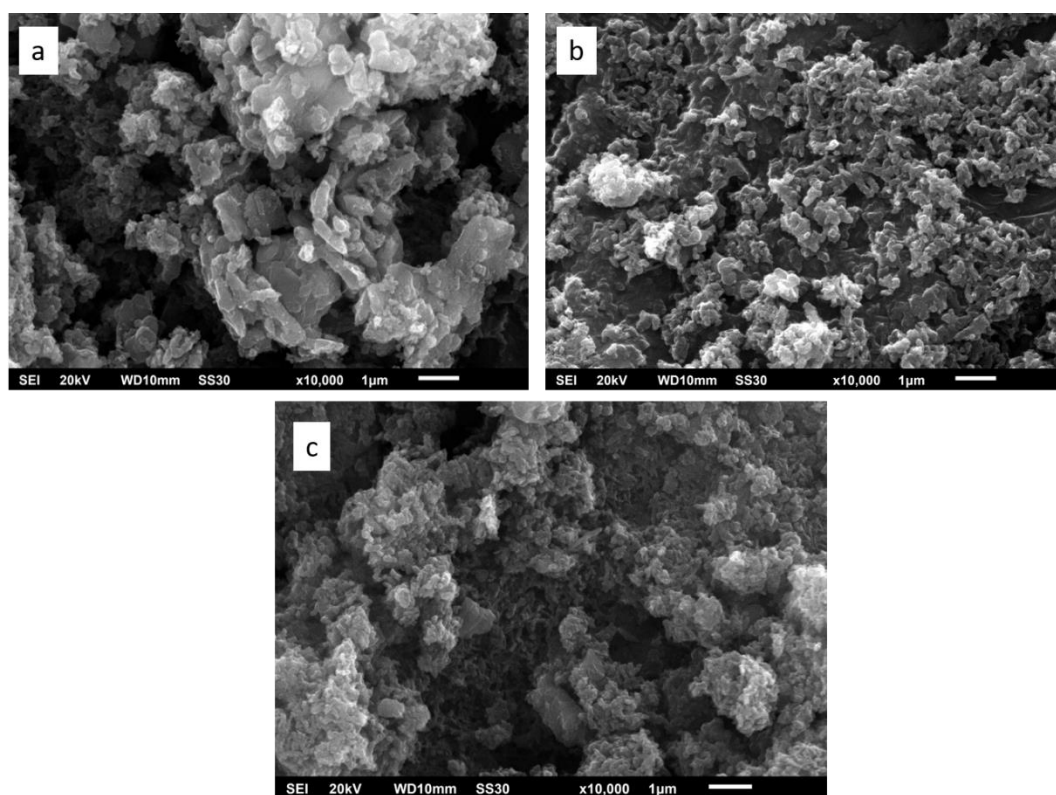


Figure 1. SEM images of (a) PANI, (b) PANI/ZnO (5% w/w) and (c) PANI/ZnO (10%).

3.2. Energy Dispersive X-Ray Analyzer (EDX)

Table 1 shows the most elements in polyaniline, PANI/ZnO (5% w/w) and PANI/ZnO (10% w/w) nanocomposites are carbon elements. The carbon element comes from polyaniline which is formed by the molecular formula $C_6H_5NH_2$ with an average weight% of 72.97%; 73.28%; and 73.15%, respectively. The results of the analysis show that the presence of oxygen and sulphur is thought to originate from ammonium peroxodisulfate $((NH_4)_2S_2O_8)$. Then the presence of chlorine as much as 0.88-1.05% by weight is estimated to come from hydrochloric acid (HCl) which is a material to produce protonated emeraldine. While the Zinc element is only found in PANI/ZnO (5% w/w) and PANI/ZnO (10% w/w) nanocomposites which shows that these nanocomposites can be formed by the interfacial polymerization method of a two-phase organic/aqueous solutions.

Table 1. Average weight (%) of elements in EDX testing.

Elements	Weight Average (%)		
	Poliyaniline	PANI/ZnO 5%	PANI/ZnO 10%
C	72.97	73.28	73.15
N	16.36	15.29	14.35
O	9.39	10.37	11.15
S	0.19	0.10	0.11
Cl	1.09	0.88	1.02
Zn	0.00	0.08	0.22

3.3. Fourier Transform InfraRed (FTIR)

To understand the structure of the PANI and PANI/ZnO nanocomposites, FTIR analysis also carried out. Fig.2 shows the FTIR pattern of PANI and PANI/ZnO (5% w/w) and PANI/ZnO (10% w/w) nanocomposites and the absorption peaks are given in Table 2.

As seen in Fig.2, the PANI exhibits characteristic peaks around 3448.72 cm^{-1} attributed to N-H stretching mode [5], the C-N stretching of quinoid unit occur at 1581.63 cm^{-1} , 1128.43 cm^{-1} due to the quinoid of PANI. In addition, the band 817.82 cm^{-1} and 594.08 cm^{-1} correspond to C-H out of plane bonding in aromatic rings and C-N-C bonding mode of aromatic rings respectively. The PANI/ZnO nanocomposites showed the similar characteristic peaks with PANI. However, there is an evidence of peak displacement when ZnO are added to the PANI. The shifts included 1481.33 cm^{-1} , 1566.20 cm^{-1} , and 1141.86 cm^{-1} [11]. According to the patterns of peaks, absorption intensity increased by adding ZnO in nanocomposites due to uniform distribution of ZnO in nanocomposites matrix and elimination of agglomeration.

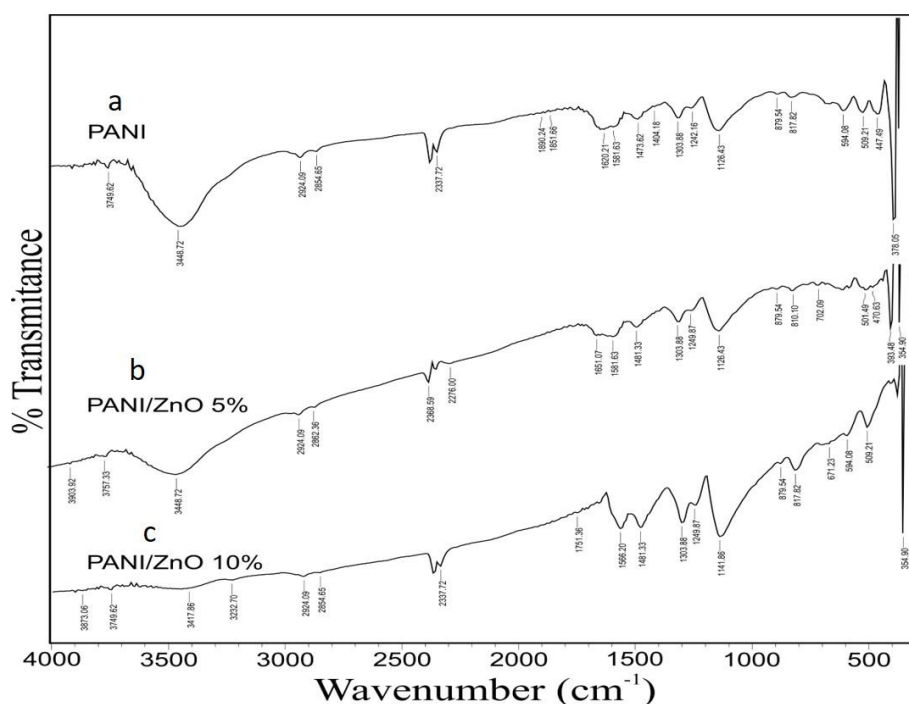


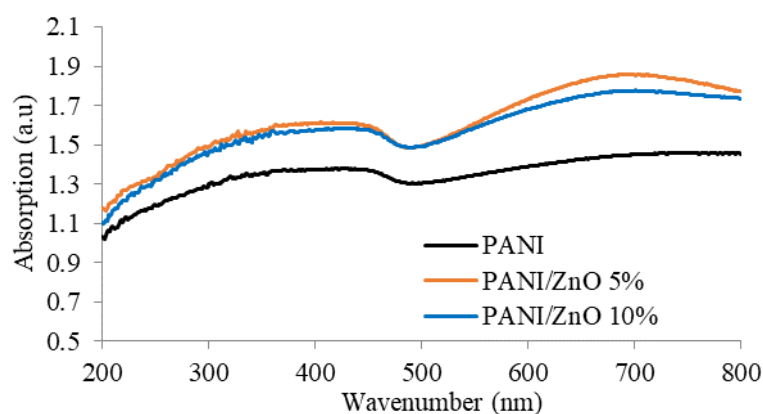
Figure 2. FTIR spectra of (a) PANI, (b) PANI/ZnO (5% w/w) nanocomposites, and (c) PANI/ZnO (10% w/w) nanocomposites.

Table 2. Characteristic absorption peaks obtained from FTIR spectrum of PANI and PANI/ZnO nanocomposite.

Wave number (cm ⁻¹)	Functionality
515-595	C-N-C bonding of aromatic ring
810-880	C-H out of plane bonding in benzenoid ring
1128.43	The quinoid of PANI
1141.86	Spectra of PANI-ZnO
1566.20	C=C stretching of quinoid ring
1581.63	C=N stretching of quinoid ring
3232.70	Interaction of ZnO and PANI by formation of hydrogen bonding between H-N and oxygen of ZnO
3448.72	N-H stretching

3.4. UV-Vis Spectroscopy

Fig. 3 shows there are three peaks of uptake at about 370 nm, 450 nm, and 700 nm indicating that the precipitate formed is a protonated emeraldine salt (ES). The absorption at about 370 nm corresponds to the transition $\pi \rightarrow \pi^*$ of the benzenoid part, the absorption at about 450 nm corresponds to the polaron transition $\rightarrow \pi^*$, while the transition at about 700 nm corresponds to the ribbon transition $\pi \rightarrow$ polaron. The polaron energy levels seen from polaron transitions $\rightarrow \pi^*$ and $\pi \rightarrow$ polaron indicate that the polyaniline produced is polyaniline in protonated emeraldine (ES) form. Polaron is an orbital between the valence band and the conduction band and has a slightly larger energy than the valence band due to cation radical. Cationic radicals could have electron delocalisation on ES, so PANI in the form of ES is conductor [14].

**Figure 3.** UV-Vis Spectra of PANI and PANI/ZnO nanocomposites.

The interaction between ZnO and polyaniline causes an increase in absorbance in the UV light region (200-400 nm) and visible light areas (400-800 nm) seen on PANI/ZnO curves of 5% and 10%. According to Shukla *et al.* [12], the interaction between PANI and ZnO occurs because ZnO is a Lewis acid compound and aniline is a Lewis base. Aniline in PANI will donate free electron pairs to ZnO and form a complex compound. This will form a polymeric ionization chain and produce an efficient electron exchange effect.

3.5. UV-Vis Diffuse Reflectance Spectroscopy (DRS)

The band gap energy can be calculated by using the following Tauc equation [15]:

$$(\alpha h\nu) = A (h\nu - E_g)^{n/2}$$

Where α , h , and ν are the adsorption coefficient, Planck constant, light frequency, respectively, while A is a constant and the value of n depend on whether the transition is direct ($n=1$) or indirect ($n=2$).

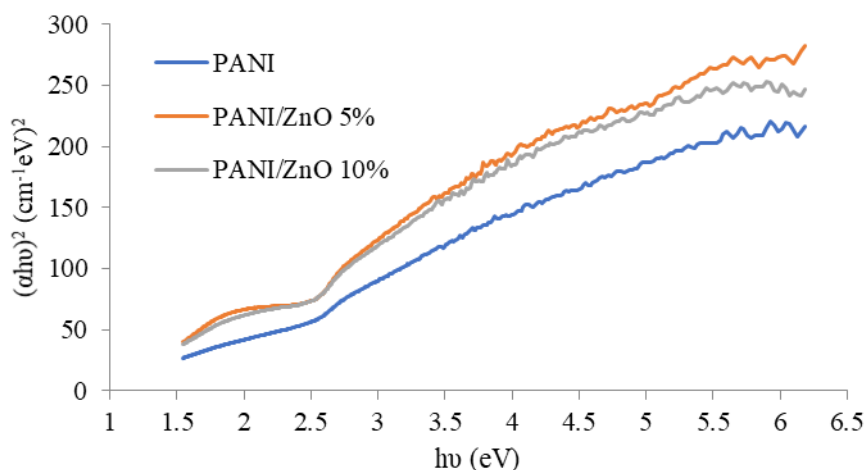


Figure 4. Determination of band gap using the Tauc Plot method.

According to Fig. 4, the value of the gap energy of PANI and the PANI/ZnO nanocomposite were obtained by drawing a straight line on the slope of the curve until it cuts the x axis. The intersection of a straight line on the slope of the curve with the x-axis shows the value of the bandgap energy. The band gap yield obtained in PANI, PANI/ZnO (5% w/w) and PANI/ZnO (10% w/w) nanocomposites were 2.029 eV; 2.026 eV; and 2.006 eV, respectively. The results obtained can be seen that more ZnO addition to PANI, the band gap energy will decrease. According to Kant *et al.* [16] the interaction between PANI and ZnO causes changes in electron density (electron density) of the polyaniline chain. These changes cause red shift where there is a shift in absorption to a longer wavelength.

4. Conclusions

Polyaniline (PANI) emeraldine salt (ES) and PANI/ZnO nanocomposite compounds were successfully made using two phase organic/water interfacial polymerization methods under acidic conditions. Characterization using UV-Vis DRS, FT-IR, and SEM-EDX showed the presence of PANI and PANI/ZnO nanocomposites.

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