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UV Cured Polymeric Optical Fluorescence Sensor for the Determination of Au (III)

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Summary: The recognition and sensing of the biologically and environmentally important metal ions has emerged as a significant goal in the field of chemical sensors in recent years. Among the various analytical methods, fluorescence has been a powerful tool due to its simplicity, high detection limit and application to bio imaging.In this study, UV cured polymeric optical sensor for Au (III) ion based on a fluorescence membrane has been developed. The response characteristics of the sensor including dynamic range, pH effect and response time were systematically investigated. The influences of the conditions such as pH, response time on the metal ion binding capacity of membrane were also tested.

Keywords: Au (III); fluorescence spectroscopy; membrane; optical sensor; UV-curing

Introduction

Noble metals, especially gold, are widely used in jewelry, catalysts, fuel cells and dental materials. However, contamination of water systems and soil may occur due to frequent use of these substances. Hence, it is crucial to develop highly sensitive and selective gold analysis methods in environmental and industrial waste waters.[1]

There are several analytical techniques have been adopted to analysis of trace amounts of gold such as atomic absorption spectrometry, electrochemical, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry and various spectrophotometric methods using complexing reagents including acid-bas indicators. However, these methods have certain disadvantages; they are time consuming, expensive and suffer from several matrix effects.[2–4]

The sensitivity and selectivity of the analysis method could be greatly enhanced by using fluorescent and chemilumiscent probes. Fluorescent chemical sensors, employing a fluorophore or a fluorescent species as read-out functions, have been frequently used in environmental monitoring, medical diagnosis and forensic analysis. Therefore, the high sensitivity, ease of data collection, and the wide range of target molecules make fluorescent chemical sensors highly desirable in the development of sensing systems.[5]

In our study a spectrofluorimetric method for the determination of Au (III) in aqueous samples based on photosynthesized polymeric membrane was developed for the first time and analytical parameters have been determined.

Experimental Part

Materials and Reagents

The commercial monomers trimethylolpropane tris(3-mercaptopropionate) (3–SH), hydroxyethylmethacrylate (HEMA), 2,4,6-triallyloxy-1,3,5-triazine (TAT) and the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma. Atomic absorption spectrophotometry standard solution of 1000 mg L^{-1} Au (III) was purchased from Merck. All the other chemicals such as buffer components were of analytical grade and used without further purification.

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The pH values of the solutions were checked using a digital pH meter (WTW) calibrated with standard buffer solutions of Merck. All of the experiments were operated at room temperature, 25 ± 1 °C. All water used in the experiments was purified using a Milli Q-water purification system (Millipore, İncekaralar-Turkey). The resulting purified water has a resistivity of 18.2 MΩ cm.

Preparation of Sensor

The sensor film based on trimethylolpropane tris (3-mercaptopropionate) (3–SH), 2-hydroxyethyl acrylate (HEMA) and 2,4,6-triallyloxy-1,3,5-triazine (TAT) were synthesized by free radical crosslinking copolymerization with a crosslinker and 2,2-dimethoxy-2-phenylacetophenone (DMPA) was added as a photoinitiator. The films were prepared by UV-curing technique as follows. The feed compositions are given in Table 1. The UV-cured membranes were taken out from the mold and immersed in a large excess of deionized water for a 1 day to wash out any unreacted monomers and initiators and then dried in a vacuum oven at 30° C until reaching a constant weight.

Characterization

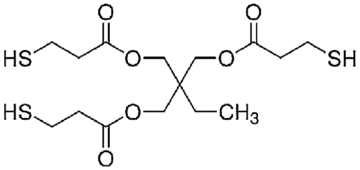
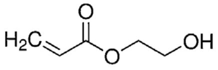
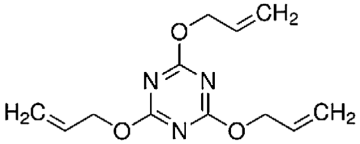
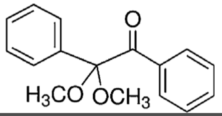
The functional groups of synthesized membrane were analyzed by Attenuated Total Reflection Infrared Spectroscopy (Perkin-Elmer ATR-FTIR spectrophotometer) in the range of 4000–400 cm–1. SEM imaging of the hydrogel was performed on a Philips XL30 ESEM-FEG/EDAX. The membranes were initially dried in vacuum air at 30 °C for 3 days before being analyzed. The specimens were prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å. The surface of the sample was then scanned at the desired magnification to study the morphology of the membranes.

Results and Discussion

Characterization of the Polymeric Material

FTIR spectrum of P(3SH/HEMA/TAT) membrane was taken (Figure 1). These can be summarized as the peak at 3396 cm^{-1} shows the hydroxyl group of HEMA, the peak at 2924 cm^{-1} which is due to the presence of –C–H band, the strong peak at 1728 cm^{-1} indicates the carbonyl group, the

Table 1.
Feed composition of polymeric sensor

Chemicals	Formula	mmol
3-SH		10,04
HEMA		17,22
TAT		10,04
DMPA		0,51

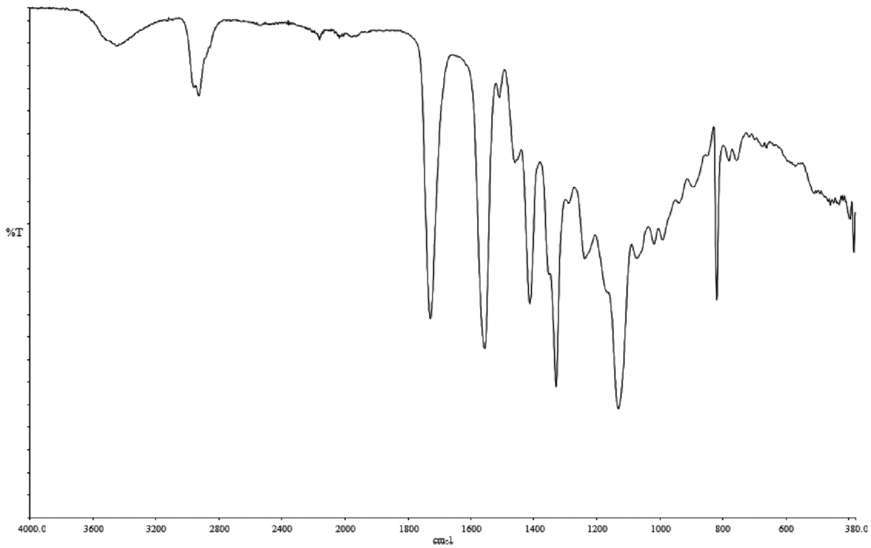


Figure 1.
FTIR spectrum of P(3SH/HEMA/TAT) membrane.

peak at 1556 cm^{-1} shows the triazine ring vibration bands.

The surface morphology of the membrane is an important factor The Figure 2a and 2b demonstrate the SEM images of the Au (III) sensing membrane. The surface morphology of the membrane was observed up to magnification factors 5000–20000. For all magnification factors, the same structure was observed. As it could be seen from the SEM images, a homogenous and nonporous Au (III) membrane was obtained.

Spectral Characterization of Sensor

Al fluorescence measurements were performed with a Varian Eclipse spectrofluorimeter. The sensor response in the presence and in the absence of Au (III) was measured. Fluorescence emission spectra of the sensing membrane exposed to the solution containing different concentration Au (III). Fluorescence spectra showed that the excitation/emission maxima of the membrane are at 379/425 nm, respectively.

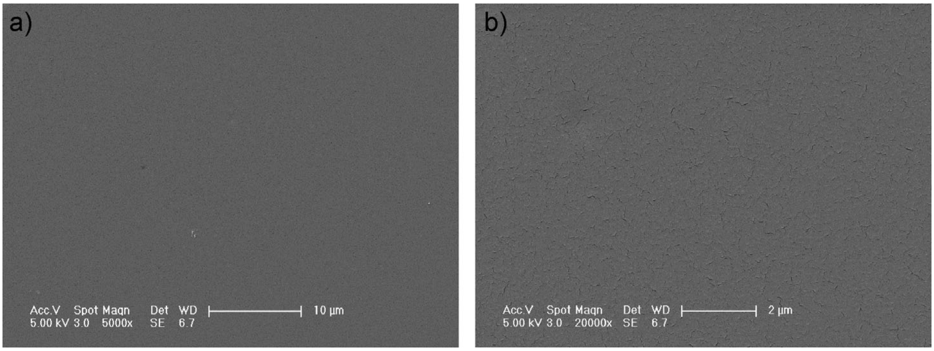


Figure 2.
SEM micrograph of Au (III) sensing membrane, (a) at 5000× magnification. (b) at 20000× magnification.

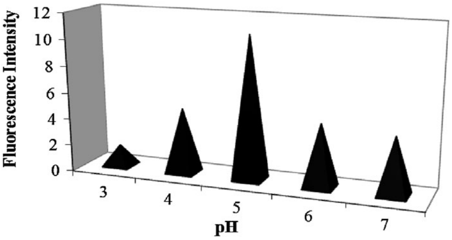


Figure 3.
Effect of pH of the gold solution (0.025 ppm) on the fluorescence intensity of the gold (III) sensor (λ_{ex}: 379 nm and λ_{em}: 425 nm).

Investigation of Sensor Response to Au (III) Ions

The influences of the conditions pH, response time on the metal ion binding capacity of membrane were also tested.

The effect of solution pH on the fluorescence response of the proposed sensor was investigated in the pH range from 3.0 to 5.0 in the presence of 0.025 ppm Au (III). As is obvious from Figure 3, the fluorescence intensity increased with increasing pH up to 3.0 from 5.0. It can be seen that the fluorescence intensity decreased when pH value higher than pH 5.0. According to Figure 3, pH = 5 was selected for further experiments. A solution of pH 5 adjusted 0.1 M acetate buffer solution was selected as an ideal experimental condition.

Fluorescence intensities of the sensor increased with increasing Au (III) concentrations up to 0.005 ppm, a fluorescence determination was carried out in the Au (III) concentration range from 0.005 ppm to 0.05 ppm. A significant decrease in fluorescence intensity of the sensor was observed upon increasing Au (III) concentration in this range (Figure 4). Sensor has a very low limit of detection which is 0.062 ppm which also is lower than the other fluorescent sensor methods reported in the literature.

The approximate response time was measured as 30 second. After the contact of the sensor membrane with Au (III) solution, it must be regenerated using distilled water. A single membrane film is given to reproducible results about 25 times.

Conclusion

Highly cost effective and fully reversible membrane sensor has been successfully prepared. The experimental procedures

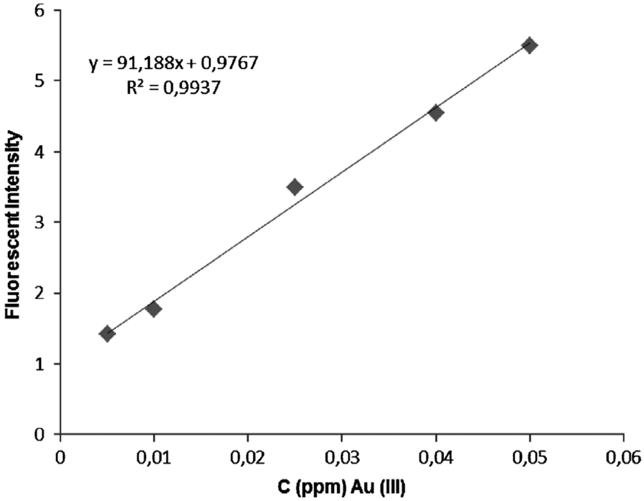


Figure 4.
Fluorescence response of sensor on exposure to Au (III) solution at pH 5.0 measured at an excitation wavelength of 379 nm and an emission wavelength of 425 nm.

developed in the present work have enabled the determination of Au (III) in solution over a wide concentration range (0.005 ppm – 0.05 ppm), the relative standard deviation (RSD) was 0.27% (95% confidence levels, n= 6) for an average exposure time of 30 second at pH 5. The working pH range for all the sensors studied was between 3.0 and 7.0 for a 0.025 ppm Au (III) solution. The method is simple, sensitive, and can be performed with available and cheap chemicals. Therefore, the method could be proposed for clinical and toxicological practice to determine trace amounts of Au (III) in various solutions and samples. For further studies, application of this sensor to the determination of Au (III) in environmental samples is ongoing in our laboratory.

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[1] Y. Jeong, J. Yoon, *Inorg. Chim. Acta* **2012**, *381*, 2–14.
[2] L. Ducret, H. Maurel, *Anal. Chim. Acta* **1959**, *21*, 74–79.
[3] Y. Wu, Z. Jiang, B. Hu, J. Duan, *Talanta* **2004**, *63*, 585–592.
[4] Y. Fazli, J. Hassan, M. H. Karbasib, M. Sarkouhic, *Minerals Engineering* **2009**, *22*, 210–212.
[5] I. Ding, Y. Fang, *Chem. Soc. Rev.* **2010**, *39*, 4258–4273.