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A Novel Solid-State Copper (II) Thin-Film Micro-Sensor Based on Organic Membrane and Titanium Dioxide Nano-Composites

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Micro-fabrication and characterization of new organic membrane and titanium dioxide nano-particles hybrid based copper (II) micro-sensor have been demonstrated. The realized nano-composites based thin-film micro-sensor incorporates titanium dioxide nano-particles as sensitive materials, poly (vinyl chloride) as supporting matrix and 2-nitrophenyl octyl ether as plasticizer. The micro-sensor based on these materials provides near Nernestian response for copper (II) ions (sensitivity of 23 ± 0.5 mV/ concentration decade) covering the range of 10^{-1}-10^{-5} mole L^{-1} and detection limit of 4.75×10^{-6}. The developed thin-film micro-sensors was successfully used in the determination of copper (II) in some samples with high accuracy (97%) and precision (<3%).

Keywords: Titanium dioxide, Nano-particles, Composites, Thin-film, Micro-sensor, Copper determination

1. INTRODUCTION

The extensive developments in analytical techniques for quality control of food, agriculture, military and particularly, medical applications have been increased in recent years. Thus, rapid, reliable, low cost, and in some cases, continuous measurement of analytes have been a major goal in analytical sciences. In this context, ion selective electrodes and potentiometric micro-sensors offer many advantages over conventional analytical techniques in terms of simplicity, detection limit, specificity, sensitivity, reliability, reusability, stability, and usually small [1-5]. Therefore, the development of such devices for analytical purposes has attracted a great deal of interest in recent years [6-8]. Recently, the development of miniaturized and micro-sized sensors based on organic sensitive membrane has been introduced to overcome the cross sensitivity problem of the chalcogenide and inorganic based thin-film micro-sensors [5]. However, there is an additional problem that the adhesion of the organic membrane to the thin-film substrate is usually poor, which produces an early degradation of those micro-sensors. To solve this problem, we had recently developed a new approach (Arida Approach) for the organic based sensors micro-fabrications [12]. In this technique, the organic membrane sensitive layer has been nebulized in combination with the substrate surface treatment. Using these two steps in combination has dramatically enhance the adhesion of the wafer surface, decrease the leaching of the ionophore and plasticizer, and stabilize the organic membrane and consequently increase the microelectrode life-time.

It is also well known that nano-structured materials display properties which they do not show in the bulk phase namely, high sensitivity and selectivity. These materials possess unique and interesting properties brought by the high surface to volume ratio. Therefore, they were utilized in various fields of human activities – e.g. in electronics, medicine, cosmonautics, car industry etc [13-15]. Moreover, there is a great deal of interest in the preparation and characterization of organic–inorganic nano-composite materials for potential applications in the field of electronics, biochemistry, materials, and medicine [16,17]. These materials have superior electrically conducting behavior, high conductivity and excellent ion-exchange behavior [18,19]. The most obvious advantage of organic and inorganic hybrids is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material [20,21]. Most of the organic-inorganic hybrid materials are nano-composite materials in which the inorganic part and the organic entities interact at molecular level in the nanoscopic domain. This kind of materials often present the best properties of each of its components in a synergic way, offering a unique opportunity to prepare tailor-made new materials with chemical, physical and mechanical properties of a high performance. As an example of such material, titanium dioxide bulk and nano-particles have been prepared and characterized [22-26]. This material has been used as sensitive element in fabrication of low coast solid-stat pH sensor [23,24] and high temperature carbon monoxide selective sensor [25]. The nanostructure of titanium dioxide has been used as coating in photocatalysis and sensor application [26]. Further, it was reported that the titanium dioxide nano-particles exhibits high adsorption capacity to copper (II) ions from aqueous media [27].

On the other hand, many sophisticated instrumental analysis were reviewed for copper (II) determination [28-31]. The ion selective electrodes and potentiometric sensors of copper (II) were also reported [32,33]. However, research on micro-sensors based on organic-inorganic nano-composite materials is not reported yet, despite the fact that they are playing an increasingly important role in biological, industrial strategies and agricultural production, process control and environmental monitoring. The advantages brought by these new microelectrodes are a reduced size, small sample volume and miniaturization feasibility. Furthermore, the integration of micro-sensors can be realized easily for multianalyte detection.

For this purpose, in the present study, titanium dioxide nano-particles embedded in PVC membrane is used as sensitive membrane in preparation of thin-film based copper (II) micro-sensor. Micro-fabrication methodology as well as characterization and application of the proposed new microchips are described.

2. EXPERIMENTAL SECTION

2.1. Reagents and materials

All reagents used were of analytical reagents grade, unless otherwise stated. Further, deionized water with a Milli-Q water purification system (Millipore, 18.3 MΩ cm^{-1}) was used in the preparation of the reagents and rinsing the glassware throughout. All the standard solutions of cations were prepared from their analytical reagent grade chemicals in de-ionized water. Nitrate or chloride salts of the metal used were purchased from Riedel-de Haën. A silicon-planner thin-film gold micro-chips was used as the substrate electrode.

Titanium (IV) oxide anatase (99.9%, 32 nm) powder was purchased from Alfa Aesar (GmbH, Germany). Lipophylic additive potassium tetrakis(4-chlorophenyl) borate and solvent mediator, 2-nitrophenyl octyl ether were purchased from Sigma-Aldrich (CH-9471 Buchs, Switzerland). The membrane solvent, THF (tetrahydrofurane) and the membrane support matrix, high molecular weight (220,000) poly(vinyl chloride) carboxylated were purchased from Riedel-de Haën chemical Company (Germany).

2.2. Instruments

Analytical scanning electron microscope (JEOL, model JSM-6390 LA) was employed to study the surface morphology of the thin-film membrane of the prepared micro-sensor. All electrochemical measurements of the proposed thin-film micro-sensor were performed by Jenway (model 3510) pH/mV meter.

2.3. Micro-fabrication and evaluation of the copper micro-sensor

Gold thin-film silicon planner microchips was used as substrates in the micro-sensors fabrication. Prior to the deposition of the organic membrane/titanium dioxide nano-particles hybrid, the gold thin-film microchips substrate were chemically treated by soaking in concentrated HNO_3 for 2 min., washed with deionized water and then rinsed with ethanol to remove the chemical contaminants on the surface. The treated microchip substrates were immediately transferred to the deposition cell containing 10^{-3}mol L^{-1} $AgNo_3$ to deposit a thin-layer from Ag precipitate as described elsewhere [12]. The cocktail coating mixture was prepared by thoroughly mixing 14 mg of nano-TiO_2, 6 mg of potassium tetrakis(4-chlorophenyl) borate, 114 mg of 2-nitrophenyl octyl ether and 66 mg of PVC in 6 mL HF and used as a nano-composite sensitive material. The deposition of the nano-composite sensitive materials on the thin-film microchips was performed using our new nebulization technique in combination with substrate surface treatment recently developed [12]. After fabrication, the micro-sensor was then air dried at room temperature overnight before being characterized.

All potentiometric measurements were performed using the fabricated nano-TiO_2 sensitive membrane based microchips as working electrode in conjunction with a commercial Ag/AgCl reference electrode immersed in stirred test solutions. Both the stirring rate and temperature (25 ± 5

^{o}C) were kept constant during the potential measurements. The response characteristics and the selectivity coefficient $K^{pot}_{Cu,M}$ (obtained by separate solution method) of the thin-film copper micro-electrode have been measured according to IUPAC recommendations.

3. RESULTS AND DISCUSSION

The prepared thin-film microchips based on titanium dioxide nanoparticles / organic membrane hybrid was integrated, characterized and evaluated as copper (II) micro-electrode. The silicon micro-chips is about 10 mm× 10 mm and the diameter of the thin-film micro-electrode is about 2 mm. A video-microscopic picture of the realized TiO_2/organic hybrid membrane-based thin-film micro-sensor is shown in Fig. 1.

Figure 1. Video microscopic picture of the nano-composites based thin-film copper (II) micro-sensor.

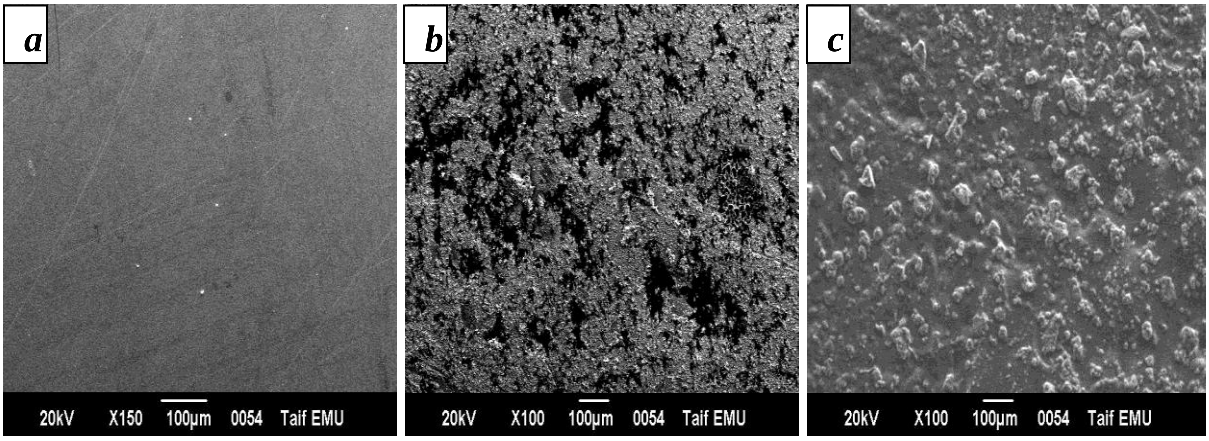

Figure 2. Typical SEM micrograph of gold thin-film surface before treatment (a), after electrochemical treatment (b) and after applying nanocomposites organic membrane sensitive layer (c).

Prior to the electrochemical characterization of the proposed micro-chips, scanning electron microscope was employed to characterize the surface morphology of the gold substrate before treatment, after the electrochemical treatment and after applying the nano-TiO_2/organic membrane sensitive layer. For comparison the results obtained were presented in Fig. 2. The surface structure of each tested film was fairly uniform and do not present any observable defects. While, the untreated film (a) appears very smooth with poor adhesive properties, the treated substrate surface (b) becomes more mountain-like with high roughness and consequently, good adhesion to the organic membrane. The nano-TiO_2/organic hybrid based sensitive film (c) seems homogenous and uniformly distributed. This significantly enhances the stability and consequently, the life time of the suggested micro-sensor.

Table 1. Electroanalytical characterization of the copper (II) micro-sensor.

Parameter	Copper microchips
Slope, mV/decade	23
Response time, s	<5
Linear range, mol L^{-1}	$1x10^{-5}$-$1x10^{-1}$
Detection limit, mol L^{-1}	$4.75x10^{-6}$
pH range	5.7-7.6
Life span, months	>4

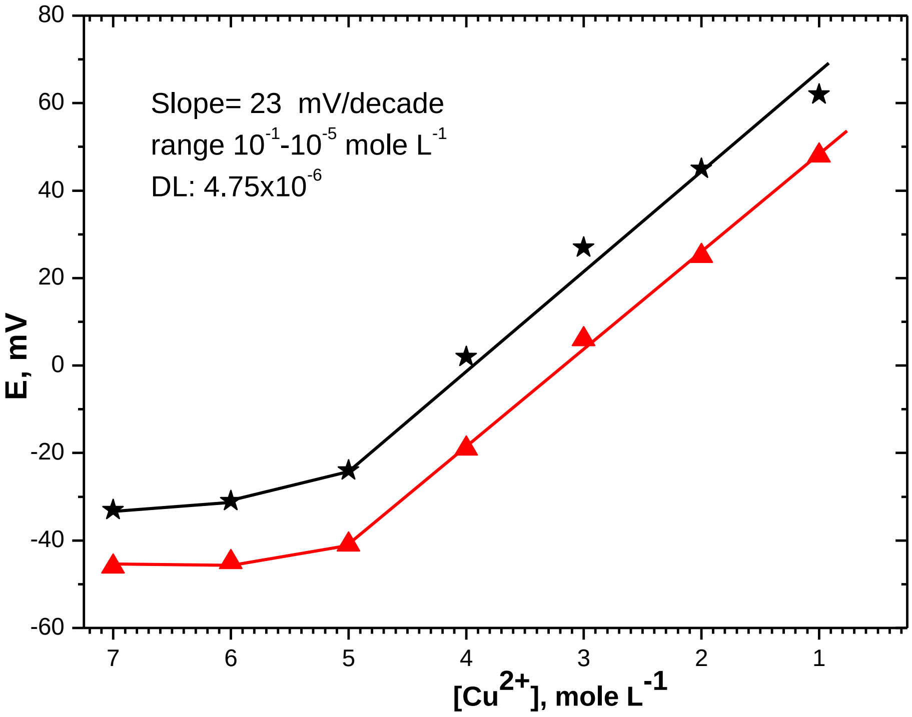

Figure 3. Duplicate potentiometric response of TiO_2 Nano-composite based Cu^{2+} micro-sensor.

In order to characterize the performance of the microelectrode, various operation parameters were tested viz., sensitivity, selectivity, response time, working pH range. The results obtained are summarized in Table 1. The integrated micro-sensor showed an average near-Nernstian sensitivity in the linear concentration range of copper (II) between 1x10^{-5} and 1x10^{-1} mol L^{-1} (Fig. 3), with a fast response time (<5 s) and cationic slope of 23 ± 0.5 mV per concentration decade. The deviation from the ideal theoretical sensitivity is generally reported for the thin-film microchips based electrodes [9]. The limit of detection, determined from the intersection of the two extrapolated segments of the calibration as recommended by IUPAC, was 4.75x10^{-6} mol L^{-1}. The electrochemical treatment of the substrate surface in combination with the nebulization of the organic membrane-sensitive layer dramatically enhance the adhesion to the wafer surface, decrease the leaching out of the ionophore and plasticizer, stabilize the organic membrane and consequently increase the microelectrode life-time (4> months).

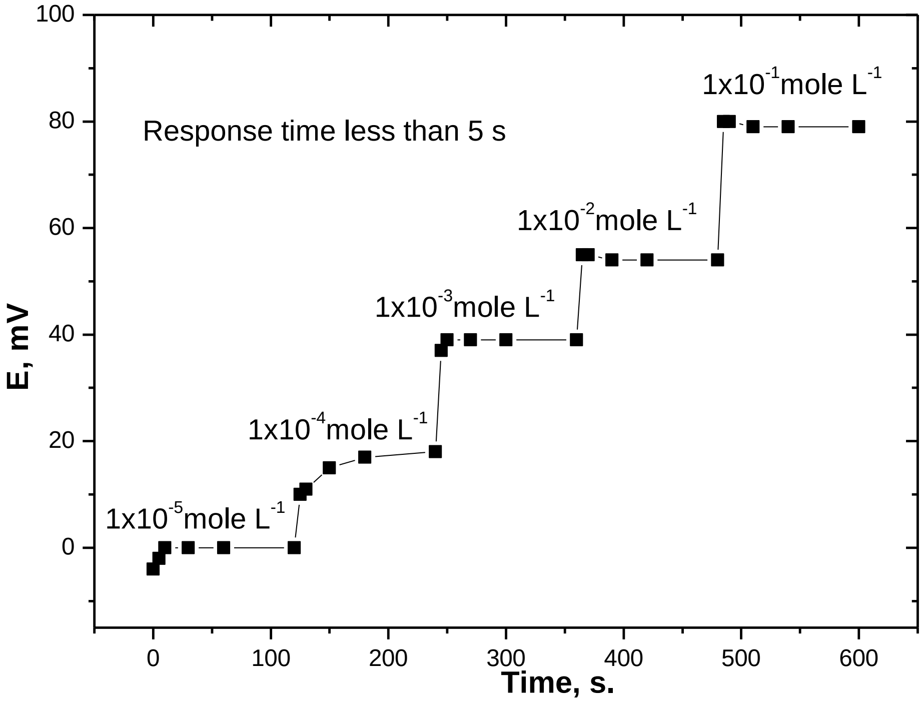

Figure 4. Potentiometric dynamic response of TiO_2 Nano-composite based Cu^{2+} micro-sensor.

In order to assess the dynamic response time, the suggested micro-sensor and the reference electrode were immersed in small beaker containing 10 mL of deionized water followed by stepwise addition of very small aliquots of concentrated copper (II) stock solution to increase the concentration of the test solution tenfold from 1×10^{-5} to 1×10^{-1} mole L^{-1}. The potential responses were recorded versus time after each addition and the results obtained were presented in Fig. 4. As one can observe, the 95% of the output potential is obtained in less than 5 s. Thus the suggested micro-sensor provides very fast response time compared to the bulk organic membrane based electrodes [1-4] and solid state microelectrode [5,6].

The pH effect on the potential of the proposed microchips was investigated in the pH range 1-13 by adding very small aliquots of concentrated nitric acid and/or sodium hydroxide to the test copper solutions (1×10^{-2} and 1×10^{-3} mol L^{-1}). The results obtained were depicted in Fig. 5. As can be seen, the potential remains constant over the pH range from pH 5.7 to 7.6 for both 1.0×10^{-3} and 1.0×10^{-2} mol L^{-1} copper (II) test solutions. The significant effect of the potential at low pH <5 could be related to abundant of the H^+ ions, since the titanium dioxide particles have a certain affinity to H^+ ions [23,24]. Decreasing of the potential at higher pH values may be due to the hydrolysis of copper (II) ions, leading to a decrease in its concentration $\{Cu^{++} \leftrightarrow CuOH^{+}+H^{+} \leftrightarrow Cu(OH)_2+2H^{+}\}$. As a result, the pH range of 5.7-7.6 can be taken as the working pH range for the suggested TiO_2/organic hybrid nano-composites based micro-sensor.

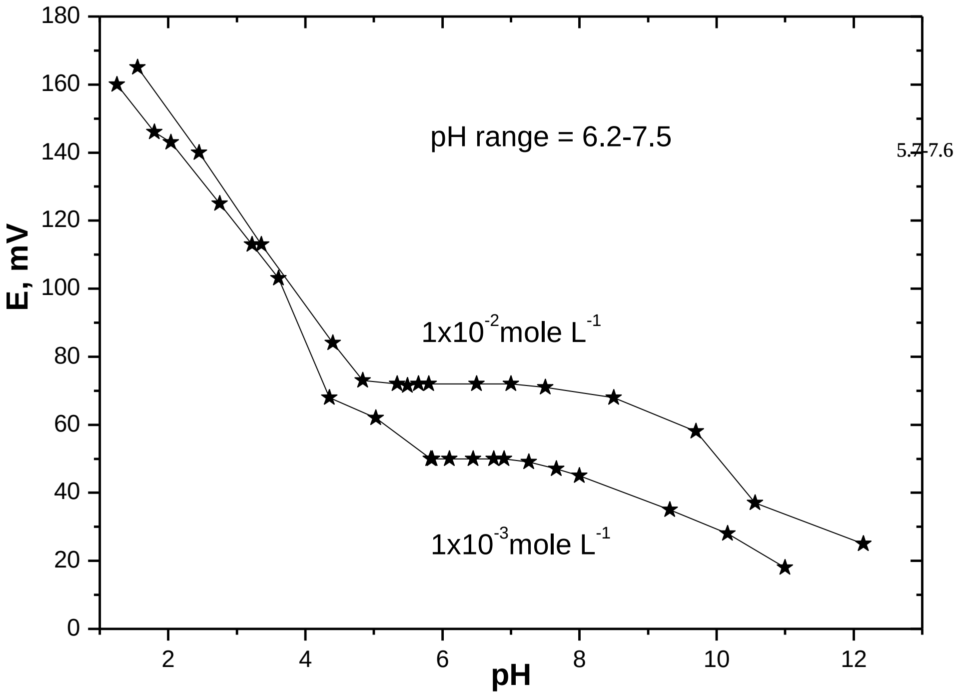

Figure 5. Effect of pH on the response of TiO_2 Nano-composite based Cu^{2+} micro-sensor.

Table 2. Selectivity coefficient of the nano-composites based Cu^{2+} microsensor.

Interfering species (B)	$K^{Pot.}_{Cu^{2+},B}$	Interfering species (B)	$K^{Pot.}_{Cu^{2+},B}$
Cu^{2+}	1.0	NH_4^+	5.5×10^{-2}
Na^+	5.0×10^{-2}	Mg^+	3.6×10^{-2}
K^+	11.0×10^{-2}	Cd^{2+}	6.0×10^{-2}
Ag^+	13.5×10^{-2}	Ca^{2+}	3.0×10^{-2}
Li^+	3.7×10^{-2}	Cr^{3+}	7.4×10^{-2}

The performance of the TiO_2/organic membrane hybrid nano-composites based electrode in the presence of some tested monovalent, divalent and trivalent cations was studied by the separate solution method according to IUPAC recommendations. The selectivity coefficients $K^{Pot}_{Cu^{2+},B}$, presented in Table (2), indicated that the electrode offer a reasonable selectivity for the copper (II) over most of the tested species. The sensitivity and selectivity of nano-TiO_2 hybrid based micro-sensor may be attributed to the high adsorption affinity of TiO_2 to copper (II) compared to other tested cations [27].

The analytical usefulness of the proposed microchips was successfully assessed by the determination of some simulated copper (II) samples using the nano-TiO_2 hybrid based micro-sensor. The results obtained showed that the suggested micro-sensor exhibits repeatable and reliable results with good accuracy (recovery, 97 ± 1%) and precision (relative standard deviation, < 3%). Moreover, the realization of such nano-composites based microchips significantly enhances the integration and automation feasibility in flow injection analysis (FIA) and network systems.

4. CONCLUSIONS

The fabrication, characterization and analytical application of new nan-TiO_2/organic hybrid based copper (II) micro-chips have been described here in this work. The micro-fabrication of the nano-composites based micro-sensor has been realized using new nebulization of the organic membrane sensitive layer in combination with electrochemical treatment of the substrate surface, recently developed. The developed micro-sensor exhibits near-Nernestian sensitivity (23 mV/concentration decade) covering the linear concentration range of $1x10^{-5}$-$1x10^{-1}$ mol L^{-1}, fast response time (<5 s.) and long life span (>4 months). The developed micro-sensor has been successfully applied in the determination of some copper samples with high accuracy and precision.

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