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RESEARCH ARTICLE

Synthesis and characterization of composite polyaniline as hydrogen gas detector

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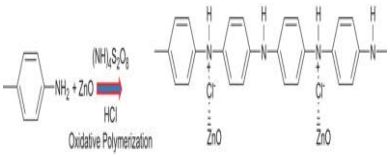
Graphical abstract



Abstract

Composite polymer consisting polyaniline (PANI) and zinc oxide (ZnO) were synthesized via oxidative polymerization of aniline. The composite PANI thin films were characterized by FTIR spectroscopy and their optical properties towards hydrogen gas were investigated using UV-vis spectroscopy. The FTIR spectra obtained verified the synthesis PANI/ZnO composite. From the experimental results, it was found that with increasing zinc oxide content in the composite cause the transmittance to decrease. The transmittance of the thin films slightly increased after exposed to hydrogen gas. PANI-ZnO (10%w.t.) exhibited best response compared to other composition with the highest transmittance peak difference of 11.4%.

Keywords: Polyaniline, zinc oxide, oxidative polymerization, palladium, hydrogen sensing thin film

INTRODUCTION

Hydrogen gas as one of the cleanest source of energy has attracted attentions from all over the world though there are still many safety concerns, especially associated with the probable linkage risk (Chen *et al.*, 2014). Wherever hydrogen is used, and wherever it can mix with air and ignite, monitoring for leaks is necessary to avoid catastrophes. Hydrogens also are known to have excellent combustible and explosive properties but also have a high tendency to leak through container or pipe lines due to its small molecular size (Kumar *et al*., 2010). Large quantities of hydrogen are safely used in industry today, but it is hard to contain and difficult to detect leaks. This is because of the natural characteristics of hydrogen gas which is colourless, odourless, has high propensity to leak, low ignition energy, invisible flame, high energy content and it is a highly explosive gas. When consumption and demand of hydrogen are growing, they will lead to the development of massive infrastructures composed of hydrogen energy system, such as large-scale storage tanks, liquid hydrogen tankers, electrolysis plants, long pipelines and fuel cell power. Therefore, a sensitive hydrogen gas sensor with low limit detectability, reliable and low cost is extremely required to sense the leakage over a wide area as fast as possible.

Mechanisms for detection of hydrogen are dependent on the type of sensors which are based on the detectable change of physical or chemical property of sensing element. Example of detectable changes such as resistance, electric current, temperature, capacitance, voltage, reflectance, bending and frequency (Hubert *et al.*, 2011). Therefore, hydrogen sensors can be classified into several types such as thermal, catalytic, electrochemical, resistive, mechanical, acoustic and optical.

Electrochemical hydrogen sensor is based on the changes of electrical properties caused by an electrochemical reaction at the electrode. Low concentration (ppm level) of hydrogen gas can be sensed using this type of sensor and does not require heating (Li *et al*., 2015). Resistive hydrogen gas sensor is based on the change of resistance of semiconductors. This change is due to the increase of surface electrons by oxygen adsorption which will later react with hydrogen gas.

PANI is one of many conducting polymers that had gained attention for various applications such batteries, electrochromic glasses and actuators (Boeva *et al.*, 2014) due to its high environmental stability and easy synthesis process. One of the unique attribute of PANI is the doping process. It can exist in three different states of oxidation. Leucoemeraldine being the most reduced form and pernigraniline the most oxidized form are poor conductors and not environmentally stable. Common use of PANI exists in the form of emeraldine, the halfly oxidized form. In this form, emeraldine can undergo easy acid/base doping which can interchange the PANI in conducting form which is the emeraldine salt and insulating form which is the emeraldine base. The properties of PANI can be tuned by adding dopant such as metals to improve selectivity (Athawale *et a*l., 2006) and acid to induce greater solubility (Cao *et al.*, 1992)

Due to the easy processibility of PANI which made it suitable to be fabricated as thin film (Kang *et al.*, 1998) allows zinc oxide to be incorporated into PANI which acts as the gas sensing reaction site due to its high surface area while ZnO linked the polymer chain to increase the stability of the composite (Shukla *et al*., 2013). PANI-ZnO had been reported to be used as ammonia gas sensor that showed room temperature operation and fast response (Talwar *et al.*, 2014). In this work, composite PANI-ZnO were synthesized by oxidative polymerization of aniline by ammonium persulfate with different weight percentage of zinc oxide. The selectivity toward hydrogen gas is assisted by addition of palladium. The resulting composite polymer is fabricated into thin films to be tested as hydrogen gas sensing material.

EXPERIMENTAL

Materials

Aniline (ACS reagent 99.5%), 1-methyl-2-pyrrolidinone (NMP, 99.5%), ammonium persulfate (APS, 98%) were purchased from Sigma-Aldrich. Palladium (II) chloride (59%) was purchased from Merck Sdn. Bhd. Zinc oxide (AR Grade) was obtained from QREC. Sodium hydroxide (ACS reagent) was purchased from R&M Chemicals. Hydrochloric acid (37%) was obtained from RCI Labscan Limited.

Synthesis of PANI-ZnO

Zinc oxide powder of 5%, 10%, 20% and 30%wt to aniline were added into 400mL of 0.1M aniline in 1M HCl. Each sample were labelled according to the weight percentage of added zinc oxide into the monomer which are Z5 (5%wt), Z10 (10%wt), Z20 (20%wt) and Z30 (30%wt). APS in 1M HCl was added in dropwise for 30 minutes while stirring vigorously and the molar ratio of monomer to oxidant was maintained at 2:1. The stirring was continued for 8 hours before the solution was left to settle overnight. The precipitate was filtered and washed with distilled water and methanol for the second wash. The precipitate was left to dry in air for 24 hours. The obtained powder was subjected to 1M sodium hydroxide treatment to convert to emeraldine base form.

Fabrication of thin film

The composite polymer powder was mixed with palladium chloride at 1:1 ratio. The mixture was dissolved in NMP to create 1% polymer solution. The solution was drop casted onto the glass slides before set to dry in an oven of 50°C until the solvent evaporated completely.

Testing rig

The fabricated thin films were tested inside a small glass chamber which allow hydrogen to pass through directly onto the surface of the thin films. The rig was as shown in Fig. 1.

Fig. 1 Experimental rig of hydrogen sensing

RESULTS AND DISCUSSION

FTIR Analysis of Polyaniline-Zinc Oxide composite

FTIR spectra of PANI-ZnO composite were observed for each sample in the range of 500–4000 cm−1 to confirm the polymerization of polyaniline. Spectra in Fig. 2 for 5wt% of ZnO in PANI-zinc oxide composite were taken as base to observe functional groups present in the composite. FTIR spectra of PANI-ZnO exhibit characteristic bands at 3200-3300, 2115, 1637, 1583, 1489, 1289, 1160 and 825 cm-1. The band at 3200-3300 cm-1 is due to the N-H stretching of PANI in PANI-ZnO. Peak at 1637 is assigned as NH_2 bending vibration. The appearance of peaks at 1583 and 1489 cm-1 is attributed to the C=C stretching of quinoid and benzenoid rings, respectively. The band at 1289 cm-1 is assigned to the emeraldine base structure. Furthermore, the band at 1160 cm-1 is due to N=Q=N, where Q represents the quinoid ring present in the PANI-ZnO nanocomposite (Alvi F. *et al.*, 2010). The peak at 825 is attributed to para disubtituted benzene. Similar spectra of different compositions of PANI-ZnO are shown Fig. 3.

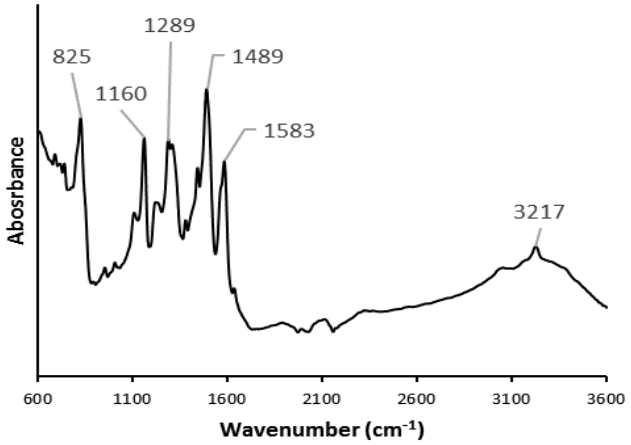


Fig. 2 FTIR spectra for 5wt% of ZnO in PANI-zinc oxide composite.

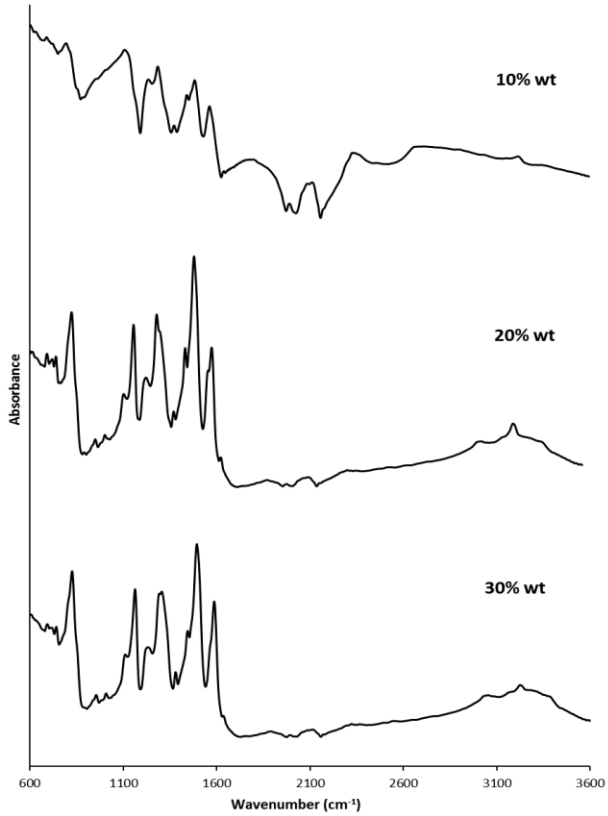


Fig. 3 FTIR spectra for different composition of PANI-ZnO

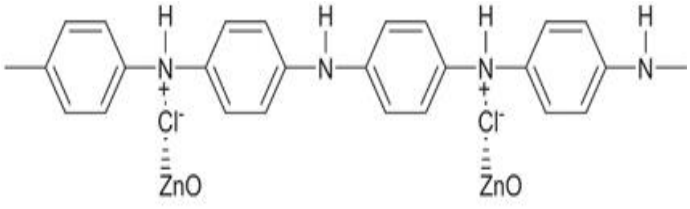


Fig. 4 Chemical structure of PANI-ZnO

Evaluation of hydrogen sensing

Based on the results, it was found that increasing amount of zinc oxide in the composite will cause the transmittance to decrease as shown in Figu. 5. Fig. 6 shows UV-vis spectrum of PANI-ZnO thin film after exposure to hydrogen gas. Samples showed strong peaks at about 580nm which attributed to transition between benzoid and quinoid ring. The peaks slightly shifted to lower wavelength as the metal oxide content increases.

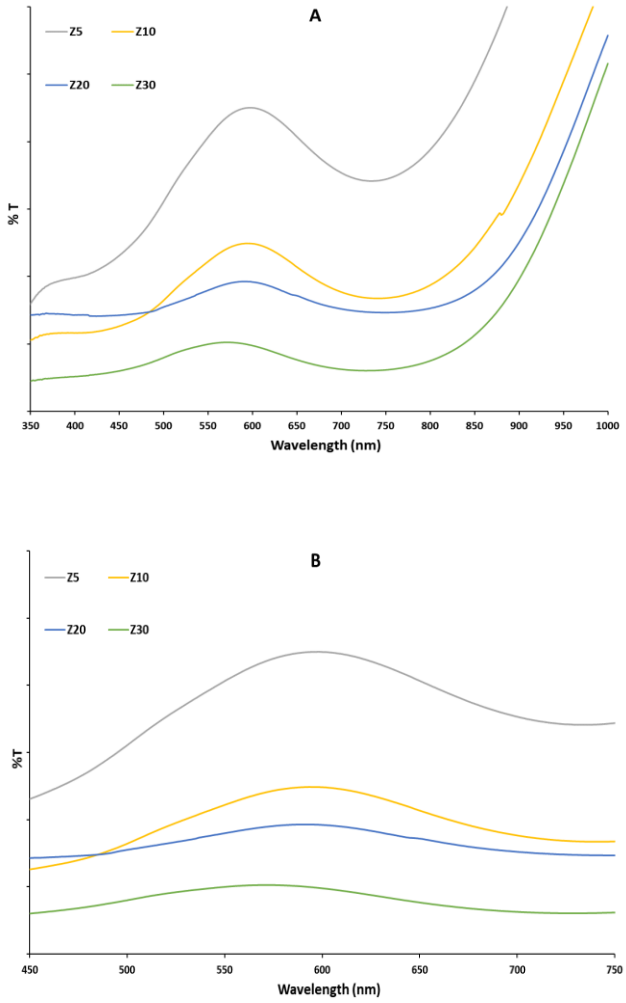


Fig. 5 (A) Wide UV-vis spectrum before H_2 exposure; **(B)** Zoomed in spectrum before H_2 exposure

Fig. 7 shows the difference in terms of transmittance for before and after the samples were passed through hydrogen gas. It can be seen that Z10 has the highest difference up to 11.4 % compared to other composition. The findings obtained is the same with the ones researched by (Ameen S. et al., 2011), where peak intensity gradually decreases with the increasing weight percent ratio of ZnO which indicates that the generations of singlet excitons are reduced due to the presence of the ZnO and might interact with the inter-chain of PANI species.

The response of thin film when exposed to hydrogen gas maybe due to the doping of PANI. When hydrogen gas comes into contact with palladium, it dissociates into hydrogen atom which then adsorbed into the matrix of PANI-ZnO. These atoms may induced protonation of PANI. From the results, the response of each samples is not yet viable to be used. This may due to the reduction of palladium chloride by emeraldine base while simultaneously changed to emeraldine salt (Khanna et al., 2008). Clear observation was made when the casting solution changed colour from blue (emeraldine base) to green (emeraldine salt) after a few days. This means the thin films of emeraldine base were already partially protonated by itself before the exposure. Since the detection depends on the initial oxidation state of PANI (Lange *et al.*, 2008), further study is needed to investigate the sensing mechanism of this composite polymer.

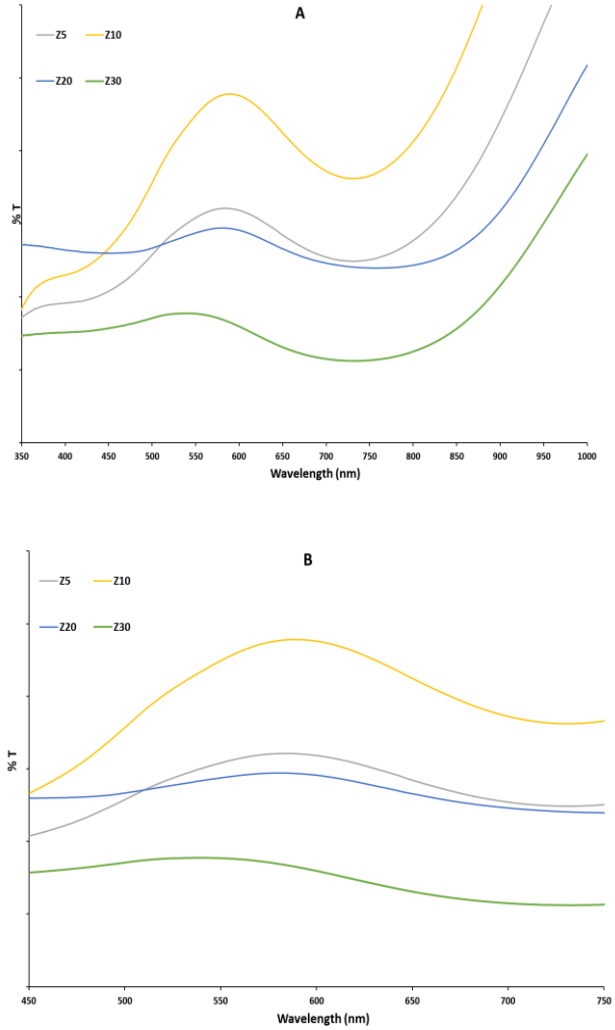


Fig. 6 (A) WideUV-vis spectrum after H_2 exposure; **(B)** Zoomed in spectrum after H_2 exposure

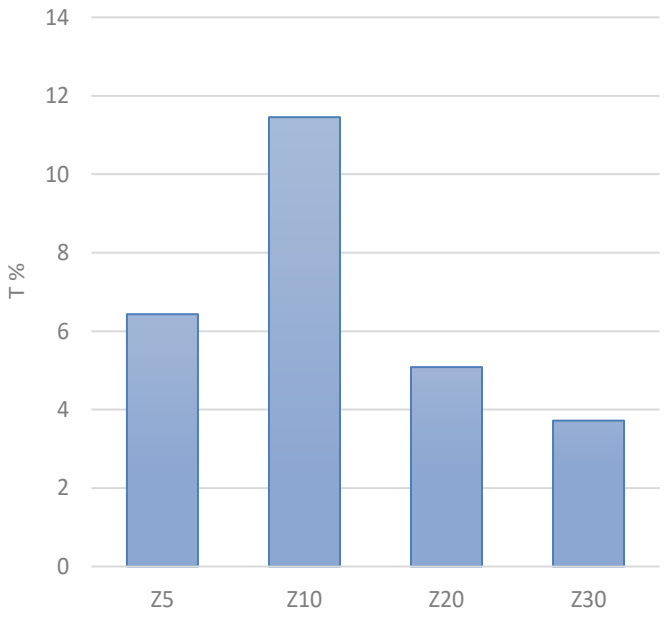


Fig. 7 Transmittance difference

CONCLUSION

PANI-ZnO with different weight percentage of zinc oxide were successfully synthesized and tested for hydrogen gas sensing. The FTIR spectra verfied the functional groups of polyaniline while the UV-vis spectrum is used to measure the response of PANI-ZnO thin film towards exposure to hydrogen gas. It was concluded that PANI-ZnO (10% w.t) showed the best response compared to other composition. This composite showed the potential of being used as hydrogen gas sensing material with further optimization of material and fabrication process.

ACKNOWLEDGEMENT

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