An Optical pH Sensor Construction Based on Polyaniline Nanoparticles (PANI NPs)

Muawia Alqasaimeh[1], Lee Yook Heng[2], Musa Ahmad[3] and Randa AL-AS'AD[1]

[1]Faculty of Science, Al-Hussein Bin Talal University, Jordan
[2]Southeast Asia Disaster Prevention Research Initiative (SEADPRI-UKM), LESTARI, Universiti Kebangsaan Malaysia, Selangor D.E., Malaysia
[3]Industrial Chemical Technology Programme, Faculty of Science and Technology, Universiti Sains Islam, Malaysia
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ABSTRACT

Polyaniline nanoparticles (PANI NPs) with size 45 nm were prepared based on chemical oxidation polymerization of aniline in acidic aqueous media by using ammoniumpersulfates an oxidant. Based on FTIR and XRD analysis for PANI NPs the structure was confirmed. The XRD analysis for PANI NPs shows the 100 and 110 crystallographic planes of the partially crystalline PANI NPs. PANI NPs color changeability property with acid/base forms exploited for optical pH sensor construction. At PANI optimum conditions, the pH sensor demonstrated a wide linear pH response range between pH 4−13 in 50 mM PBS. The pH sensor shows two linear calibration curves; at 870 nm and 425 nm where the optimum sensitivity of the pH sensor of 0.055 and the correlation coefficient (R^2) of 0.98 (n=3) and %RSD=7.1 were achieved at 870 nm wavelength.

Keywords: Polyaniline; Nanoparticles; pH sensor; Coating
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INTRODUCTION

The measurements for pH, is important in many fields of applications such as common industrial, environmental analysis, medical [1] and process control [2]. There are many methods for the determination of pH, these methods have many disadvantages, e.g. complicated sample pre-treatment, required skillful operator, high cost of instrumentation and sometimes they require long analysis time [3]. These disadvantages can be overcome by using sensors.

Nanoparticles are interesting materials that bridge the gap between individual molecules and bulk materials. They exhibit electronic, magnetic, ionization potentials and optical properties that differ from the bulk material. They can improve the mechanical properties of bulk or composite materials [4; 5]. Polyaniline (PANI) is a nano polymer that is easy to prepare, has a good stability, and has high surface area. PANI has color changeability with acid/base forms [6], this acid/base switching ability could be exploited for pH sensor construction.

In this work Polyaniline NPs (PANI NPs) was studied for their potential in the development of new pH sensors. The optical pH sensor was designed successfully and constructed based on PANI NPs. The pH sensor was constructed by dip-coating PANI NPs onto a transparent plastic slide and the PANI NPs was immobilized onto transparent plastic slide by adsorption method. When the sensor dipped into a solution based on the pH value of the solution media, the immobilized PANI NPs color will be changed which can be proverb as an optical signal.

MATERIALS AND METHODS

Chemicals
Polyvinylpyrrolidone (PVP) (Mwt: 40,000) was purchased from Sigma-Aldrich. Aniline (99.5%) was purchased from MERCK. Hydrochloric acid (HCl, 37%) was obtained from J.T.Baker. Ammoniumpersulfate (98%) was purchased from MERCK, KH_2PO_4 (99.5%) and K_2HPO_4 (98%) were purchased from Fluka, Pure water was used in all solution preparations with a resistivity of 18.2 MΩcm. All chemicals were used without further purification.

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Instrumentation
UV-Visible Spectrophotometer: Varian Cary 50 UV-Visible spectrophotometer was used for UV-Visible measurements. A personal computer was used for online data collection. The instrumental parameters were controlled by Cary Win UV Software and the data were collected and processed.

P^H Meter: P^H meter model Ω Metrohm 827 was used for pH value measurements. The pH electrode was dipped into any solution for pH determination and the values were recorded when a stable reading was reached.

Scanning Electron Microscope (SEM): The nanomaterial samples were investigated using VPSSEM 1450 at UKM. The samples were firstly coated with a metal that readily reflected electrons, and then the coated samples were placed in the SEM. An electron beam was focused onto the sample surface. The electrons that bounced from the surface of the specimen were collected by an imaging screen. The nanoparticles sizes and the nanoparticles distribution were evaluated from the collected image.

Fourier Transform Infrared Spectroscopy (FTIR): The transmission FTIR spectra for nanoparticles samples was carried out and analyzed using Perkin Elmer Infrared Spectroscopy model GX in the range 400-4000 cm^{-1} with 4 cm^{-1} resolution using KBr pellets.

X-Ray Diffraction Spectroscopy (XRD): The XRD measurements were carried out using Phillips X-pert MPD PW3040, with running step = 0.02° in the range of 10-80° 2-theta, using monochromatized Cu Kα (λ=0.154) materials by using the phenomenon of diffraction. The samples were kept in the tray of the system and the scanning was done in the range of 10-80° 2-theta, and then the data were collected and plotted as diffraction intensity versus 2θ.

PANI NPs Preparation: PANI NPs was prepared as described in literature with some modifications [7-11]: 4.0g PVP was dissolved in 150.0 mL water and heated for 30 min at 80 °C under vigorous stirring. Under vigorous stirring, 1.0 ml of aniline was added and stirred in 5 min until the solution became homogenous. 5.0 mL of concentrated HCl was added and then 10.0 mL 0.5 g/mL of ammoniumpersulfate was added under vigorous stirring. The final green produced solution was left overnight under room temperature with vigorous stirring. For pure PANI NPs purification, the resultant PANI NPs were then purified by using water in eight cycles of centrifugation, decantation, and resuspension. The solution was centrifuged (4000 rpm, 10 min). The resultant nanoparticles were dried in a vacuum oven at 60 °C.

P^H Sensor Construction Based on PANI NPs The optical pH sensor was prepared by dip-coating a transparent slide into a suspended PANI solution. Then, the resultant pH sensor was left to dry. PANI NPs concentration were varied in the range of 16-65 mg/mL for pH sensor construction to determine the optimum response for the pH sensor. Three sensors were prepared from the following PANI concentration: 17.78, 20.32, 23.22, 26.54, 30.33, 34.67, 39.62, 42.93, 49.06, 56.07, and 64.08 mg PANI per ml water. For every constructed sensor, the UV-Visible were scanned in the range of 200-900 nm at pH 1.00 and pH 13 using 50 mM PBS. The averages of the corrected base line absorbance difference (ΔAverage at 870 nm corrected by 200 nm base line) between pH 1 and pH 13 were calculated and plotted against PANI amounts. At optimum PANI amounts, a calibration curve for the pH sensor was constructed in the range of 1-13 pH values using 50 mM PBS.

RESULTS AND DISCUSSION

Polyaniline nanoparticles (PANI NPs)
Polyaniline (PANI) nanoparticles were obtained via chemical-oxidation polymerization of aniline in acidic aqueous media using ammoniumpersulfate (APS) as an oxidant [12-14]. A characterization for PANI NPs was conducted. PANI nanoparticles were used successfully for pH sensor construction.

PANI nanoparticles morphology study
The morphologies of the synthesized PANI NPs were examined by using a scanning electron microscope (SEM). Figure 1 shows the SEM image for PANI NPs. The average size of the PANI NPs was 45 nm, which was calculated based on 10 particles.
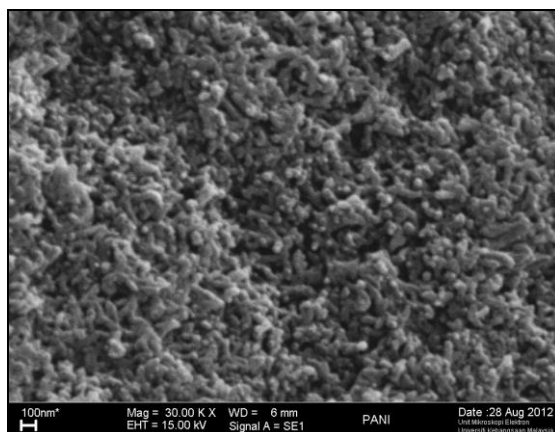
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Figure 1: The SEM image for PANI NPs

FTIR spectroscopy analysis

Figure 2 shows FTIR spectrum of PANI NPs. Table 1 shows that the peak locations related to the corresponding chemical bonds are in good agreement with those reported in the literature.
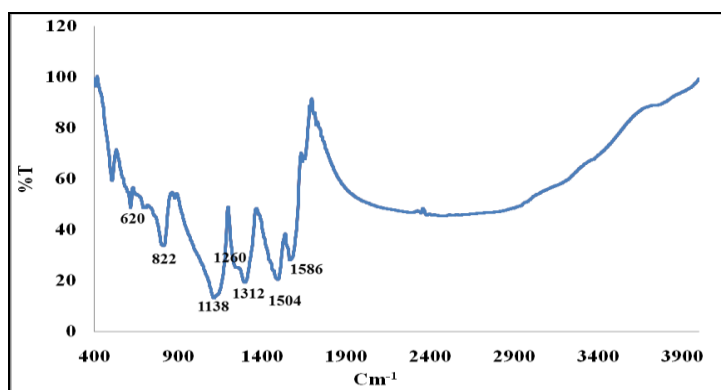

Figure 2: FTIR spectrum of PANI NPs

Table 1: Characteristic frequencies of PANI NPs

Wave no. (cm-1)	Band characteristic	Reference
620	C–H out of plane bending vibration	[15]
822	Paradisubstituted aromatic rings indicating polymer formation	[15;16]
1138	C–H in plane bending vibration	[15; 16]
1260	Aromatic C-N stretching indicating secondary aromatic amine group	[16; 17]
1312	C=N stretching	[16; 17]
1504	C–N stretching of benzenoid rings	[15-17]
1586	C–N stretching of quinoid rings	[15-17]
1312	C=N stretching	[16; 17]

XRD analysis

Figure 3 shows XRD spectrum of PANI NPs. Abroad peaks are observed at 2θ value of 20°C and 25°C, which are ascribed to the periodicity parallel to the polymer chains of PANI. The two characteristic peaks indicate that PANI had crystallinity to a certain extent [18; 19]. The two broad peaks correspond to the 100and 110 crystallographic planes of the partially crystalline PANI [20].
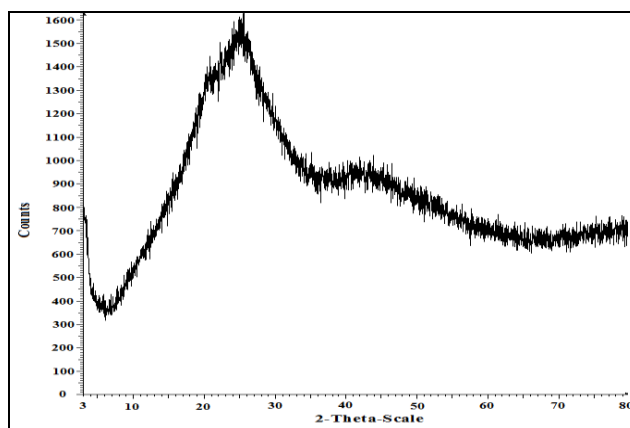
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Figure 3: XRD spectrum of PANI NPs

Fabrication of pH sensor based on PANI NPs

Due to PANI ability to change color from green (ES) to blue (EB), an optical pH sensor was constructed as described in section 2.4. To obtain optimum response, the PANI NPs were optimized by varying the PANI NPs weight between 16.0-65.0µg. For every sensor constructed, the UV-Visible spectra were scanned in the range 200–900 nm at pH 1and pH 13using 50 mM PBS buffer. Base line correction for every pH sensor at pH 1 and pH 13 was calculated. The corrected absorbance difference between pH 1 and pH 13 (ΔA) was calculated and plotted against PANI NPs weight to determine the optimum response. Figure 4 illustrates the relationship between the PANI amounts and the pH sensor response. The figure shows that the optimum response was achieved by using 460.8 µg of PANI NPs.
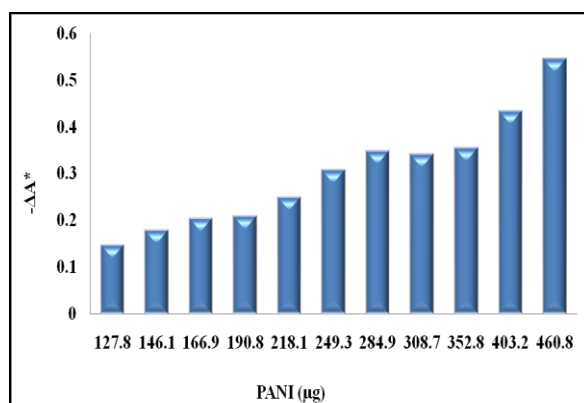

Figure 4: The relationship between PANI amounts and optical pH sensor response (n=3)
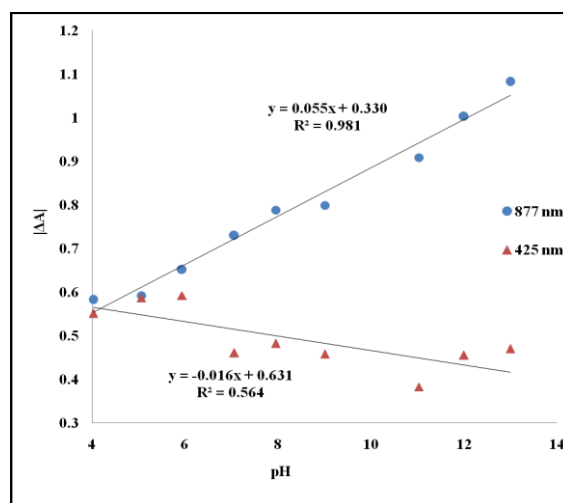

Figure 5: The optical pH sensor calibration curve (A measurable with base line at 870 nm and 425 nm correction) using 50 mM PBS

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At PANI optimum conditions, the pH sensor demonstrated a wider linear pH response range and thus a calibration curve could be constructed between pH 4−13 in 50 mM PBS. Figure 5 shows the pH sensor calibration curve at 870 nm and 425 nm where the optimum sensitivity of the pH sensor of 0.055 and the correlation coefficient (R^2) of 0.98 (n=3) and %RSD=7.1 were achieved at 870 nm wavelength. Figure 6 shows the absorbance spectrum of the optical pH sensor at different pH values using 50 mM PBS. The pH sensor response time was within seconds.
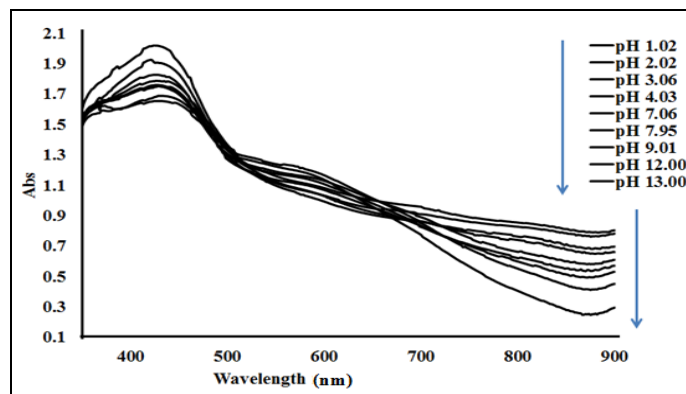

Figure 6: The absorbance spectrum of the optical pH sensor at different pH values using 50 mM PBS

Figure 6 shows the absorbance spectrum of the optical pH sensor at different pH values using 50 mM PBS. The figure apparently illustrates that two specific bands of PANI NPs appear at 425 and 870 nm, which can be attributed to π-π^* and π-polar on transitions, respectively [21].When nitrogen atoms in imine groups are protonated, nitrogen and its neighboring quinoid ring become a semiquinoid radical cation, causing a decrease in the exciton absorption peak intensity and generation of the absorption peaks at about 425 and 870 nm due to the presence of polaron/bipolaron [22; 23].

CONCLUSION

PANI NPs properties were exploited to construct an optical pH sensor. The optical pH sensor was fabricated by dip-coating a transparent plastic slide onto suspended PANI NPs solution. At wavelength of 425 and 870 nm, a specific band of the optical pH sensor was observed due to π-π^* and π-polar on transitions of immobilized PANI NPs and a change of these peaks was related to polaron/bipolaron of PANI NPs conformations. At optimum conditions, the optical pH sensor showed a response toward pH values change in the range of 1−13 at 870 nm with less than 10 s of response time.

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