

Polypyrrole Chitosan Cobalt Ferrite Nanoparticles Composite Layer for Measuring the Low Concentration of Fluorene Using Surface Plasmon Resonance

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Fluorene is a polycyclic aromatic hydrocarbon, which is a hazardous toxic chemical in the environment. The measurement of low concentrations of fluorene is a subject of intense interest in chemistry and in the environment. Polypyrrole chitosan cobalt ferrite nanoparticles are prepared using the electrochemical method. The prepared layers are characterized using field emission scanning electron microscopy, Fourier transform infrared spectroscopy, and energy dispersive spectroscopy. The layers are used to detect fluorene using the surface plasmon resonance technique at room temperature. The composite layer is evaluated after detection of fluorene using atomic force microscopy. The fluorene is bound on the layer, and the shift of the resonance angle is about 0.0052° , corresponding to the limitation of 0.01 ppm.

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Magnetic nanoparticles based on ferrite component are non-toxic materials, and they have high mass transference and a large surface area.^[1] They are thermally and chemically stable,^[2] hence they are used in sensors and biosensors, because they have several beneficial analytical features including low detection limits, enhanced sensitivity and selectivity, and high signal-to-noise ratios.^[3,4] Spinel CoFe_2O_4 -nanoparticles (CoFe_2O_4 -NPs) are of interest because they can be used as catalysts,^[5] and they have applications in several other fields, including biomedical^[6] and audio, videotape, and high-density digital recording disks.^[7,8] Spinel CoFe_2O_4 -NPs are utilized in magnetic bio-separation and detection of biological entities (cells, protein, nucleic acids, enzymes, bacterial, viruses, and others),^[9] and they are used in clinical diagnoses, such as magnetic resonance images and magnetic fluid hyperthermia, targeted drug delivery, and biological labels.^[10] Fluorene is a type of polycyclic aromatic hydrocarbon (PAH) with two benzene rings that are coplanar with the central carbon, and the chemical formula is $\text{C}_{13}\text{H}_{10}$. It is obtained from coal tar, and it is soluble in organic solutions.^[11] Fluorene has an aromatic nature, thus it is an excellent candidate as a conductor based on organic components. Fluorene, polyfluorene, and other components of fluorene have more attractive applications in light emitting diodes,^[12] solar cells,^[13,14] and biosensors.^[15,16] Fluorene is a hazardous material, and it can irritate and burn the eyes and skin. Fluorene has an effect on the lungs, and it can cause cancer.^[17] Therefore, the detection and measurement of the concentration of fluorene are very important in medicine, chemistry, and environmental departments. Many methods have been introduced for measuring the concentration of fluorene. The best known methods that were used to measure low concentrations of fluorene are high performance liquid chromatography (HPLC),^[18] liquid chromatography-fluorescence detection (LC-FLD),^[19] and laser-induced fluorescence probes.^[20] These met-

hods require expensive instruments, and they require special chemical knowledge to conduct experiments and analyze the data. The surface plasmon resonance (SPR) technique is a versatile technique to detect toxic materials. The SPR sensor is based on a prism with angular modulation,^[21] and output of the sensor is the variations of the resonance angle, which can be calibrated to identify variations of refractive index or the concentration of the probe medium.^[21] In accordance, prior publication, the gold layer should be modified with an immobilized layer to improve the sensitivity of the sensor. For example, paramagnetic iron oxide (Fe_3O_4) nanoparticle and the combination of multi-walled-born nitride nanotubes and Fe_3O_4 nanoparticles were used to detect and remove arsenic in water and human blood.^[22,23] The polypyrrole-NPs/reduced graphene oxide was used to detect and measure the low concentration of the pyrene using the surface plasmon resonance.^[24] Verma *et al.*^[25] investigated the mixture of polymer and chitosan to detect the heavy metal ions using the SPR technique. They measured the low concentration of pb^{2+} and Hg^{2+} with the limitation of 0.158 nM and 0.293 nM, respectively. ZnO-polypyrrole nanocomposite was used to modify the gold layer for the detection of manganese ions using the surface plasmon resonance^[26] and recently, the surface plasmon resonance based on graphene-MoS₂ hybrid structures was used to make an ultrasensitive biosensor for detection of molecules.^[27] In this study, a polypyrrole-chitosan cobalt ferrite nanoparticle composite was prepared using the electrodeposition method. The prepared layers were characterized using scanning electron microscopy, energy dispersive spectroscopy and atomic force microscopy. The layer was used to modify the gold layer for the surface plasmon resonance sensor.

The poly(vinyl pyrrolidone) (PVP), iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, polypyrrole, chitosan, acetic acid, fluorene and sodium dodecylbenzenesulfonate (SDBS) were purchase from the Sigma Aldrich company.

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Metal nitrate reagents were used as precursors, poly(vinyl pyrrolidone) (PVP) was used as a capping agent to reduce the agglomeration of the particles, and deionized water was used as the solvent. Iron nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were purchased from Acros Organics with purities exceeding 99%. PVP (MW=29000) was purchased from Sigma Aldrich and was used without further purification. An aqueous solution of PVP was prepared by dissolving 3 g of polymer in 100 ml of deionized water at 343 K, before mixing 0.2 mmol of iron nitrate and 0.1 mmol of cobalt nitrate (Fe:Co=2:1) into the polymer solution and constantly stirring for 2 h using a magnetic stirrer until a colorless, transparent solution was obtained. The solution had a pH from 1 to 2 measured by means of a glass electrode. No precipitation of materials occurred before the heat treatment. The mixed solution was poured into a glass Petri dish and was heated at 353 K in an oven for 24 h to evaporate the water. The resulting orange solid was crushed for 15 min in a mortar to form powder. The calcinations of the powder were conducted at 673, 723, 823, and 923 K for 3 h for the decomposition of the organic compounds and the crystallization of the nanoparticles.^[28]

Prior to carrying out the experiment, the gold-coated glass slide was prepared with a sputtering coating at a thickness of 46.3 nm.

The PPy-Chi/CoFe₂O₄-NPs composite layers were synthesized using electrochemical polymerization of distilled pyrrole in the presence of NiCo₂O₄ nanoparticles. The CoFe₂O₄ nanoparticles were dissolved in a mixture of the SDBS and distilled water. The CoFe₂O₄ nanoparticles had a 0.04% weight ratio to pyrrole monomer, and they were dispersed in an SDBS solution that was sonicated for 7 h to enhance the disaggregation of any nanoparticle bundles. The ratio of CoFe₂O₄ nanoparticles to SDBS was 1:9.

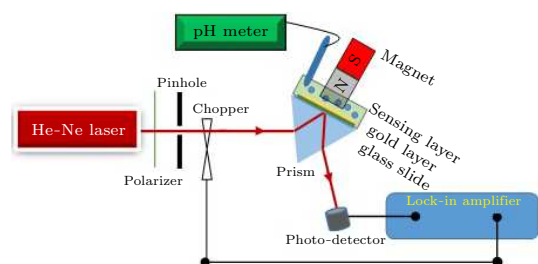


Fig. 1. The SPR setup contains a He-Ne laser, a polariser, a pinhole, a chopper, a high index prism, a photo-detector and a lock-in amplifier.

The 0.7% w/v of chitosan was dissolved in acetic acid at room temperature prior to the electrodeposition of the layer. Then, the mixture of CoFe₂O₄-NPs and SDBS solution was dispersed into the chitosan solution, and during mechanical stirring, the pyrrole was added to the mixture. The premixed solution of Py-Chi-CoFe₂O₄-NPs was electropolymerized at +1.2 V in a three-electrode electrochemical cell. A gold-coated glass slide electrode was used as the working electrode. A graphite rod and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The electro-deposition of the layer was carried out at

room temperature using an electrochemical instrument (Versa stat 3, Ametek, Princeton Supplied Research), and the deposition time was 74 s. The final PPy-Chi/CoFe₂O₄-NPs thin layer was washed with water and methanol to remove the electrolyte solution and was dried under a vacuum at 23°C for 24 h. The layer of PPy-Chi/CoFe₂O₄-NPs was characterized using a field emission scanning electron microscope (FE-SEM, Hitachi, SU8000 Series), an energy dispersive spectroscopy (EDX, Oxford Instrument, X-Max) and an x-ray diffraction spectroscope (WITec, Alpha 300R).

The surface plasmon resonance setup contains a He-Ne laser (633 nm), a pinhole, a polarizer, a precision rotation stage, a high index prism, a silicon detector, a chopper, and a lock in-amplifier (Fig. 1). The gold layer was coated on a glass slide that was attached to a prism using liquid index gel. The prism was placed on the precision rotation stage, and the liquid was flowed in the tank that was attached to the prism. The silicon detector registered variations in the laser beam during the rotation of the precision stage up to 40°. The SPR signals were analyzed using the Fresnel theory based on the matrix method for the system of multilayer using a computer program.^[29]

The aqueous solutions of fluorene were prepared by using 1 g of fluorene dissolved in 1 L of carbon disulfide. The final solution contained 1000 ppm of fluorene. Then, other concentrations, i.e., 0.01, 0.1, 1, 3, 5 and 10 ppm, were obtained by dilution of the 1000 ppm C₁₃H₁₀ solution.

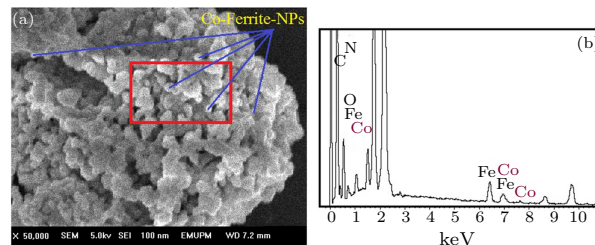


Fig. 2. (a) The FE-SEM image showing the morphology of the PPy/CO-ferrite-NPs composite layer. (b) The EDX results showing Co and Fe formed in the composite layer.

Figures 2(a) and 2(b) show the FE-SEM image and the EDX result of the PPy-Chi/CoFe₂O₄-NPs composite layer, respectively. The square area was utilized for the EDX test. Figure 2(a) shows that the chitosan agglomerated the pyrrole and Co-ferrite-NPs during the electrodeposition process, and the polymer encompassed the Co-ferrite-NPs and formed a thin layer. Figure 2(b) shows the EDX results corresponding to PPy-Chi/CoFe₂O₄-NPs. The peaks appeared at 0.3, 0.4, 0.5, 0.6, 6.4, 7.0 and 7.7 keV. The peaks at 0.3, 0.4 and 0.5 were related to C, N, and O, respectively, which are components of the polymer. The peaks at 0.6, 6.4, 7.0, 7.1 and 7.7 keV corresponded to Fe and Co, respectively. The wt% values of C, N, O, Fe, and Co were 48.31, 19.45, 20.72, 4.17, and 7.35 wt%, respectively. The peaks at 7.0 and 7.7 keV corresponded to Co, and the peaks at 6.4 and 7.1 keV were related to Fe. The contributions of Co and Fe to the total weight were 4.17 and 7.35%, respectively. Consequently, the Co ferrite NPs were formed in the mixture of polypyr-

role and chitosan.

PPy-Chi/CoFe₂O₄ NPs were deposited on a gold coated glass slide. The morphology and the thickness of the gold/(PPy-Chi/CoFe₂O₄ NP sensing layer was obtained using an atomic force microscopy and a high surface profilometer (AMBIOS Technology XP-200). The thickness of the gold layer was 46.3 nm. Figure 3 shows the roughness and thickness of the gold/(PPy-Chi/CoFe₂O₄-NPs before the experiment. As a result, the average height was 4.1 nm, and the thickness of gold/(PPy-Chi/CoFe₂O₄-NPs was 64.7 nm. Consequently, the thickness of the PPy-Chi/CoFe₂O₄-NPs composite layer was 18.4 nm.

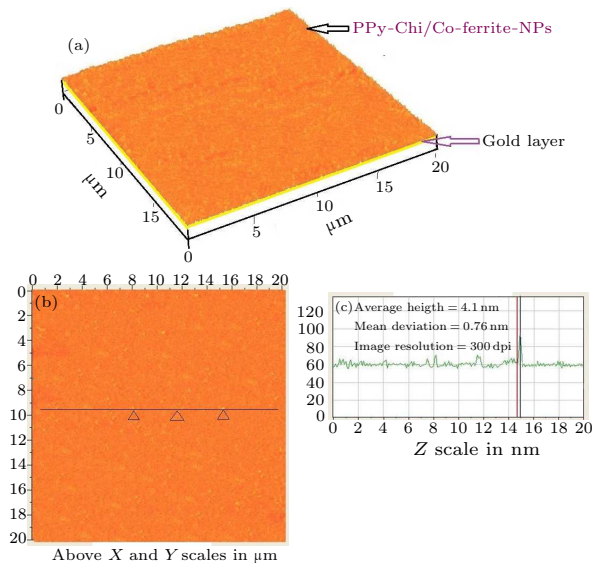


Fig. 3. (a) The SPR signal related to determination of the refractive index of the sensing layer. (b) The SPR signal at the baseline, with the resonance angle 75.963°.

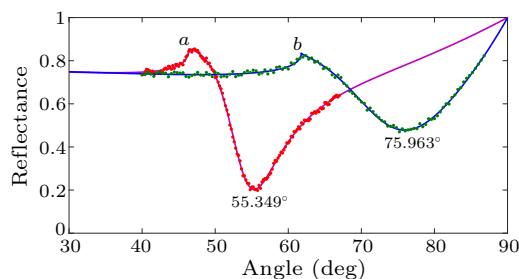


Fig. 4. The morphology of the sensing layer depicting the roughness of the PPy-Chi/Co-ferrite NP layer before the detection of fluorene.

To determine the refractive index of the sensing layer, deionized water ($n = 1.3316$) was poured into the tank prior to carrying out the experiment. The SPR signal was registered, and the resonance angle and refractive index of the layer were determined by the analysis of the SPR using the Fresnel equation based on matrix methods.^[30,31] Curve *a* in Fig. 4 shows the SPR signal in the presence of deionized water ($\text{pH} = 7.62 \pm 0.02$). The resonance angle was 55.349°, which corresponded to the $1.5214 + 0.168i$ refractive index. To detect different concentrations of fluorene, the baseline was found using pure carbon disulfide (CS₂). The probe of the pH meter was attached to the flow

tank to measure the pH during the experiment. Curve *b* in Fig. 4 shows the SPR signal in the presence of pure carbon disulfide at a pH of 7.72, and the resonance angle was 75.963° in the baseline.

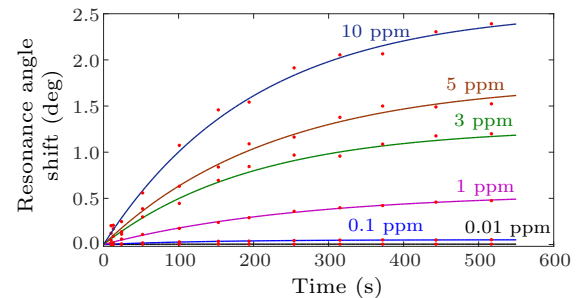


Fig. 5. Sensogram for detecting fluorene using PPy-Chi/CoFe₂O₄-NPs. Dotted points are the resonance angle shifts obtained from experiments at different times.

Different concentrations of fluorene were poured into the tank separately, and the SPR signal was registered. The experiment was repeated 10 times for each solution to obtain the resonance angle at different times. The SPR signals were analyzed using the Fresnel theory, and sensograms were drawn, as shown in Fig. 5. The variations of the resonance angle shift in different concentrations were a function of time, and the experimental data were fitted well to Langmuir's first-order adsorption model as follows:^[32,33]

$$\Delta\theta = \Delta\theta_{\text{sat}}(1 - \exp(-k_a t)), \quad (1)$$

where $\Delta\theta_{\text{sat}}$, k_a and t are the saturated value of resonance angle shift, the rate constant, and the response time of the sensor, respectively. Figure 5 shows the resonance angle shifts related to 10, 5, 3, 1, 0.1, and 0.01 ppm. The resonance angle shift corresponding to the concentration of fluorene less than 0.01 ppm was zero (the red line on the horizontal axis). As a result, the minimum fluorene concentration detected by the sensor was 0.01 ppm.

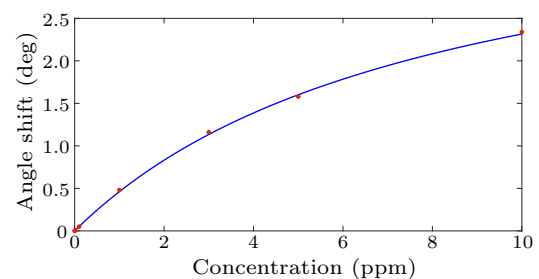


Fig. 6. Variation of the resonance angle shift with the concentration of fluorene.

Figure 6 shows the variation of the saturated value of resonance angle shift versus the concentration of fluorene. The experimental data were fitted to the Langmuir equation $\Delta\theta_{\text{sat}} = \frac{\Delta\theta_{\text{max}} \times C \times K}{1 + K C}$,^[34] and the maximum shift of the resonance angle ($\Delta\theta_{\text{max}}$) and the affinity constant (K) of the sensing layer for detection of fluorene were 4.183° and 0.124, respectively. As a result, it was found that the saturation of the sensing layer occurred at a high concentration.

The sensing layer was tested using an atomic force microscope (AFM) after the experiment. When the

fluorene solution contacted the sensing layer, the molecules of fluorene were binding to PPy-Chi/CoFe₂O₄ NPs in the dissociation process, thus the roughness and thickness of the sensing layer were changed.

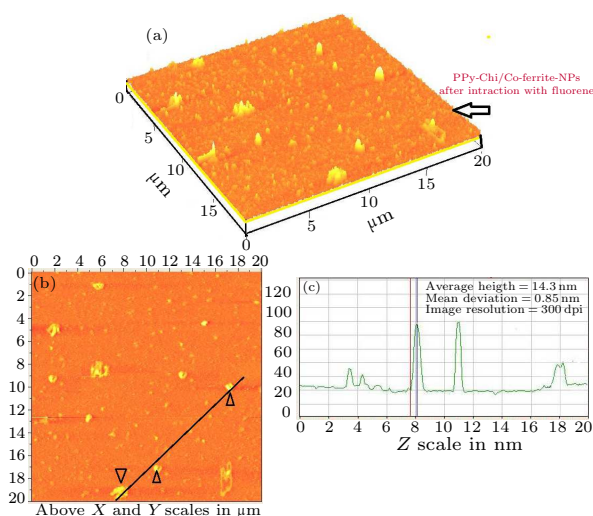


Fig. 7. AFM image after the experiment. The fluorene was attached to the surface of the PPy-Chi/CoFe₂O₄ NP sensing layer.

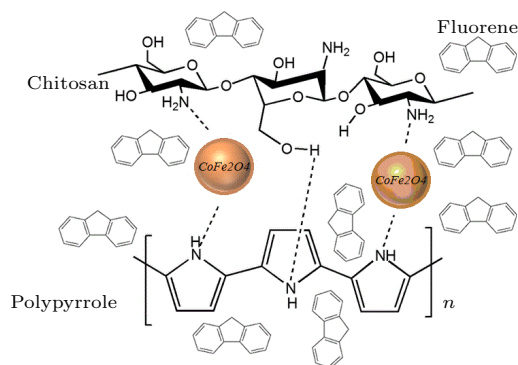


Fig. 8. Adsorption of fluorene with the PPy-Chi/CoFe₂O₄ NP sensing layer.

Figure 7 shows the AFM image after the binding occurred. The average height of the surface was increased from 4.1 nm to 14.3 nm. Consequently, the fluorene interacted with the PPy-Chi/CoFe₂O₄ NP sensing layer, and the roughness of the layer was changed.

PPy-Chi/CoFe₂O₄ NPs have more π -bonds,^[22,35,36] and this provides active sites for π - π stacking interactions between the PPy-Chi/CoFe₂O₄ NPs and PAHs. Moreover, the protonation of -NH₂ and -NH- group of PPy-Chi/CoFe₂O₄ NPs to -NH₃⁺ and -NH₂⁺ causes the electro static interaction^[37] between sensing layer and fluorene.

Figure 8 shows the mechanism of binding, and this interaction will heighten the sensitivity of PPy-Chi/CoFe₂O₄ NPs toward fluorene, due to the electrostatic and influence of the delocalized electrons between the sensing layer and fluorene.

In summary, the polypyrrole-chitosan/CoFe₂O₄ NP composite layer was deposited on a gold coated glass slide using the electrodeposition of pyrrole

in the presence of chitosan and CoFe₂O₄ NPs. As a result, Co-ferrite nanoparticles were formed in the layer. The roughness of the surface was about 4 nm, thus the surface was approximately smooth. The sensograms, which were derived from the SPR signals, depicted that the sensing layer was able to detect low concentrations of fluorene. Therefore, the PPy-Chi/CoFe₂O₄-NPs composite layer adsorbed the fluorene and the AFM image illuminated the binding of fluorine, and the limitation of the sensor was about 0.01 ppm.

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