



Core-shell nanoparticles optical sensors - Rational design of zinc ions fluorescent nanoprobe of improved analytical performance



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ABSTRACT

In this work the effect of affinity of an analyte to a receptor on the response of nanostructural fluorimetric probes is discussed. Core-shell nanoparticles sensors are prepared that benefit from the properties of the phases involved leading to improved analytical performance.

The optical transduction system chosen is independent of pH, thus the change of sample pH can be used to control the analyte - receptor affinity through the “conditional” binding constant prevailing within the lipophilic phase. It is shown that by affecting the “conditional” binding constant the performance of the sensor can be fine-tuned.

As expected, increase in “conditional” affinity of the ligand embedded in the lipophilic phase to the analyte results in higher sensitivity over narrow concentration range – bulk reaction and sigmoidal shape response of emission intensity vs. logarithm of concentration changes.

To induce a linear dependence of emission intensity vs. logarithm of analyte concentration covering a broad concentration range, a spatial confinement of the reaction zone is proposed, and application of core-shell nanostructures. The core material, polypyrrole nanospheres, is effectively not permeable for the analyte - ligand complex, thus the reaction is limited to the outer shell layer of the polymer prepared from poly(maleic anhydride-alt-1-octadecene). For herein introduced system a linear dependence of emission intensity vs. logarithm of Zn^{2+} concentration was obtained within the range from 10^{-7} to 10^{-1} M.

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1. Introduction

Optical sensors are established tools of analytical chemistry. Among different systems, miniature probes, with a dye embedded in the lipophilic matrix, offer significant benefits, e.g. Refs. [1,2]. They allow localized fluorimetric signal change observation, however often take advantage of highly selective but optically silent receptors – e.g. ionophores originally developed for ion-selective electrodes [3–8]. These compounds are used together with a suitable optical transducer, and are together embedded within a lipophilic micro- or nanospheres moiety. Most often the mechanism relies on a competition between the analyte and hydrogen ions, using pH-sensitive dyes as optical transducers [2–7]. This well established approach (optode) suffers from significant limitation in accessible pH range and needs to assure a stable pH value during

determination [2–7]. For these systems the possibility to affect the prevailing analyte – receptor stability constant is highly limited.

An alternative approach proposed in our group [9] benefits from pH independent optical transducer characterized with emission spectra overlapping with absorption spectra of free ligand. Formation of a ligand-analyte complex with absorption maximum different from that of free ligand, allows observation of increase in transducer emission intensity, for increasing analyte concentration in the solution [9]. Another advantage of this system was exceptional broad and linear dependence of observed emission intensity on logarithm of analyte concentration changes in a sample [9]. This effect resulted from limitation in diffusion of the formed receptor-analyte complex within the microsphere leading to a linear dependence of fluorimetric response on logarithm of analyte concentration covering seven orders of magnitude [9].

A similar effect of broad linear dependence range of emission intensity on change of analyte concentration in a solution was observed for nanoscale optodes of surface rich in carboxyl groups

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[6,7]. Electrostatic interactions between analyte cations – e.g. potassium or calcium ions – and nanoprobe surface negative charges result in linear responses covering a few orders of magnitude concentration range [6,7]. However, in a longer time scale (28 h compared to 10 min) the response pattern was evolving to a classical optode sigmoidal dependence of signal vs. logarithm of analyte concentration. Binding equilibrium prevailing in the system ultimately resulted in incorporation of potassium ions to the bulk of nanoprobe, leading to sigmoidal shape dependence of emission on analyte contents. A similar behavior was also observed by others for a system with surface negative charges applied as potassium ion sensor [10]. For optodes operating under special experiment conditions (exhaustive mode) linear responses were also reported [11], however, usually they are observed in a narrow concentration range.

Clearly, the possibility of tailoring responses of optical sensors by affecting both analyte transport into the inside of the probe and binding affinity (between receptor and analyte) in the probe is challenging, but relatively unexplored research subject. In this work we propose a novel core-shell nanospheres arrangement that due to outer-shell confined reaction zone offers improved analytical performance. The model system studied was core-shell nanospheres prepared by covering conducting polymer nanoparticles, synthesized according to our procedure [12], by a polymeric outer shell. The outer layer was obtained in a similar manner as used previously to transfer quantum dots to water phase [13,14]. Application of poly(maleic anhydride-alt-1-octadecene) (PMAO) as a starting material was found successful to result in highly stable optical sensors even without the presence of other material inside the nanostructure [6,7,15].

Different core-shell structures have been reported in literature, however to the best of our knowledge, neither core-shell nanoparticles based on oxidized conducting polymer core nor shell based on poly(maleic anhydride-alt-1-octadecene) (PMAO) have been reported previously as a material for optical sensing purposes.

In this work Zn^{2+} ions sensors based on pH independent optical signal transduction were used as a model system [9].

2. Experimental

2.1. Reagents

Poly(maleic anhydride-alt-1-octadecene) (average molar mass 30000–50000 $g\ mol^{-1}$) (PMAO), bis(hexamethylene)triamine (BHMTA), pyrene (puriss p.a., for fluorescence), 1-(2-pyridylazo)-2-naphthol (PAN) (Fig. S1), pyrrole, poly(vinyl alcohol) (PVA), tris(hydroxymethyl)aminomethane (Tris), tetrahydrofuran (THF), chloroform, were from Aldrich (Germany).

All salts used, as well as hydrochloric acid, were of analytical grade and were obtained from POCh (Gliwice, Poland). Doubly distilled and freshly deionized water (resistance 18.2 $M\Omega\ cm$, Milli-Qplus, Millipore, Austria) was used throughout this work.

The following pH buffers were used: 10^{-3} M Tris (adjusted with HCl) buffer of pH = 7.4, and acetate (0.1 M sodium acetate + acetic acid) buffer, pH = 5.2.

2.2. Apparatus

Fluorimetric experiments were performed using a spectrofluorimeter Cary Eclipse (Varian). After exposure at excitation wavelength of 337 nm emission intensity was recorded within the range from 350 to 500 nm. The slits used were 5 nm both for excitation and emission, while the detector voltage was maintained at 690 V.

Emulsions were prepared using a homogenizer from Hielscher, model UP 200S.

The obtained nanostructures were separated from solutions using centrifuge MPW-251 Centrifuge (MPW Med. Instruments).

To obtain TEM images of the prepared nanospheres, a Zeiss LIBRA 120 TEM (HT = 120 kV, LaB₆ cathode) apparatus was used.

For dynamic light scattering measurements Malvern Zetasizer Nano ZS (scattering angle 173°) was used.

A home-made coulometric analyzer (current range 0.03–100 mA, voltage output 19 V) was used for all coulometric experiments. The pH-meter and combine glass electrode, both from Seven Multi Mettler Toledo were used in coulometric titration to follow pH changes. The generator electrode was made of platinum foil with a surface area of 2 cm^2 . The surface area of the generating silver anode was chosen so that the current density could be changed in the range from 0.1 to 10 $mA\ cm^{-2}$. The silver anode had a surface area of about 4 cm^2 .

2.3. Synthesis and loading of polymeric nanospheres with pyrene and PAN

Synthesis of PMAO nanospheres was carried out according to the procedure developed in our group [6,7,15]: 500 μ l of a solution of PMAO in chloroform (22 $mg\ ml^{-1}$) was slowly added, dropwise, to 5 ml of a 1% (w/w) PVA aqueous solution containing 10 mg of dissolved BHMTA under sonication (cycle 0.5, power 70%). Sonication was continued for another 5 min. Then the mixture was placed on a stirring plate, 400 μ l of 0.18 M H_2SO_4 aqueous solution was added and the mixture was left overnight on the stirring plate.

Synthesis of polypyrrole nanospheres was performed according to the procedure reported earlier [12]. To 5 ml of water 432 μ l of pyrrole was added. Then 1 ml of poly(n-butyl acrylate) suspension was added to this mixture. After 20 min at ultrasound bath, microspheres were transferred to a solution containing 3 ml of the oxidizing agent – 0.1 M iron(III) toluenesulphonate (TSH). The monomer was gradually and spontaneously released from the microspheres and was readily oxidized at/close to the surface of the microsphere, positively charged oligomers were formed. The mixture was left overnight on a stirring plate and then the nanospheres were centrifuged and the resulting polypyrrole nanospheres were suspended in 750 μ l of chloroform.

To synthesize PMAO-nanoPPy core-shell nanostructures a mixture of: 500 μ l polypyrrole nanospheres suspension in chloroform and 500 μ l of PMAO dispersion in chloroform (22 $mg\ ml^{-1}$) was slowly added, dropwise, to 5 ml of a 1% (w/w) PVA aqueous solution containing 10 mg of dissolved BHMTA under sonication (cycle 0.5, power 70%). Sonication was continued for another 5 min. Then the mixture was placed on a stirring plate, 400 μ l of 0.18 M H_2SO_4 aqueous solution was added and the mixture was left overnight on a stirring plate.

Absorption of dyes (pyrene and PAN) was performed by adding to 1 ml of either water suspension of nanospheres (either polypyrrole or PMAO) or of core-shell nanostructures 200 μ l of THF solution containing 0.12 mg ($4.9 \cdot 10^{-7}$ mol) of PAN and pyrene: 0.1 mg ($4.9 \cdot 10^{-7}$ mol) (resulting in 1:1 M ratio). The mixture was left for 20 min in an ultrasound bath for absorption to occur. Then the nanostructures were centrifuged and the harvest nanostructures were suspended in 1 ml of 1% (w/v) PVA solution.

2.4. Coulometric titration of nanospheres

A platinum electrode was placed in a coulometric cell together with silver electrode [16]. In course of electrolysis OH^- anions generated were reacting with carboxyl groups of nanospheres. Dissolved oxygen was removed from the sample by a stream of pure argon to prevent oxygen taking part in the cathode reaction, the argon stream also removed dissolved carbon dioxide.

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