

Design and Characteristics of an Optical Nanosensor Based on Immobilization of MWCNTs-g-PCA-Au on a Triacetylcellulose Membrane for Determination Trace Amounts of Thiourea

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ABSTRACT

The characterization of an optical absorption based one-shot sensor is described for the determination of thiourea based on the immobilization of new nanocomposite of MWCNT-graft-poly(citric acid)/Au on a triacetylcellulose membrane. MWCNT-g-PCA/Au is covalently bonded to a transparent triacetylcellulose film. Thiourea reacts with the immobilized nanocomposite and causes a decrease in the absorbance of the film at 300 nm. The response time of sensing phase is within 5 min depending on the concentration of thiourea. This sensing phase has a linear range of 40-250 and 250-1000 mgL⁻¹ for thiourea with a limit of detection of 11 mgL⁻¹ at a wavelength of 300 nm. The nanosensor was successfully applied for the determination of thiourea in spring water and orange peel.

Keywords: thiourea, Au nanoparticles, optical sensor, triacetylcellulose membrane, functionalized MWCNTs

1 INTRODUCTION

Thiourea is a reagent in organic synthesis. The main application of thiourea is in textile processing, the synthesis of pharmaceuticals and insecticides. Their toxic and hazardous effects seem to arise from a disturbance of carbohydrate metabolism [1] and could result in chronic goitrogenic and other glandular difficulties in humans [2]. Furthermore, TU and its derivatives have also been screened as allergenic [3], and it was shown that their presence inhibits nitrification in soil and water [4]. Carbon nanotubes (CNTs) are unique one-dimensional materials, being the focus of current research due to their special structure dependent electrical, mechanical, and optical properties [5, 6]. These unique properties make CNTs very useful for supporting metal nanoparticles (NPs) in many potential applications, ranging from advanced catalytic systems through very sensitive electrochemical sensors to highly efficient fuel cells [7-9]. Gold nanoparticles since a long time are motive of intense research because of their special optical properties and electrochemical activity and heretofore produced with difficult methods [10-13]. The

sorptive property of CNT is an important factor in its sensing behavior [14]. The development of optical sensors is of great interest because of their possible application in biology, biotechnology and ecology [15-18]. In this work for the first time, we used the optical sensor for measurement of thiourea. So Multiwalled carbon nanotubes were functionalized and gold nanoparticles were encapsulated on CNT-g-PCA. Then we discuss the application of MWCNTs-g-PCA-Au as a reagent which immobilized on a triacetylcellulose membrane for fabrication of an optical absorption based one-shot sensor for the determination of thiourea.

2 EXPERIMENTAL

2.1 Apparatus

A Shimadzu model UV-1650PC UV-Visible spectrophotometer with 1-cm glass cells was used for recording the absorption spectra and absorbance measurements. The sensing membrane was placed and fixed inside the cuvette using a special frame with an opening of 7mm×40mm and all measurements were performed in a batch mode. The control sample was stretched in the same way inside the cuvette using a frame of the same size. A Jenway 3020 pH-meter was used to adjust the pH solutions.

2.2 Reagents

Triply distilled water and analytical-reagent grade chemicals were used. The multi-wall carbon nanotubes (MWCNT, <95%) and HAuCl₄.3H₂O was purchased from Notrino and sigma respectively. Ethylene diamine and other materials were supplied from Merck. A stock solution of 3000 mg l⁻¹ thiourea was prepared by dissolving 0.150 g thiourea (Merck) in distilled water and diluted to the mark in a 50mL volumetric flask. A 0.2M Phosphate buffer solution of pH 5.0 was prepared.

2.3 Preparation of MWCNT-g-PCA-Au nanocomposites

CNTs were opened and then citric acid was Polymerized onto functionalized carbon nanotubes according to the reported procedures in literatures [19]. Briefly, MWCNTs were activated in nitric acid solutions to give carboxyl group modified MWCNTs (MWCNT-COOH), followed by reaction with monohydrate citric acid, resulting in hyperbranched poly (citric acid) grafted onto MWCNT (CNT-g-PCA).

The prepared MWCNT-g-PCA composites were mixed with moderate concentration chloroauric acid (HAuCl_4) and placed in an ultrasonic bath for 20 min in order to well disperse metal ions in the polymeric shell of nanocomposite. The solution was then stirred at room temperature for 8 h.

2.4 Preparation of the sensing phase

The immobilized indicator on the triacetylcellulose membrane was prepared according to the following procedure [20]. The transparent triacetylcellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove colored gelatinous layers. The films were treated with ethylenediamine for 3min at ambient temperature then they were placed in a MWCNTs-g-PCA-Au solution and in an ultrasonic bath for 30 min. At the next step, films were placed for 24 hours in the MWCNTs-g-PCA-Au solution. Then they washed with water for removing excess solution and achieve fix absorbance. Prepared membranes were kept under water when not in use.

3 RESULTS AND DISCUSSION

Figure 1 shows the UV spectra of complexation of Au and MWCNT-poly (citric acid) for different period of time. The weak absorption peak centered at 530 nm in the spectrum of MWCNT/gold nanocomposite was in good agreement with the reported values for gold NPs [11].

Figure 2 shows the TEM image of encapsulated gold nanoparticles in the PCA shell of the CNT-g-PCA. It is clear that nanoparticles are placed on the surface of CNTs which confirmed nanoparticles are fitted on the CNT wall by PCA shell.

The surface topology of modified membranes were characterized by SEM images. Fig. 3 shows the SEM images of MWCNTs-g-PCA-Au on a triacetylcellulose membrane. It is clear that gold nanoparticles in the PCA shell of CNT-g-PCA are placed on triacetylcellulose membrane and disperse very well. Figure 4 shows image of nanosensor before and after reaction with analyte. As can be seen, nanosensor's color has changed to light brown

after reaction with thiourea and the formation of complex after one day, color change depend on the thiourea concentration. Figure 5 shows the SEM images of nanosensor after reaction with analyte. As can be seen in the figure, there is a few gold nanoparticles remained on triacetylcellulose membrane because complex formation of gold nanoparticles with thiourea.

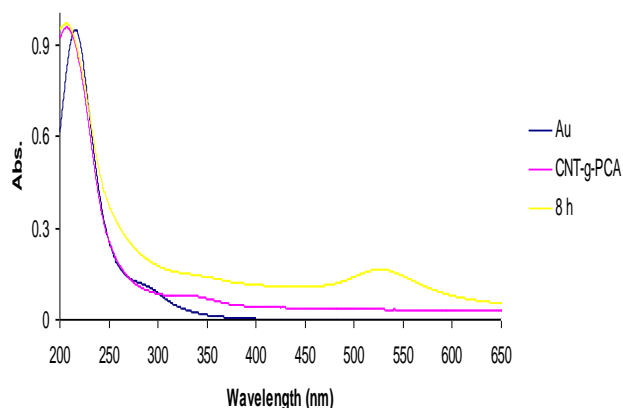


Fig.1. UV-vis absorption spectra.

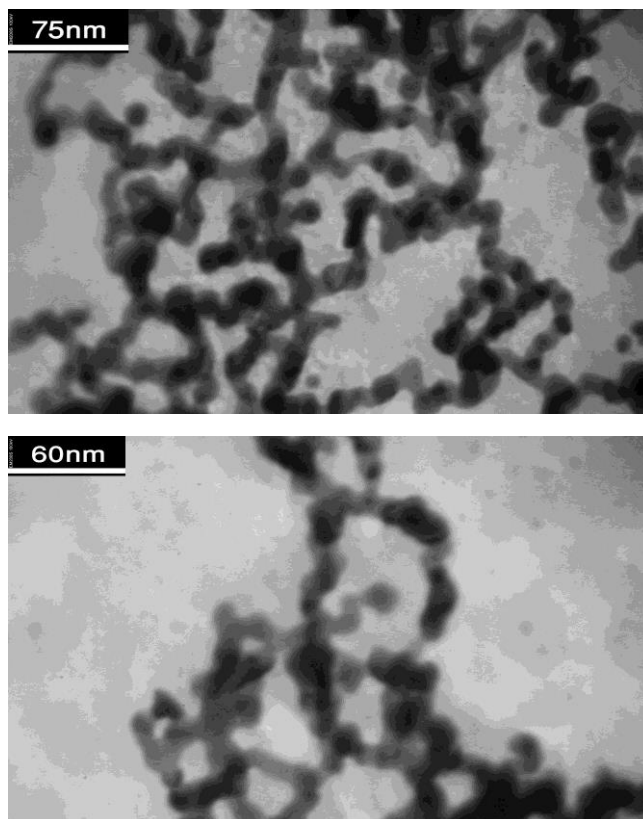


Fig.2. TEM images of CNT-g-PCA-Au.

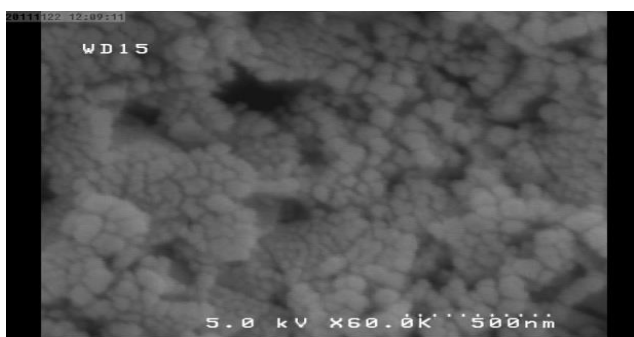
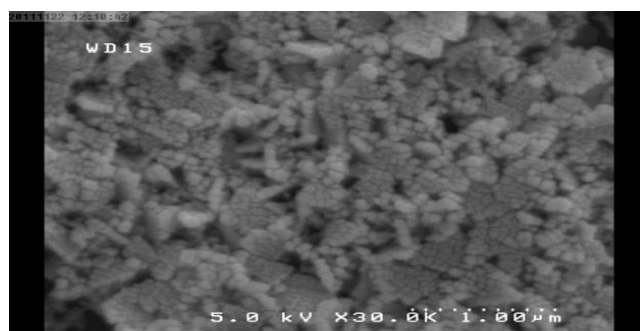


Fig.3: SEM images of immobilization of MWCNTs-g-PCA-Au on a triacetylcellulose membrane.

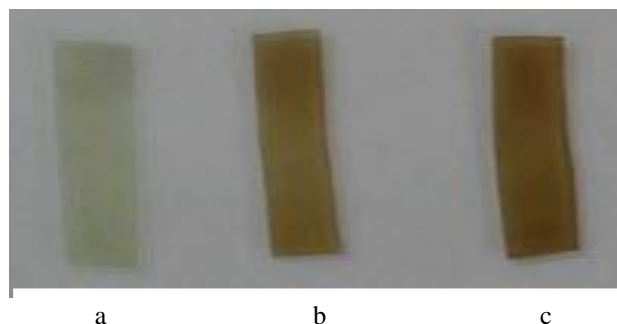


Fig.4: images of nanosensor(a) before reaction, (b) after reaction with 50 mg L⁻¹ thiourea, (c) 100 mg L⁻¹.

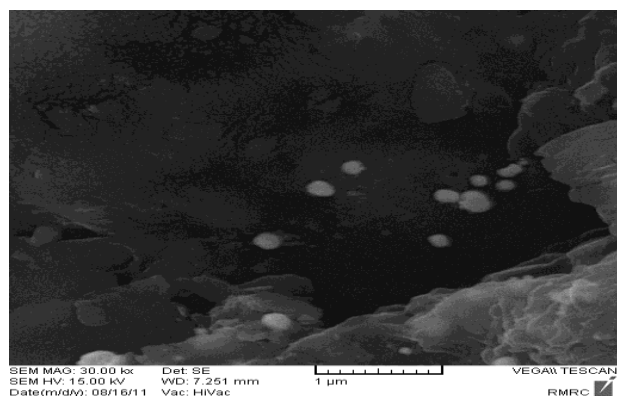


Fig.5: SEM images of membrane after reaction with thiourea 50 mg L⁻¹.

Fig. 6 shows the absorption spectra of immobilized MWCNTs-g-PCA-Au, which were obtained after being equilibrated in buffer solution (pH 5) containing different concentrations of thiourea. The spectral changes is result of the reaction of thiourea with MWCNTs-g-PCA-Au. The absorbance maxima of the immobilized MWCNTs-g-PCA-Au are located at 300 nm. As can be seen from Fig. 6 the decrease in the absorbance at 300 nm is more pronounced in the membrane as the thiourea concentration increases. The wavelength of 300 nm was selected for further studies because of higher sensitivity at this wavelength.

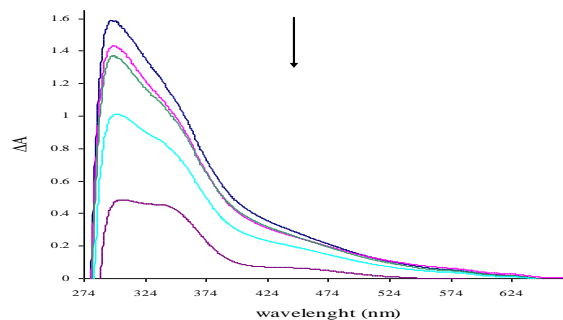


Fig.6: Absorption spectra for sensing phase film in the presence of, from top to bottom, 0, 50, 60, 100, 200 mg L⁻¹ thioureaat .

3.1 Response time

An important analytical feature of any sensing phase is its response time. The response time of the present sensing phase is controlled by the time required for the analyte to diffuse from the bulk of the solution to the membrane interface and to associate with the indicator. The response time was tested by recording the absorbance change from a pure buffer (pH 5) to buffered reaction solutions in the presence of 100 and 300 mg L⁻¹ thiourea.

The membrane was found to reach 95% of the final signal at 3–5 min depending on the concentration of thiourea.

3.2 Application

Because of its high sensitivity and selectivity, the proposed method was directly applied to the determination of water and orange peel samples. The dried orange peels were crushed into fine powder and dissolved in concentrated sulfuric acid. This solution wash filtered using Whatman 42 paper. Then 5.0mL of this solution transferred to a volumetric flask, diluted to 100mL and analyzed following the recommended procedure[21]. The recovery results for the analysis of some real samples are shown in Table 1. The results show that this method is suitable for determination of thiourea concentrations in such samples.

Table 1 Determination of thiourea in real samples.

sample	Thioureae (mg L ⁻¹)	
	Added	Found ^a
golestan spring water	-	^b ND
	40	40.35±0.009
	300	300.33±0.02
Orange peel	-	^b ND
	40	40.27±0.01
	300	300.44±0.02

^a Average of three determinations±standard deviation.

^b Not detected.

4 CONCLUSION

The optical one-shot nanosensor described in this work is easily prepared and provides a simple means for determination of free thiourea. The membrane responds to thiourea by decreasing sensing phase absorbance. It has a long lifetime and the sensing phase presented a relatively good selectivity for thiourea. The proposed method is quick, inexpensive, and uses conventional instrumentation only. To the best of our knowledge this is the first report on the fabrication of one-shot sensor for determination of thiourea.

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