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The Development of Optical Sensors for Heavy Metal Ions detection on Nanocellulose substrate

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Summary:

This study presents two novel all-solid-state optodes, emloyed for detecting different heavy metal ions (HMIs) in waters. For this reason, PVC-based polymeric membranes, containing tetraphenylporphyrin (TPP) and Zn(II)TPP-1,3-bis(2-pyridylimino)isoindoline-Crown (ZnPC) as cation-sensitive ionophores, were embedded in nanocellulose substrate. In addition, a water-soluble porphyrin and silver nanoparticles (AgNPs) were doped with nanocellulose to devise an aqueous sensing suspension. The optical response of these chemical sensors displayed a successful detection of multiple HMIs.

Keywords: Chemical sensors, Nanocellulose, Porphyrin ligands, HMIs, Optical detection

Background, Motivation and Objective

A rise in the level of HMIs in water resources, mainly due to industrial activities, has caused mounting concern about human health. Accordingly, the fabrication of sensing platforms aimed at monitoring HMIs has attracted researchers´ attention [1]. Among all, optical sensors are of substantial interest owing to their privileges, including fast response, excellent sensitivity, and easy usage. Porphyrins and their analogues have been actively used as a sensing materials for the development of chemical sensors over the last decades [2]. It is noteworthy to mention that the utilization of porphyrin ligands in optical sensors opens up new possibilities in detecting HMIs thanks to their ability in hosting and chelating several ions [3]. On the other hand, Nanocellulose, offering unique properties, like biodegradablity, non-toxicity, and sustainablity, can be a promising candidate in sensing platforms [4]. As a result, the integration of porphyrin ligands in nanocellulose substrate leads to a selectivite, sensitivite and biocompatible optical sensor.

The objective of this work is the development of optical sensing platforms in which porphyrin ligands are incorporated in PVC-based polymeric matrix; and nanocellulose applied as a solid support is investigated as well. It should be noted that these are the first steps of series of experiments for development of optical sensors for HMIs with nanocellulose as a solid support, the further studies are in progress.

Two sensing materials based on plasticized PVC membranes were prepared by incorporating 1 wt% of one of the porphyrin ligands and 5 wt% of TpClPBK cation exchanger as it was reported previously [3]. The membrane cocktails in THF (2 µl) were deposited on the small round pieces of freeze-dried nanocellulose (~d= 0.5 cm), isolated from bleached eucalyptus pulp by using high-pressure homogenizer (100-700 bar, 20 cycles, 10 $L.h^{-1}$). The performance of the obtained sensing platform in recognizing different concentrations (10^{-7}-10^{-1} M) of variant HMIs (Ni^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}) were examined. For this reason, 5 µl of all the concentrations of each HMIs were deposited on the prepared sensing optodes.

Additionally, NC was used to facilitate the upload of free base 5, 10, 15, 20 tetrasulpho-penyl porphyrin (TPP-$(SO_3)_4$) on AgNPs. The TPP-$(SO_3)_4$/NC@AgNPs suspension was then used for HMIs optical sensing. The suspension was synthesized according to the literature [5,6] in one-pot procedure through drop-by-drop addition of sodium citrate (2.4×10^{-3} M) into aqueous suspension of NC (0.1 wt%, at boiling point) to which $AgNO_3$ and TPP-$(SO_3)_4$ in 10:1 mass ratio were dissolved. The mixture was refluxed for 40 min. To investigate the performance of the sensing suspension, the HMIs mentioned before were added to it so that obtaining different concentrations of them (10^{-5}-10^{-3} M) in the suspension.

Description of the New Method or System

To the best knowledge of the authors, this is the first time that nanocellulose is exploited as a substrate for porphyrin ligands. Besides, a naked-eye observation in the attained sensing suspension opens a perspective for newly developed NC-based composite materials doped with porphyrins for development of optical sensors for HMIs detection.

Results

Fig. 1(a, b) depicts the images of TPP- and ZnPC-based optodes in response to all the concentrations of the aforementioned HMIS. As can be seen in Fig. 1a, the optical response of the TPP-based optode to all the ions except Zn^{2+} is visible by naked-eye and appears in color change from red to green by increase in their concentrations, attributed to the formation of the sitting-a-top complex of porphyrin with HMIs [2]. In contrary, Fig. 1b depicts that ZnPC-based optode does not have an observable response to the HMIs. However, grayscale color model showed the considerable change in the intensity of its color in the presence of Cu^{2+}, Hg^{2+} and Zn^{2+}. In this case, the response of the ZnPC ligand corresponds to the binding of HMIs by the crown ether cavity [3]. The data extracted by means of ImageJ software [8].

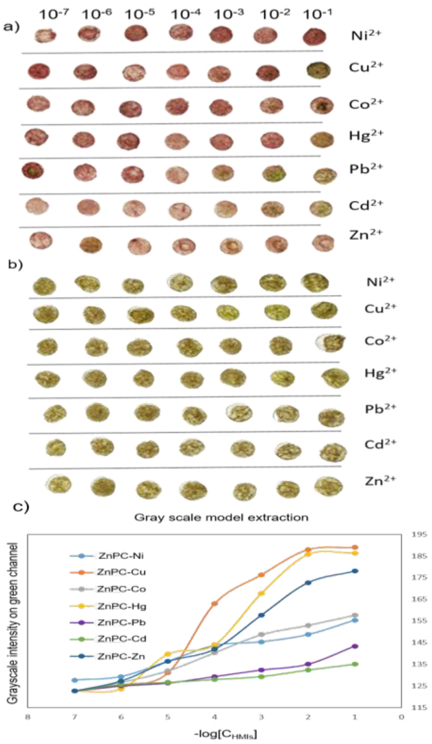

Fig. 1. The images of a) TPP-, b) ZnPC-based optodes in the presence of HMIs in a 10^{-7}-10^{-1} M range of concentrations, c) Plotted data extracted from ZnPC-based optodes by Grayscale model.

Fig. 2a indicates the UV-Vis spectra of TPP-$(SO_3)_4$/NC@AgNPs in the presence of growing concentrations of Hg^{2+}, and the variation of peak intensity as well as red shift of Soret band (typical for porphyrin complexes). Moreover, as can be seen in Fig. 2b, the evident color change of the sensing suspension upon the addition of 10^{-3} M Co^{2+}, Hg^{2+} and Cd^{2+} can be observed. More details on optical signal extraction and HMIs quantitative analysis will be discussed in our presentation.

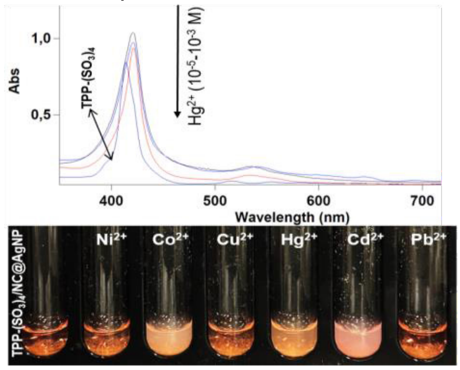

Fig. 2. a) UV-vis spectra of TPP-$(SO_3)_4$/NC@AgNPs aqueous solution in the presence of growing concentrations of Hg^{2+}, b) the image of as synthesized TPP-$(SO_3)_4$/NC@AgNPs, upon the addition of 10^{-3} M solutions of different HMIs.

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