# Imprinted nanobead-based disposable screen-printed potentiometric sensor for highly sensitive detection of 2-naphthoic acid

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## ARTICLE INFO

## ABSTRACT

Currently, potentiometric sensors based on various molecularly imprinted polymer (MIP) receptors have been successfully fabricated for detection of organic species. However, almost all of the previously developed potentiometric sensors based on MIPs are in traditional liquid-contact mode in which lower detection limits have been restricted by zero-current transmembrane ion fluxes. Herein, a screen-printed potentiometric sensor for determination of 2-naphthoic acid has been developed. It is based on the MIP nanobeads as the selective receptor and the electrochemically reduced graphene oxide film as the solid contact. Compared with the classical potentiometric sensor, the proposed sensor based on nonequilibrium sensing mechanism exhibits remarkably improved detection sensitivity for 2-naphthoic acid with a low detection limit of $6.9 \times 10^{-11}$ M.

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## 1. Introduction

In recent years, polymeric membrane ion-selective electrodes (ISEs) have become an attractive tool for determination of ionic species in clinical diagnostics and trace-level environmental monitoring due to their intrinsic advantages including excellent selectivity, ease of use and high reliability [1–4]. To date, many ISE-based clinical analyzers have been commercially available for monitoring electrolyte ions in clinical laboratories and at the bedside of critically ill patients. However, it should be noted that most of these potentiometric sensors are used for determination of inorganic ions such as the electrolyte ions. So far, potentiometric sensors for detection of organic species have not been widely reported.

Nowadays, molecularly imprinted polymer (MIP)-based potentiometric sensor is exhibiting a great potential to significantly change this situation. MIPs are synthetic receptors which are seemingly general materials for selective binding of a wide range of analytes with affinities and selectivities similar to their biological counterparts [5–8]. Above all, they are stable, less costly and easier to produce [9]. Currently, potentiometric sensors based on various MIP receptors have been successfully fabricated for determination of organic species in their ionic and neutral forms [10].

Despite their success in organics detection, almost all of the previously developed ISEs based on MIPs are in traditional liquid-contact mode in which lower detection limits have been restricted by zero-current transmembrane ion fluxes [11]. This has serious limits for their use in environmental trace-level analysis.

Solid-contact polymeric membrane ISEs which eliminate the inner filling solution have some unique characteristics such as convenient storage and maintenance, and ease of electrode miniaturization [12]. Especially, it has been established that the ISE membrane with a solid contact rather than a traditional liquid inner contact can yield a lower detection limit because of diminished ion fluxes [13]. As one of solid-contact electrodes, disposable screen-printed electrodes have shown to be a powerful technique for the fabrication of miniaturized solid-contact sensors. Compared to the conventional solid-contact electrodes, they are more simple, cheaper and easier for mass production [14]. Additionally, the screen-printed multiple-electrode systems can overcome the operation difficulties of the single-electrode system in the online monitoring processes, which can further expand the application of the solid-contact electrodes in environmental monitoring [15]. These characteristics make such electrode particularly promising for detection of organic species. So far, no research findings about screen-printed potentiometric sensors based on MIPs have been reported yet.

Herein, we present a novel MIP-based screen-printed potentiometric sensor. 2-Naphthoic acid which is the first-grade

decomposition product of naphthalene is selected as a model of organic species. The electrochemically reduced graphene oxide film is used as the solid contact [16]. The MIP nanobeads are incorporated into the sensing membrane and employed as the receptors for the selective recognition of 2-naphthoic acid. It will be shown that the MIP nanobead-based polymeric membrane screen-printed ISEs could offer a high sensitivity for potentiometric detection of 2-naphthoic acid.

## 2. Experimental

The 2-naphthoic acid MIP nanobeads were synthesized by the precipitation method. Briefly, the template 2-naphthoic acid (1.0 mmol), acrylamide (AA, 2.5 mmol), methyl methacrylate (MMA, 4.0 mmol), divinylbenzene (DVB, 60 μL), trimethylolpropanetrimethacrylate (TRIM, 320 μL) and free-radical initiator 2,2′-azobisisobutyronitrle (AIBN, 0.5 mmol) were dissolved in acetonitrile (40 mL) in a 50 mL flask and sonicated for 10 min to maintain homogeneity. Then the solution was purged with gentle flow of $N_2$ for 10 min and sealed under $N_2$ atmosphere. The temperature was increased from 20 to 75 °C within 30 min and maintained at 75 °C for 24 h. After polymerization, the template was removed by the batch-mode solvent extractions with methanol/acetic acid (8/2, v/v) and methanol until no absorption of the methanol was observed with a Beckman DU-800 UV spectrophotometer. The successful removal of the template was confirmed by the Fourier-transform infrared spectroscopy (FT-IR) (Fig. S1). The resulting polymer was dried for 24 h in vacuum at 40 °C. Non-imprinted polymer (NIP) was prepared under identical conditions except for omission of the template. The detailed descriptions for preparations of the solid contact and the MIP-based screen-printed electrode were given in the Supporting Information.

## 3. Results and discussion

The MIP nanobeads were synthesized by the precipitation method [17] using AA as the functional monomer, MMA as the comonomer and TRIM and DVB as the cross-linkers. The schematic representation of the imprinting process is shown in Scheme S1. In this process, the amine group of AA can interact via strong hydrogen bonding with the carboxyl group of 2-naphthoic acid. In addition, a charge-transfer complexing interaction takes place between the electron-deficient aromatic ring of the template 2-naphthoic acid and the electron-rich amino group (—$CONH_2$) of AA [18]. The micrographs of the obtained imprinted nanobeads were investigated by scanning electron microscopy (SEM). As shown in Fig. 1a, the 2-naphthoic acid imprinted nanobeads are spherical with a diameter distribution of 200–300 nm. It can be expected

that these nanobeads not only can be well dispersed in the polymeric ISE membrane but also have a higher binding capability than the traditional microparticles (Fig. 1b). These will lead to more available binding sites in the sensing membrane and thus result in better response performance [10].

The electrochemically reduced graphene oxide-based solid-contact film was formed on the screen-printed electrode directly from the graphene oxide dispersion by a one-step electrodeposition technique. The morphology of the obtained graphene film on the screen-printed electrode surface was characterized by SEM. As illustrated (Fig. S2 in the Supporting Information), the graphene layer has been successfully deposited onto the surface of the screen-printed electrode. In contrast to the bare carbon substrate which is rough and porous (Fig. S2a), the image of the graphene layer covered electrode (Fig. S2b) clearly exhibits an even and uniform surface.

Since many factors can affect the sensor performance, experimental parameters including the particle size and the MIP amount (see Fig. S3 and S4 in the Supporting Information for the detailed description) were optimized. Under the optimized conditions, the typical time-dependent potential response of the proposed screen-printed potentiometric sensor based on the MIP nanobeads to the deprotonated 2-naphthoic acid is shown in Fig. 2. The proposed sensor shows a Nernstian response of −59.0 mV/decade over the concentration range of $1.0 \times 10^{-5}$–$3.0 \times 10^{-4}$ M with a detection limit of 2.2 μM. Here, the detection limit is defined by the cross-section of the two extrapolated linear calibration curves according to the IUPAC recommendation. Evidently, our approach is effective for determination of ionic 2-naphthoic acid. However, it should be pointed out that the obtained detection limit is poor and unable to satisfy the needs for trace-level analysis.

In order to overcome this, the nonequilibrium potentiometric method was then employed for further improvement of the detection sensitivity [19]. For a traditional ISE, the sensing membrane is usually conditioned with the primary ion and the electrodes are measured under classical equilibrium conditions for the Nernstian sensor response. While for the non-classical potentiometric sensor, before measurements, the electrode is conditioned with a highly discriminated ion (i.e., $Cl^-$) rather than the primary ion. When the electrode is in contact with the primary ion (i.e., deprotonated 2-naphthoic acid), the interfering ions in the membrane surface can be rapidly displaced by the primary ions because of the favorable host-guest interaction with the MIP nanobeads in the membrane. This displacement can induce a nonequilibrium steady-state potential response. Such nonequilibrium sensing method has been successfully applied to sensitive detection of inorganic and organic ions [10,19,20], Fig. S5 shows the potential response of the proposed sensor associated with the nonequilibrium sensing
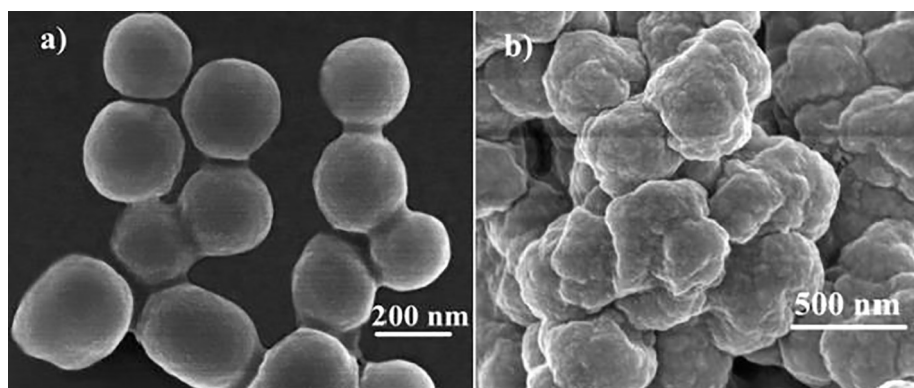


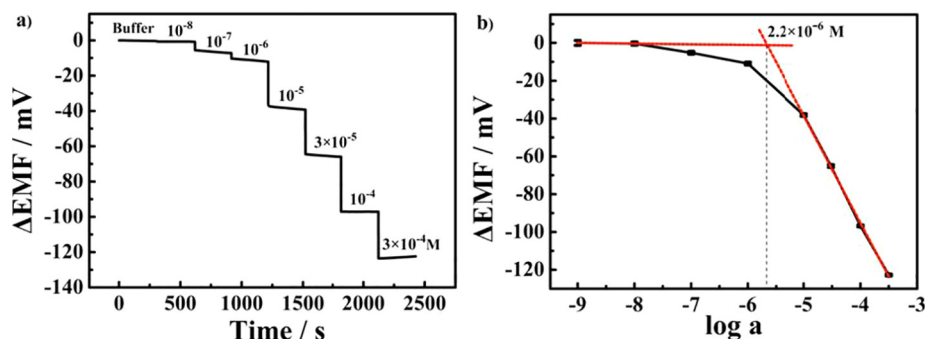**Fig. 1.** SEM images of the 2-naphthoic acid MIP nanobeads (a) and MIP microparticles (b).

**Fig. 2.** Potentiometric responses (a) and corresponding calibration curve (b) of the proposed sensor based on the MIP nanobeads to deprotonated 2-naphthoic acid. Experimental conditions: detection background, 30 mM phosphate buffer solution (PBS) of pH 7.0; conditioning solution, $10^{-4}$ M 2-naphthoic acid in 30 mM PBS of pH 7.0. Error bars represent one standard deviation for three measurements.
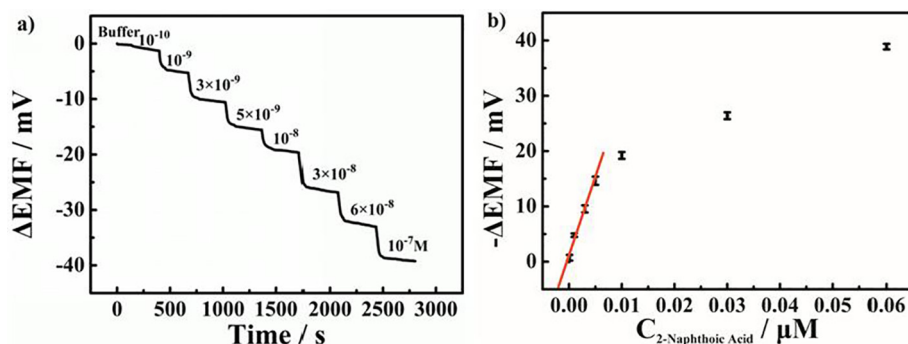


**Fig. 3.** Time-dependent EMF response traces (a) and corresponding calibration curve (b) of the proposed sensor based on nonequilibrium sensing mechanism for measuring deprotonated 2-naphthoic acid. Error bars represent one standard deviation for three measurements. The other conditions are as provided in Fig. S5.

mechanism. As expected, the sensor exhibits a significant improvement in the detection sensitivity (curve a). For measurement of 2-naphthoic acid at $10^{-8}$ M, a negligible EMF change can be observed for the classical Nernstian electrode while that for the nonequilibrium electrode is approximately 15 mV, which indicates that the nonequilibrium potentiometric method is effective for the sensitive detection of deprotonated 2-naphthoic acid.

As a control, the potential response of NIP nanobead-based sensor was also tested (curve b in Fig. S5). Compared with the response of MIP nanobead-based sensor, a worse response performance in terms of a smaller total EMF change for all measuring concentrations can be obtained for NIP nanobead-based sensor under identical conditions, which confirms that the potential signals are indeed induced by the specific recognition interactions between the MIP binding sites in the membrane and the target 2-naphthoic acid.

Under the optimized conditions, the potential response of the screen-printed potentiometric sensor based on the MIP nanobeads for measuring 2-naphthoic acid at concentrations ranging from $10^{-7}$ to $10^{-10}$ M in nonequilibrium mode is shown in Fig. 3. Further analysis of the experimental results reveals that there is a linear dependence of the EMF change on the concentration of 2-naphthoic acid in the range of $1.0 \times 10^{-10}$–$5.0 \times 10^{-9}$ M with a detection limit of $6.9 \times 10^{-11}$ M ($3\sigma$). This detection limit is near five orders of magnitude lower than the classical ISE, which makes it feasible to perform trace-level measurements. In addition, experiments show that the proposed electrode exhibits excellent selectivity to 2-naphthoic acid over its analogs such as 1-naphthoic acid and benzoic acid and some inorganic anions such as OH$^-$ and Cl$^-$ (see Table S1 in the Supporting Information). Also, the sensor has satisfactory recoveries (between 96% and 105%) for real soil samples (Table S2). See the Supporting Information for more

detailed discussion about the selectivity and the real sample analysis.

## 4. Conclusions

Compared with the classical potentiometric sensor, the proposed sensor based on nonequilibrium sensing mechanism exhibits remarkably improved sensitivity for detection of 2-naphthoic acid with a low detection limit of $6.9 \times 10^{-11}$ M. It is expected that various organic ions at trace levels can be determined by using different MIPs. Further, a sensor array using different screen-printed ISEs based on MIPs may be fabricated for simultaneously potentiometric detection of a series of organic species.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2018.04.119.

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