

Construction a Novel Optode for Quantitative Measurement of Ag⁺ Cation in Solutions Based on Covalent Immobilization of Thiazole Yellow on Triacetyl Cellulose Films

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Abstract

To measure the concentration of Ag⁺ cation in solutions, a new optical chemical sensor was fabricated by covalent immobilization of Thiazole yellow dye on a triacetyl cellulose film via a linker, called epichlorohydrin. The interaction between the Ag⁺ cation and immobilized Thiazol yellow molecules was investigated using UV-Vis spectrophotometry. The fabricated optode indicated a range from 3×10^{-7} to 2.5×10^{-5} M regarding to the concentration of Ag⁺ cation at pH 6 and the detection limit was searched to be: 0.8×10^{-7} M. The constructed optical chemical sensor, shows a long-term stability, good reproducibility and repeatability, and also satisfied selectivity and sensitivity. The sensor response to Ag⁺ cation is absolutely invertible and it can be reproduced simply with a solution of EDTA (ethylenediamine tetra acetic acid) in about 5 minutes. The response time is 10 minutes. The fabricated optode can be employed successfully to determine the concentration of Ag⁺ cation in actual sample solutions.

Keywords: Epichlorohydrin; Optode; Silver (I) ion; Thiazole yellow; Triacetyl cellulose; Covalent immobilization.

Introduction

Today, the silver amount in environmental specimens has increased with the rise in the utilization of silver and its compounds in industry such as batteries structure, photographic material, electronic devices, electroplating for industrial applications, semiconductors, besides to the other applications such as mirrors, decorative, medicine, jewelry, and cloud seeding [1-4]. Because of impressive anti-bacterial properties of Ag, it is being widely used to disinfect the beverage water plus applying it in the pharmaceutical

and dental preparations [5, 6]. Silver enters from the industrial water into the environment, since it exists in zinc, arsenic and copper industries as an impurity [7]. In addition, in marine environments, silver was known as a toxic material [8]. As Bowen proposed, the silver may act as a water pollutant due to lack of recycling of the extracted silver [9]. Thus, determining the silver trace values has a high importance for a vast areas of chemical analysis.

Up to date, several procedures have been proposed in the texts for quantitatively determining the silver ions in various medicinal, industrial, and environmental

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samples, employing Solid Phase Extraction (SPE) [10-13], Spectrophotometry [14], Cloud Point Extraction (CPE) [15], Ion-pair extraction [16], Catalytic method [17], Ion-selective electrodes [18-24], and also Bulk optodes [25-29].

A chemical material, called Thiazole yellow (TY) with the formula $C_{28}H_{19}N_5Na_2O_6S_4$, is a triazene dye, being applied as a fluorescent indicator and a stain in microscopy [30]. It can also be applied as an albumin detector [31] and proteins detector [32]. Moreover, it is employed as a reagent to determine the Mg^{2+} [33, 34] and as an acid-base indicator, too, because between pH 12 and pH 13, its color shifts from yellow to red.

Besides, many researchers have worked in the area of pH measuring via the optodes, prepared from TY molecules at high pH levels [35-38].

One of the methods for stabilizing some of the chemical reagents on the substrates of optodes is using the covalent bond, having some advantages such as considerable film stabilization in relation to the other stabilizing methods. However, a disadvantage of this method is that the covalent bond reduces the sensitivity of the reagent in relation to the analyte and the response time of the sensor becomes longer. Furthermore, only the reagents with the agent groups and special characteristics could be stabilized on the substrate with this system. Nevertheless, if it is possible to prepare a sensor with appropriate efficiency with the help of covalent bond, the advantage of proper stabilization dominates the disadvantage, since in this situation, we can trust more on the sensor responses and besides, we can prepare a sensor with the longer life. In the literatures about these fields, different

process are mentioned for covalent bond formation between the reagent and optode substrate that are mostly from the acetate cellulose material.

One of the procedure to produce the bond is employing some reagents containing at least one amine groups or a nucleophile with carbohydrate compounds, being rich of hydroxyl group. Epichlorohydrin acts as a bridge or an intermediate agent between these compounds and reagent.

Since, also in the substrate of cellulose three acetate, after hydrolysis of ester groups, hydroxyl group is formed, it was decided to perform on the area of such substrates activation, applying epichlorohydrin. Hence, after the analysis and optimization of affecting parameters on cellulose acetate films hydrolysis and optimizing the influencing parameters on the reaction between hydrolyzed films and epichlorohydrin, it was tried to prepare the optimum condition for activation of such films.

In this study, we have immobilized the Thiazole yellow dye molecules on the triacetyl cellulose (TAC) membrane to fabricate a sensitive, durable, and selective optode to determine the concentration of Ag^+ in the aqueous environment. Up to now, the application of Thiazole yellow for estimation of silver(I) ion and fabrication of an optode to do so, is not researched yet. Moreover, the immobilization procedure of amino dyes on TAC membranes via epichlorohydrin (as a linker) has been studied [39]. Figure 1 reveals the chemical reaction between TY molecules and epichlorohydrin activated TAC beds.

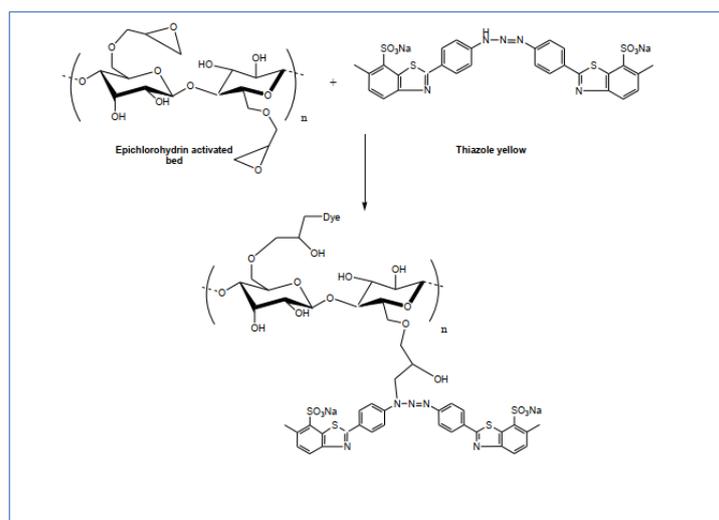


Figure 1. The chemical reaction between the epichlorohydrin, activated on TAC beds and the Thiazole yellow.

Materials and Methods

Reagents

Epichlorohydrin, thiazole yellow, potassium dihydrogen phosphate, sodium hydroxide, silver nitrate, borax, disodium hydrogen phosphate, and hydrochloric acid were produced from Merck chemical company. Waste photographic film tapes (Kodak) were used to prepare the TAC membranes. Universal aqueous pH buffer solutions were made based on the CRC handbook recommendations [40]. For adjusting the pH of the solutions, we used 1.0 molar solutions of hydrochloric acid and sodium hydroxide. Deionized distilled water was employed for all of our experiments.

Instruments

To measure the solutions' pH, the Metrohm 827 pH meter was applied. To measure the spectrophotometric requirements, a double-beam Lambda 25 UV/ Vis spectrophotometer was employed. To estimate the materials' weight, a Sartorius laboratory balance with 0.0001 gr accuracy is used. IKA®RH basic 2 heater/stirrer is also employed for our work.

Sensor membranes production

Waste photograph film tapes have been used to produce the transparent TAC membranes. The substrate of photographic films from the various brands is may formed from different materials. However, two of the most famous fundamental materials of such films include polystyrene and cellulose three acetate. The polystyrene membrane is not appropriate for stabilizing our considering reagents, because no reaction is happened between these reagents and these substrates, whether in the direct form or with the help of intermediate activator molecules, used for this purpose. Nonetheless, acetate cellulose films, after the hydrolysis, obtain the ability to react with several reagents, having the proper agent groups, after their activation.

Commercial sodium hypochlorite is also used for numerous seconds to pick up the gelatinous layer from the membranes.

Faucet water and distilled water were used to wash the membranes, respectively. Thence, the membranes were hydrolyzed in a 0.2 M solution of sodium hydroxide at 30^oC for 24 hours to increase the porosity of the membranes and de-acetylate the esteric groups. Epichlorohydrin solution was used to treat the hydrolyzed membranes in a basic environment as follows: At 25^oC, 2.5 g epichlorohydrin was added to 150 ml of 1M sodium hydroxide solution, and the solution was mixed enough to achieve a clear and

homogeneous solution. Next, 3g of the hydrolyzed membranes was transferred into a reactor and a magnetic stirrer was used to mix the solution for 3 hours at 25^oC. Then the activated films were drowned in 500 ml distilled water for 30 min. Next, it was washed adequately with distilled water. Eventually, they were dried at room temperature. Then, the dried activated films were cut into several pieces with the weight around 0.04 g (8 × 35 mm pieces).

To make sure that the TY is immobile on the activated films surface, 10 film pieces were moved into a vacuum bottle and 10 ml of a 0.025M solution of potassium dihydrogen phosphate was added into it afterwards. In the next step, 0.007 g of Thiazole yellow was added into the solution to produce a mixture with 1.0×10⁻³ M dye concentration. Subsequently, the pH of the solution was adjusted to about 12.8-13 by adding solid sodium hydroxide, gradually. The resulted solution was stirred for 2 hours at 60^oC and then 22 hours at 45^oC. The immobilized films were washed with distilled water. Thereafter, they were positioned in 35 ml of a buffer solution for 3 times with pH 6 and mixed for 5 hours at 30^oC. Eventually, the fabricated films were washed with distilled water and they were preserved in a buffer solution of pH 8.

Method

A section of a Hydrolyzed TAC film (raw film) was placed into a Teflon framework in vertical position in a spectrophotometric cell for spectrophotometric measurement; and it is being applied as a reference cell. The immobilized film was set in a Teflon framework and positioned into a 10 mm spectrophotometric cell, being employed as a sample cell. With scanning the spectrophotometer, the absorption spectra were recorded.

Results and Discussion

1. Optimized conditions to activate the TAC and immobilize the TY

The optimized conditions to activate the hydrolyzed TAC beds, employing epichlorohydrin were carried out based on our previous knowledge about the reaction time, and the temperature, concentration of NaOH and epichlorohydrin. These parameters were adjusted et at 3 hours, 25^o C, 0.2 M and 1M, respectively. The immobilization reaction pH was set at 13. The dye immobilization process was operated at different temperatures to find the influence of the temperature. The outcome reveals that the immobilized dye value on the film surface rises at the higher temperatures. However, because the films exposure into the higher

temperatures for a long time will deform them, it is determined to operate the reaction at 60°C for the first 2 hour and thereafter, at 45°C for 22 hour. The influence of the dye concentration on immobilization of the TY molecules was estimated, as well. To do so, first, the pH of 10 ml of a 0.025M potassium dihydrogen phosphate solution, contained a clear amount of dye was adjusted to be 13 by adding some of the solid sodium hydroxide. Next, 0.04 g epoxy activated film slide was immersed in the achieved solution.

We used 1Mm solution of the dye in the other experiments. Based on the experimental outcomes, we accomplished the immobilization reaction at the optimal conditions: pH= 13, 2 hours at 60 °C and then 22 hours at 45 °C and 1mM of TY for 10 film slide pieces.

2. The pH effect on the response of optode

Figure 2, represents the effect of the solution pH on the membrane absorption. As is evident in this figure, by rising the solution pH, the absorbance increases to its maximum value at pH 6, and then decreases. This phenomenon might be due to the fact that at lower pH values (pH < 6), the complexation process between the Ag⁺ cation and TY molecule seems to be possibly weak. At pH amounts higher than 6, the Ag⁺ cation forms hydroxide species which prevents the complexation process between this cation and TY molecule. Thus, pH 6 was selected for further studies.

3. Reproduction of the optode

One of the main destinations of constructing optodes or in fact, one of the main parameters to evaluate an appropriate optode is its ability to measure the considered property for several times. When the optode becomes single-use or it can be applied for only limited times, this problem is accounted as a defect of it. In order to apply the optode for several times, it is essential to recover it after each usage. It means, it can be possible to somehow separate the components of the bonded or reacted analyte from it and prepare the sensor for reuse.

To recover the structured optode, some of the chemical materials, being applied commonly in the same research studies for eliminating the reacted silver (I) cation with the surface are analyzed.

The impact of some chemical solutions which could be applied for reproduction of the Ag⁺ optodes, was investigated. Thiourea and S²⁻ ion might be employed for this purpose, but they seemingly precipitate on the surface of the optode with Ag⁺ cations, leading to the optode inactivation. Therefore, we applied EDTA

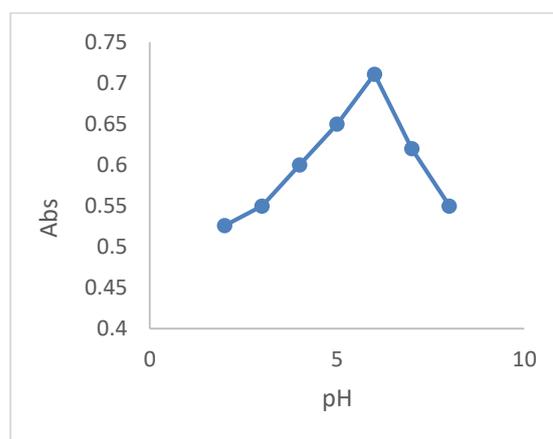


Figure 2. The influence of pH on the absorbance of a typical membrane. The concentration of Ag⁺ cation in all tests was 10⁻⁵M.

solutions with various concentrations to regenerate the optode. The experimental results indicated that the EDTA molecules are able to regenerate the constructed optode: a 2% solution of EDTA can regenerate this optical sensor in about 5 minutes at environmental temperature.

4. Optode analytical specifications

Figure 3 represents the time-dependence response of the fabricated optode at 420 nm for a 12 minutes period. As could be observed, the signal of the absorption reaches to the 95 % of its steady state in around 10 minutes. Figure 4 illustrates the response profile for the structured optode versus repetitive change in the concentration of Ag⁺ cation. As can be understood from this Figure, with increasing or lowering the Ag⁺ cation concentration, the optode shows a reversible and reproducible optical response.

To estimate the reproducibility of the optode fabrication, at the same time under optimal experimental situations, eight immobilized films were prepared. For these prepared optodes, the proportional standard deviation of the absorption signal at pH 6 and at 420 nm was found to be 2.95 %. The relative standard deviation for consecutive measurements of the Ag⁺ cation concentration, applying a single optode was determined for ten repetitive measurements at 420 nm and at the pH 6, found to be: 1.20 %. To determine the long-term stability of the constructed optode, a part of the prepared films were maintained in buffer solutions with various pH amounts between 0- 13 and in distilled water, as well. The experimental outcomes indicated that, in the pH range between 6 to 11 and specifically in the range of 6 to 9, the variation in the absorption

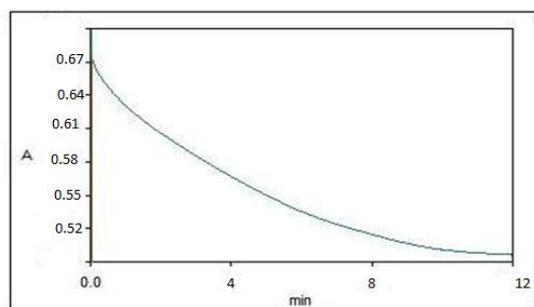


Figure 3. Time-dependence response profile for the fabricated optode at 420 nm. The concentration of Ag⁺ cation and the solution pH are 10⁻⁵M and 6, respectively.

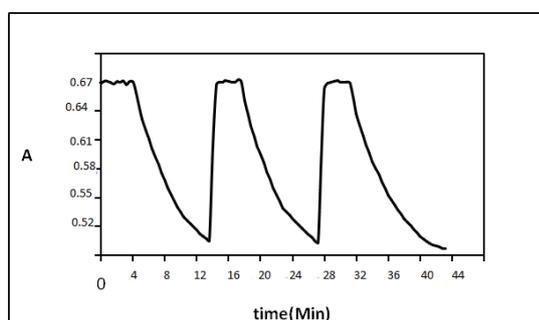


Figure 4. The response profile for the structured optode versus repetitive change in the concentration of Ag⁺ cation from 0 to 10⁻⁵ M and vice versa. The solution pH was adjusted at 6.

signal after 4.5 months was less than 5 %. Hence, pH 6 was selected to store the fabricated sensors.

Figure 5a, reveals the dependence of absorbance upon Ag⁺ cation concentration for a typical constructed optode under optimized experimental conditions. As can be found in the Figure 5, two linear ranges are observed in calibration curves from 0.3 to 1 and 1 to 25 μM, with respect to concentration of Ag⁺ cation concentration. It seems that two bond sites with different affinity are present on the surface of the optical sensor.

Figure 5b, represents the calibration graph, achieved by a fabricated optode for 3×10⁻⁷ to 2.5×10⁻⁵ M solutions of Ag⁺ with three repetitive measurements for the concentration of this cation in solutions. Figure 6 also indicates the absorption spectra for Thiazole yellow in its immobilized form at different silver (I) ion concentrations at the pH 6.

5. Selectivity

We determined the selectivity of the constructed

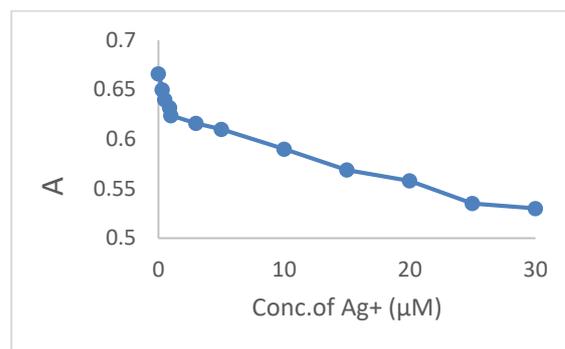


Figure 5. a) The response graph for Ag⁺ cation in the concentration range of 0 to 30 μM at pH 6

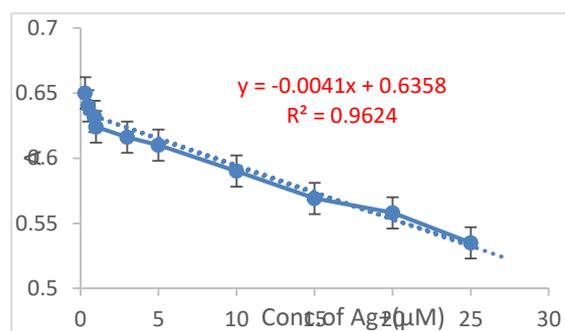


Figure 5. b) The calibration graph for the Ag⁺ cation in the concentration range of 10⁻⁶ – 2.5×10⁻⁵ M at pH 6.

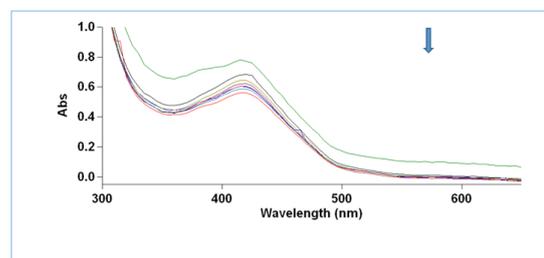
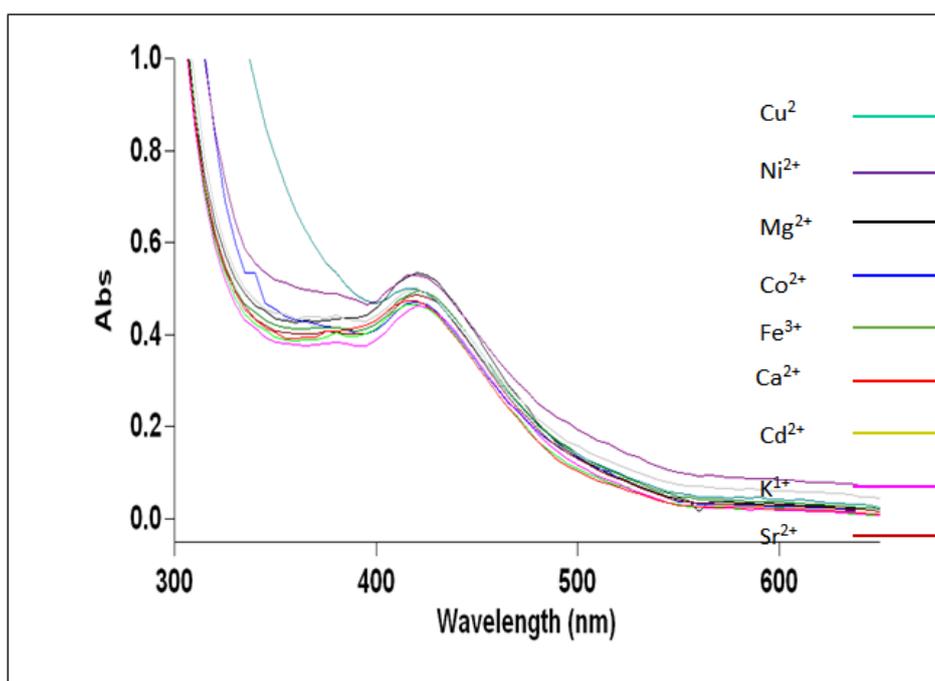


Figure 6. The Absorbance spectra of Ag-TY complex in immobilized form of the concentrations of Ag⁺ cation, being the same as the concentrations, presented in the figure 5a. The arrow in the figure indicates the increasing direction of the concentration of Ag⁺ cation in the solutions.

optode by addition of some metal cations, indexed in the Table 1 to a sample solution, including 10⁻⁶ M of Ag⁺ ions (pH =6). The toleration limit for the interfering ions is described as the concentration of the added ions, resulting less than ±5 relative errors in the absorption signal. As can be clearly seen in this Table, in measurement of Ag⁺ cation, the tested ions have not considerable interference. As a result, the fabricated optode has a well selectivity for Ag⁺ ion in aqueous

Table 1. The effect of some interferences in determining the concentration of Ag^+ cation in solutions.

Interferent	Concentration of metal cation (μM)	Concentration of Ag^+ (μM)	Error(%)
Cu^{2+}	100	1	1.39
Ni^{2+}	100	1	1.26
Mg^{2+}	100	1	1.36
Co^{2+}	100	1	1.34
Fe^{3+}	100	1	1.32
Ca^{2+}	100	1	1.33
Cd^{2+}	100	1	1.44
K^+	100	1	1.42
Sr^{2+}	100	1	1.39

**Figure 7.** The selectivity effect of the constructed optode by addition of some metal cations, listed in Table 1.

solutions. Figure 7, represents the graphical results of the optode selectivity which is influenced by adding some of the metal cations, listed in Table 1.

Some of the analytical data obtained by the constructed optical sensor and the other sensors to determine the concentration of Ag^+ cation in solutions are summarized in the Table 2. The detection limit and the linear range of the suggested optode is reasonable when compared to the other optodes. The simple method for sensor membrane preparation and also the cheapness of the chemical reagents used for construction of the present potode are the other advantages of this optical sensor.

Conclusion

In this research, a chemical optical sensor was fabricated, employing the immobilization of TY

molecules on a triacetyl cellulose film via epichlorohydrin as a linker to determine the concentration of Ag^+ cation in the aqueous solutions. The presented method is a novel way for ligands immobilization on such kinds of membranes to construct the optical sensors. Up to date, it is the first time which the Thiazole yellow molecules, are applied for constructing an optical sensor for quantitative measurement of the silver (I) ion in the aqueous solutions. The influence of the affecting parameters on the reaction of the activated film with the indicator was investigated and the parameters were optimized upon experimental conditions. The structured optode, has some advantageous such as satisfied short term and long duration stability (at least 5 months), repeatability, and reproducibility. In addition, the other benefits of

Table 2. The comparison between some analytical performance data with the reported data in literatures for determining the concentration of Ag⁺ cation in solutions.

Reagent	Bead	Samples	Linear range (M)	Detection limit (M)	Response time (min)	Ref.
Tetradecyl-14-dithiacrown-4	Pellicular octadecylsilica beads coated with a lipophilic organic liquid	-	10 ⁻⁶ -10 ⁻²	-----	8-10	[25]
Hexathia-18- crown-6 and 1, 2- benzo- 3- octadecanoylimino- 7- diethylaminophenoxazine	PVC	Drinking water sample	5×10 ⁹ -5×10 ⁻⁵	1×10 ⁻⁹	12	[28]
Tetrakis (p-chlorophenyl) borate and 1- (dansylamidopropyl)-1- aza-4, 7, 10- trithiacyclododecane	PVC	Medical radiological film, fotografical fixing solution and bleaching solution	5×10 ⁷ -1.7×10 ⁻²	1×10 ⁻⁷	8	[29]
Diphenylthiocarbazone	Transparent triacetyl cellulose (generated from waste photographic film)	Synthetic samples, different kinds if photographic solutions and pharmaceutical	Up to 3.4×10 ⁻⁴	9.2×10 ⁻⁸	4-7	[41]
Thiazole yellow G	Transparent triacetyl cellulose (generated from waste photographic film)		3 ×10 ⁻⁷ -2.5×10 ⁻⁵	0.8×10 ⁻⁶	10	Presented work

this fabricated optode, include a relatively good sensitivity, ease of construction and regeneration, and a wide linear range regarding the concentration of Ag⁺ cation in aqueous solutions.

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