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Gold nanoparticles solid contact for ion-selective electrodes of highly stable potential readings

Ewa Jaworska, Michał Wójcik, Anna Kisiel, Józef Mieczkowski, Agata Michalska*

Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

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ABSTRACT

Internal solution free ion-selective electrodes were prepared applying for the first time gold nanoparticles as a solid contact layer. The presence of a layer of gold nanoparticles stabilized with aliphatic thiols at the back side of the membrane resulted in highly stable potentiometric responses of the sensors, good selectivities and close to Nernstian slopes. Electrochemical studies have confirmed that the applied material is effectively working as capacitive solid contact, yielding high stability sensors.

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1. Introduction

Although nanostructures are of interest of electrochemical community for quite a while now, their application in ion-selective electrodes (ISEs), is a novel research topic. Some reports point out to beneficial effect of nanostructures: gold nanoparticles (GNP), introducing also ionophore modified GNPs [1–3] or platinum nanoparticles [4]. These materials present in the membrane improve performance of the sensors [1–5]. Other papers discuss recognition achieved due to interactions with carbon-nanotubes (CNTs) [6–8]. Besides search for improved/novel receptors for ISEs the research for many years now was focused on the elimination of internal liquid phase without compromising sensor performance, especially stability of potential readings (e.g. [9,10]). Different materials were tested as so called ion-to-electron transducers, solid contacts (SC) including: hydrogels (e.g. [11,12]), ferrocene organothiols [13,14], redox-active self-assembled monolayers [15], three-dimensionally ordered macroporous carbon [16] conducting polymers (CPs) [9,10,17] also in the form of layers obtained from microstructures or nanoparticles suspensions [18–20]. The most successful CPs SCs are based on polyoctylthiophene (e.g. [21–23]). High stability of potential readings achieved for this SC type is attributed to high lipophilicity of applied CP.

To our best knowledge, apart from CPs nanoparticles, other nanomaterial applied as SC in ISEs are CNTs [24–26]. CNTs transducer based ISEs are characterized with analytical parameters well comparable with those of other arrangements and good stability of potentials [24–26].

The goal of this work was to check the possibility of GNPs application as SC – transducer layer in ISEs, using as a model – potassium sensor (K-ISE). To our best knowledge GNPs have not been applied as solid-contacts; however, they seem to be interesting alternative for other materials used so far as SC in ISEs. Due to the presence of aliphatic thiols on the surface of GNP they can offer significant lipophilicity, moreover GNPs SC sensor properties can be relatively easily modified using different thiols or terminal sulphur(II) bearing compounds. Application of the GNPs transducer layer is conveniently achieved by simple drop-casing method.

2. Experimental

2.1. Apparatus

In the potentiometric experiments and electrochemical measurements experimental setup similar to described earlier [4] was used. The recorded potential values were corrected for the liquid junction potential calculated according to Henderson approximation.

2.2. Reagents

Valinomycin, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB), poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS) and terahydrofuran (THF) were from Fluka

* Corresponding author. Tel.: +48 22 8220211; fax: +48 22 822 59 96.
E-mail address: agatam@chem.uw.edu.pl (A. Michalska).

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AG (Switzerland), regioregular poly(3-octylthiophene) (POT), $AuCl_3$, sodium borohydride, methyltrioctylammonium bromide (MTOABr), octanethiol, butanethiol and chloroform were from Aldrich (Germany), dry solvents: toluene, acetone, ethanol, analytical grade salts were from POCh (Poland).

Doubly distilled and freshly deionised water (resistance 18.2 MΩ cm, Milli-Qplus, Millipore, Austria) was used throughout this work.

2.3. Synthesis of gold nanoparticles

Synthesis was carried out via modified Brust method as described previously [27,28] using either octanethiol or butylthiol (2.7 mmol) as ligands for nanoparticles prepration in course of gold reduction with sodium borohydride. Nanoparticles were purified by precipitation/centrifugation using mixture ethanol/acetone, ethanol, finally GNPs were dispersed in THF and stored in dark. GNPs obtained are denoted Au@C8 and Au@C4 for octanethiol or butylthiol used, respectively.

2.4. Preparation of solid contact electrodes

Glassy carbon (GC) electrodes of surface area 0.07 cm^2 or for control experiment Au electrodes of surface area 0.018 cm^2 were used. The substrate electrodes were polished with Al_2O_3, 0.3 μm and rinsed well in water.

GNP solid contact layers were prepared by drop casting THF based GNPs (either Au@C4 or Au@C8) solution (if not stated otherwise, 0.4 mg of GNPs/electrode) on prepared as described above GC electrode surface and left for the evaporation of THF at room temperature.

For comparison POT transducer sensors were also used, they were prepared by applying 10 μl of polymer solution in chloroform (2.75 mg/ml) instead of GNPs and left for the evaporation of POT solvent, at room temperature.

Coated wire (CW) sensors were obtained applying membrane directly on polished GC substrate.

For control experiment Au substrate electrodes modified with either C4 or C8 thiols in course of 2 h contact were used (no GNPs applied).

2.5. Ion-selective membranes

K-ISE membrane contained (by weight): 1.6% NaTFPB, 2.8% valinomycin, 64.0% DOS and 31.6% PVC. Total 200 mg were dissolved in 1.5 ml of THF.

30 μl of the membrane cocktail was applied on the top of electrodes prepared as described above (in 10 μl aliquots), when the electrode was placed in up-side down position and left for 5 h for THF to evaporate. As lowering of the detection limit was not aimed in this study all tested sensors were conditioned before measurements for at least 12 h and were stored in-between measurements in 10^{-3} M KCl.

3. Results and discussion

Application of GNPs Au@C4 as SC has resulted in sensor characterized with linear Nernstian responses within the range from 0.1 to 10^{-6} M KCl with slope equal to 55.9 ± 1.0 mV/dec (R^2 = 0.999) and detection limit (LD) equal to $10^{-6.2}$ M. For sensor prepared using Au@C8 similar responses were obtained with slope equal to 55.3 ± 0.6 mV/dec (R^2 = 0.999) and LD = $10^{-6.1}$ M. In parallel experiment equivalent responses were also obtained for POT solid contact electrode: slope 53.7 ± 0.8 mV/dec (R^2 = 0.999), LD equal to $10^{-6.1}$ M.

Table 1
Selectivity coefficients, log $K^{pot}_{K,J}$ ± SD obtained within the activities range from 10^{-1} to 10^{-3} M, separate solution method, for tested potassium selective electrodes, the values were determined using experimental electrodes slope.

	CW	Gold nanoparticles contact		POT contact sensor
		Au@C4	Au@C8	
Ion J	Log $K^{pot}_{K,J}$ ± SD			
Mg^{2+}	−4.4 ± 0.1	−4.5 ± 0.1	−4.5 ± 0.1	−4.0 ± 0.4
Ca^{2+}	−4.3 ± 0.2	−4.6 ± 0.1	−5.0 ± 0.1	−4.0 ± 0.4
H^+	−3.8 ± 0.4	−4.1 ± 0.5	−5.0 ± 0.1	−4.4 ± 0.7
Na^+	−2.8 ± 0.2	−3.1 ± 0.3	−3.5 ± 0.2	−3.5 ± 0.3
Cu^{2+}	−4.2 ± 0.2	−4.6 ± 0.2	−5.4 ± 0.1	−4.2 ± 0.2
Pb^{2+}	−4.1 ± 0.3	−4.5 ± 0.2	−4.9 ± 0.3	−4.4 ± 0.4

Selectivity coefficients, obtained for tested sensors pretreated in KCl (saturated membranes, i.e. conventional selectivities) are gathered in Table 1. Comparison of values obtained for sensors with POT or GNPs transducer Au@C4 shows that both sensors are characterized with similar selectivities within the range of experimental error. However, the improved selectivity was obtained for GNPs Au@C8 transducer. The values obtained for this sensor were, except for Mg^{2+}, significantly lower compared to POT transducer ISE. It was interesting to check if the presence of thiols ligands on the gold, is affecting sensor selectivity towards Cu^{2+} or Pb^{2+} cations. As can be seen from Table 1, relatively high selectivity for copper(II) and lead(II) was preserved (Au@C4) or even increased (Au@C8) for GNPs contact potassium ISE compared to POT SC sensor.

The prerequisite to obtain successful all-solid-state sensor is high stability of potential readings in time. Thus the potentials of GNPs and POT transducer based sensors and CW electrodes recorded within whole activity range (from 10^{-1} to 10^{-9} M) calibrations conducted over 3 weeks were compared. Fig. 1 presents mean values of recorded potentials together with SD. As can be seen from Fig. 1 both types of SC resulted in similar response pattern, however, there is a pronounced difference in potential readings stability between these electrodes and CW electrodes tested in a parallel experiment. CW type sensor was characterized with highest SD of obtained potential values for whole tested activity range, pointing to poor stability. Significantly lower SD values, especially for activities ≥10^{-4} M, were obtained for sensors with POT transducer, although for lower activities SD values equal to about 20 mV were obtained.

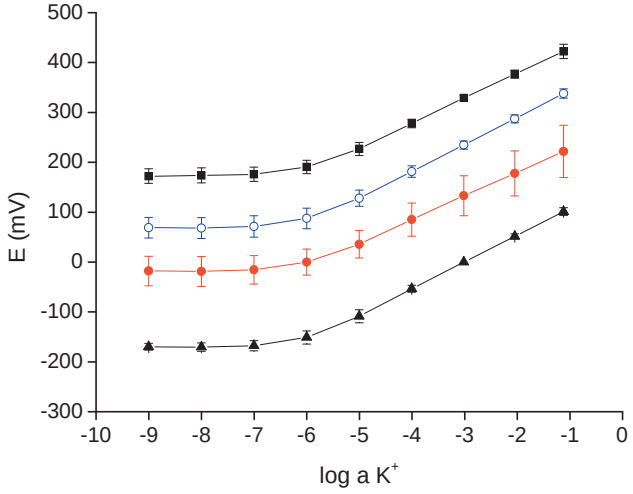

Fig. 1. Mean potential values ± SD recorded over 7 calibrations performed during 3 weeks for following types K-ISEs: (●) CW, (▲) GNP Au@C8, (■) GNP Au@C4 and (○) POT.

The lowest values of SD of potentials recorded were obtained for GNPs SC, both Au@C4 and Au@C8. Generally SD of potential values recorded for GNPs SC sensors were not exceeding 15 mV, and especially for Au@C8 used as solid contact SDs were lower than 10 mV regardless activity of solution tested. Obtained results point to the highest stability of proposed novel solid contact material among tested.

High potential stability of GNPs sensors was also observed while comparing within day stability (5 calibrations within the range from 10^{-2} to 10^{-6} M). For the above given activity range SD values of potentials recorded for Au@C4 and Au@C8 were in the range of 0.5–1.0 mV, whereas for POT transducer sensor SDs were in the range of 1–2 mV. When the K-ISE with Au substrate electrode modified with C4 or C8 thiols (but without GNPs) was used in the same experiment the SD of obtained potentials was in the range of 5–7 mV for K^+ activities higher than 10^{-4} M and even bigger for lower activities.

It is interesting to speculate on the origin of observed high stability of GNPs transducer sensor, although studies of charge transfer process at GNPs transducer is beyond scope of this communication. It seems rational to ascribe the observed effect to lipophilicity of thiol ligands present on gold surface. It is worth stressing that increase in length of thiol aliphatic chain has beneficial effect on the sensor performance, possibly due to the change of acidity of thiol [29], however deeper studies of this issue are required. Also, high surface/volume ratio of GNPs may contribute to enlarging the contact area membrane and SC similarly as for CNTs transducer [24]. A simple, rough, estimation of surface area of applied amount of GNPs (assuming all applied mass is Au and diameter of GNPs metallic core 1.5 nm [27,28]) yields value close to 8×10^2 cm^2, whereas the surface of applied Au substrate electrode (diameter 1.5 mm) is equal to 1.8×10^{-2} cm^2, i.e. the gold surface areas ratio, assuming no contact between particles would in ideal case reach a few orders of magnitude.

The superior performance as SC of GNPs compared to POT can result also from higher resistivity of GNPs for spontaneous reaction with e.g. oxygen (spontaneous charging discharging processes of conducting polymer are known to create ion fluxes through the ion-selective membrane leading to change of sensor performance in time [30,31]). In the case of POT, in the presence of liphophilic anions of ion-exchanger within the ion-selective membrane, these processes can lead to changes in potential of the sensor, especially in long term experiments (e.g. [10]).

In aqueous layer test experiment [15] conducted in 10^{-3} M KCl and NaCl solutions, Fig. 2, significantly more stable potentials (practically no drift) were recorded for GNP Au@C4 contact sensor both in KCl and in NaCl solutions, for the contact with KCl solution after transfer from interferent solution potential change was equal to 0.38 ± 0.01 mV/h. For GNP Au@C8 contact slightly higher potential change in KCl solutions (following contact with NaCl electrolyte) was obtained equal to 0.66 ± 0.01 mV/h, whereas for POT solid contact the drift was equal to -0.74 ± 0.01 mV/h. On the contrary for coated wire type electrode tested in parallel in both electrolytes solutions pronounced potential drift was recorded (for the contact with KCl solution after transfer from NaCl solution potential change was equal to 4.20 ± 0.10 mV/h). The results presented in Fig. 2 clearly show superiority of GNP contact over coated wire type sensor showing that GNP based contact can be even superior over POT type transducer.

The electrochemical stability experiment [17] (chronopotentiometric test in 10^{-3} M KCl, applying cathodic and then anodic current 10^{-9} A) has confirmed high stability of GNPs transducer sensors – lower slopes of E vs. time dependencies. Accordingly the capacitance calculated as described in [17] for GNPs: Au@C8, Au@C4 and POT transducer sensors were equal to 8×10^{-5}, 4×10^{-5} and 1.5×10^{-4} F/cm^2, respectively; 2×10^{-5} F/cm^2 was

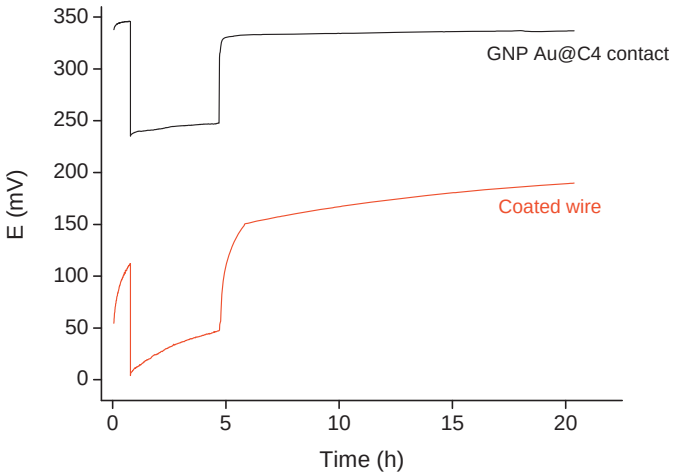

Fig. 2. The aqueous layer test experiment performed for GNP A@C4 solid contact electrode and coated wire type electrode. Experiment was performed in 10^{-3} M KCl, 10^{-3} M NaCl and 10^{-3} M KCl again.

obtained for CW type sensor. These results clearly confirm that GNPs used as SC result in favorable increase of capacitance of the sensor compared to CW arrangement; however, obtained values are slightly lower than characterizing POT SC. It should be stressed that (undoped) POT and GNPs are of different properties, thus the comparison is not straightforward. When the mass of GNPs applied as SC per electrode was doubled, the increase of capacitance of the sensor by factor slightly bigger than 2 was observed regardless if it was Au@C8 or Au@C4. On the other hand, when the Au substrate electrode modified directly with either C4 or C8 thiols (no GNPs used) and then covered with PVC based membrane was tested, the capacitance, regardless applied thiol, was lower and close to 2×10^{-5} F/cm^2, comparable with CW arrangement with GC substrate electrode.

Clearly a more detailed research on GNPs transduction mechanism, especially in the shade of higher potential stability of these sensors is required and is ongoing in our group. It should be stressed that calculated resistances [17] of GNPs: Au@C8, Au@C4, POT transducer based sensors and CW type one were equal to 6.6×10^6, 2.9×10^6, 8.5×10^6 and 1.6×10^7 Ω, respectively. These values are, within the range of experimental error, typical for PVC based membranes sensors.

The impedance spectra (EIS) obtained for both types GNPs and coated wire type sensors were similar, Fig. 3. The obtained results clearly point out to decrease of charge transfer resistance (for the same membrane thickness) in the case of application of GNPs as solid contact compared to coated wire arrangement. For GNPs (similar results were also observed for POT SC sensor, results not shown) and frequencies lower than 10^2 Hz phase angles were equal to 0 and log Z were stable reaching values between 6.5 and 7. Thus, the estimated resistance of tested sensors obtained from this experiment was comparable with the above given values obtained from chronopotentiometry.

EIS spectra for the electrode coated by gold nanoparticles (without membrane, not shown) did not represent pure capacitive behavior, and were typical for a constant phase element (CPE) most probably due to extended surface area. For CPE the impedance $Z(\mathrm{CPE}) = Y_0^{-1}(j\omega)^{-n}$, where ω is the angular frequency. Both for Au@C4 and Au@C8 the n value was close to 0.85 and the estimated Y_0 was about 10^{-3} s$^{0.85}$ Ω^{-1} cm^{-2}. Taking into account approximation in representing capacitance by Y_0, the latter value was not far from the determined low frequency capacitance of the SC. For the Au substrate electrode modified with C8 thiols, EIS spectrum revealed CPE behavior in a wide frequency range (up to 10^3 Hz) with

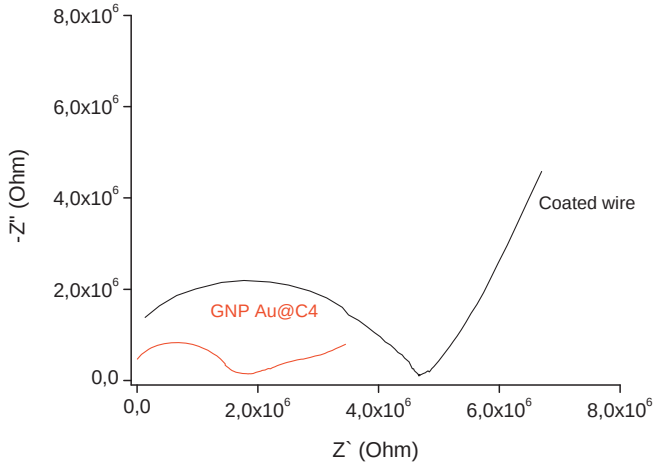

Fig. 3. Electrochemical impedance plots obtained in 0.1 M KCl solution for GNP contact electrode Au@C4 and coated wire type electrode within frequency range 10^4–10^{-2} Hz.

absolute value of phase angle slightly below 75°. Thus, n value was 0.83 and Y_0 was about 2×10^{-5} $s^{0.83}$ Ω^{-1} cm^{-2}, much lower than for electrode with GNP. The Y_0 ratio for GC electrode with GNP and Au substrate can to some extent represent the ratio of effective surface areas, this ratio was close to 50. This confirms that capacitive properties of gold nanoparticles determine to large extent the properties of the sensor, resulting in capacitive solid contact ion-selective electrode. However, the presence of ion-selective membrane reduces to some extent the beneficial difference in capacitances. Nevertheless, advantageous effect resulting in better stability is observed.

4. Conclusions

Ion-selective electrodes with gold nanoparticles solid contact were prepared in course of simple drop casting procedure. Resulting sensors were characterized with superior stability of potentials, higher compared to well known conducting polymer transducer sensors. Moreover, linear response range, slopes of dependence and selectivities were not adversely affected by the presence of GNPs at back side of the membrane, in fact for GNP with longer alkyl chain ligand (Au@C8) improvement of selectivity was observed, especially for tested heavy metal cations. Beneficial effect of GNPs presence in all-solid state sensors can be attributed to higher capacitance of sensors and to the presence of relatively lipophilic alkyl chains of used ligands. Presented results clearly demonstrate that GNPs can be attractive alternative for established solid contact materials, especially as application of other ligands opens wide possibilities of sensor properties tailoring, by tuning of transducer phase properties. Further studies on this issue are ongoing in our group.

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