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Rhodamine-based conjugated polymers: potentiometric, colorimetric and voltammetric sensing of mercury ions in aqueous medium†

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Herein, we report the synthesis and characterization of a new rhodamine-based monomer (RD-CZ), and an investigation of the optical and electrochemical properties of the corresponding polymer (P(RD-CZ)), which was electropolymerized on an ITO electrode. The resulting P(RD-CZ) polymer film was used as a simple and novel multi-signal sensor platform, which demonstrates ion-selective potentiometric, colorimetric and voltammetric responses in aqueous media for the first time. P(RD-CZ) exhibits excellent selectivity for Hg^{2+} ions compared with Cd^{2+}, Cu^{2+} Zn^{2+}, and Fe^{3+} using the potentiometric technique, which depends on the increasing charge carrier transport through rhodamine-bound Hg^{2+} with a limit of detection (LOD) of 9.77×10^{-8} M. The P(RD-CZ) polymer film also exhibits a distinct color change from orange to purple, which is detectable even by the naked eye, in the presence of Hg^{2+} ions. The LOD for Hg^{2+} ions obtained using the colorimetric method is 3.16×10^{-8} M. The same material has also been used for the voltammetric sensing of Hg^{2+} in aqueous media with a detection limit of 1×10^{-7} M. In this study, a conductive polymer-based sensor platform for detecting mercury ions *via* three different methods has been designed for the first time. By doing so, a disposable planar paper-based ion-sensing platform, which is suitable for low-cost point-of-care and in-field testing applications, could be fabricated with a highly reproducible and linear response towards different concentrations of analyte ions in aqueous and biological samples.

1. Introduction

Heavy metals are indispensable in modern technology due to them having lots of applications in industry. However, heavy metal ion pollution can cause serious problems for many years due to the severe risks to human health and the environment.[1–5] Since mercury can get into the human body *via* the skin, gastrointestinal tissues, and respiratory system without any difficulty, causes harm to the central nervous and endocrine systems, and lingers for a long time, even after the contaminant has been discarded, it leads to environmental and health problems, and has been identified as one of the most toxic heavy metals in aqueous solutions.[6]

Several techniques are available for mercury detection, such as inductively coupled plasma atomic emission spectroscopy, and atomic absorption spectroscopy. However, all of these methods need sophisticated instrumentation and inconvenient sample preparation steps. Therefore, it is significant to explore new alternative ways to detect Hg^{2+} in a simple, sensitive, effective, nondestructive, inexpensive and rapid manner. For this purpose, fluorometric, colorimetric and potentiometric techniques have been used frequently in sensory applications.[7]

Conducting polymers with exclusive semiconducting and electrical properties have played essential roles and resulted in numerous technological applications.[8–15] They have been extensively researched for novel applications such as thin film transistors,[16] fuel cells,[17,18] organic light-emitting diodes (OLEDs),[19] organic solar cells,[20] electrochromic devices[15,21–24] and chemo/bio-sensors.[25–27] In particular, their implementation in sensory systems has been widely investigated in terms of the sensing processes and transduction mechanisms.

Conducting polymers have been used as signal-transducing materials for sensory applications due to their excellent optical features and doping–dedoping mechanism. Fluorescent conjugated polymers (FCPs), which are a type of conducting polymer, are the most convenient ones for the detection of metal ions due to their high sensitivity, high selectivity and fast response features, as well as the fact that they involve electrochemical signals. One of the benefits of FCP sensors is

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