



Light-driven ion extraction of polymeric membranes for on-demand Cu(II) sensing

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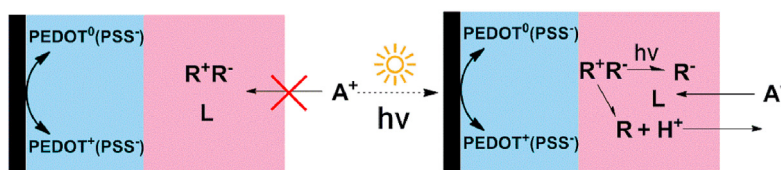
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HIGHLIGHTS

- A potentiometric sensor that exhibits dynamic response by light irradiation.
- Light-driven ion extraction of polymeric membranes can be used for ion detection.
- Potentiometry and constant potential coulometry can be used for direct ion sensing.

GRAPHICAL ABSTRACT



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ABSTRACT

The modulation of the ion-fluxes across a polymeric membrane is important for designing attractive methodologies. As an alternative to the commonly used dynamic electrochemistry approaches, light can be used as an external stimulus and provides a very convenient way to manipulate ions release and/or extraction into a polymeric membrane. Herein, we designed a solid-contact polymeric membrane ion-selective sensor that exhibits dynamic response by light irradiation at 375 nm. The electrode membrane contains a light-sensitive lipophilic salt (bis(4-tert-butylphenyl)iodonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (R^+-R^- , BTDT-TFPB) instead of traditional ion exchanger. Under light illumination, the decomposition of the lipophilic cation makes the membrane with ion-exchange properties. The solid-contact ion-selective electrodes based on potentiometry and constant potential coulometry have been explored for direct ion sensing. Copper was selected as a mode analyte and can be determined at micromole levels. The proposed dynamic ion sensors show promise for on-demand ion sensing.

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1. Introduction

Potentiometry with polymeric membrane ion-selective electrodes (ISEs) commonly works in a passive measurement mode, in

which the response of an electrode relies on a chemical equilibrium [1–3]. In recent years, dynamic electrochemistry approaches based on the modulation of the ion-fluxes across the polymeric membranes have been introduced and adopted by researchers to establish new attractive methodologies [4]. These methodologies include chronopotentiometry [5–7], thin-layer coulometry [8,9], stripping ion-transfer voltammetry [10–12], coulometric/chronopotentiometric flash titrations [13,14], and pulse current-operated reference electrodes [15]. The controlled release and/or

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uptake of ions by the polymeric membranes of ISEs can be achieved via an external voltage or current, which constitutes one of the unique features of these methods.

As an alternative approach, light can be used as an external stimulus and provides a very convenient way to manipulate ions release and/or extraction at a desired time and in a desired area [16]. Photoexcitable polymeric membranes doped with photochromic spiropyrans or photoresponsive compounds have been well studied and applied for sensor design by several groups [17–21]. These potentiometric ion sensing and biosensing systems can be regulated by light [22,23]. Moreover, photoresponsive ion extraction/release systems have recently attracted much attention by researchers [24–26]. By incorporating photoactive molecules in the polymeric membrane, dynamic ion optodes for a number of ions have been designed [27–31]. Herein, we report on the light-driven ion extraction of polymeric membrane for both potentiometric and voltametric ion sensing.

As the most promising generation of potentiometric ion sensors, solid-contact ISEs have been extensively studied [3,32,33]. Potentiometry based on solid-contact ISEs are routinely measured in an open circuit potential (OCP) mode. Very recently, Bobacka's group reported a novel signal transduction method for solid-contact ISEs based on constant potential coulometry [34,35]. Then, Bakker and Bobacka et al. established a capacitive model for coulometric readout of ISEs [36]. The method shows promise for measurements of very small changes in ion concentration (activity). While the principle is expected to be useful in the standard addition mode, its applications in the direct detection mode cannot be easily achieved. Inspired by the researches on the light-controlled ion extraction, we designed dynamic solid-contact ISEs that can be explored for direct ion sensing based on constant potential coulometry. We show that by using light as an external stimulus, the photo-generated protons can exchange with the analyte ions, which can be sensed by both zero-current potentiometry and constant potential coulometry.

2. Experimental section

2.1. Materials

High-molecular-weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), Cu^{2+} ionophore I o-xylylenebis(N,N-diisobutyldithiocarbamate), bis(4-tert-butylphenyl)iodoniumtriflate (BTDT), calcein, chromoionophore I (CH 1), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), poly(sodium 4-styrenesulfonate) (NaPSS), and 3,4-ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich (St. Louis, MO). A photoresponsive lipophilic salt bis(4-tert-butylphenyl)iodonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (R^+-R^- , BTDT-TFPB) was synthesized by a metathesis method as described before [29]. The hydrophilic counter cation of TFPB $^-$ was replaced by the photoactive ion BTDT. BTDT and NaTFPB with 2 to 1 ratio were dissolved in dichloromethane and extracted with 0.01 M sodium hydroxide aqueous solution. The presence of excess BTDT enables the complete replacement of the counter cation of TFPB $^-$. The organic phase was evaporated under reduced pressure to obtain the desired salt. All other chemical reagents were purchased from Sinopharm Chemical Reagent (Shanghai, China). The successful synthesis of the BTDT-TFPB was confirmed by mass spectrometry (Fig. S1 in the supporting information). Electrospray ionization mass spectrometry analyses were performed on a LCQ Fleet ion trap mass spectrometer (Thermo Finnigan) in positive ion mode. All chemicals were analytical grade and used without further purification.

2.2. Membrane preparation

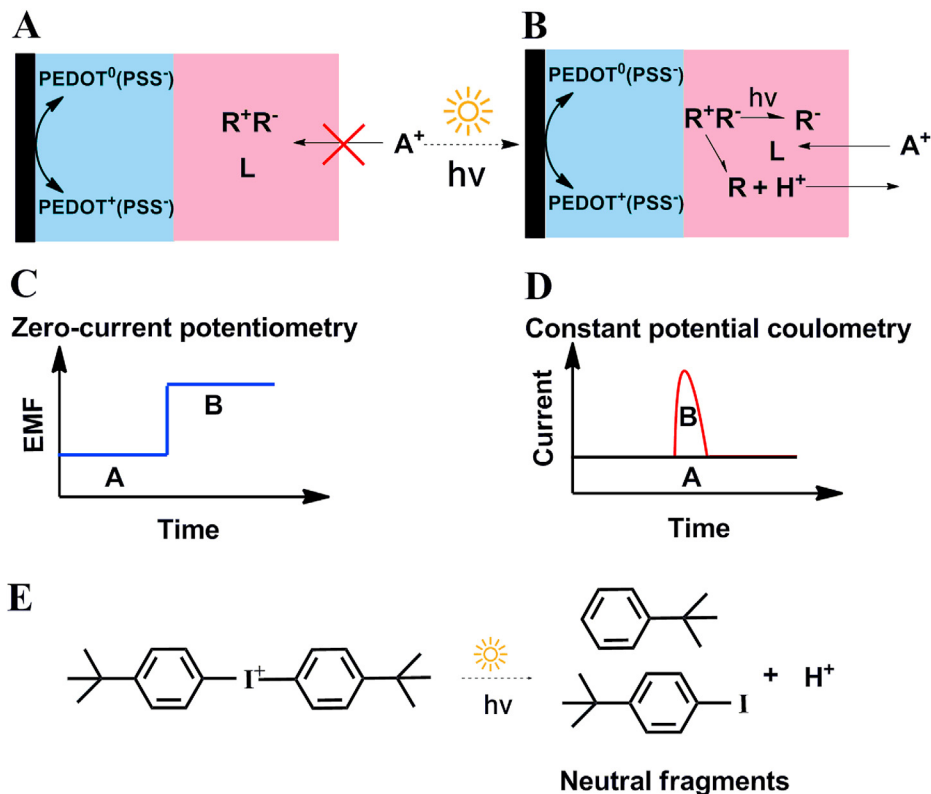
The light-sensitive ion-selective membranes containing 31.4 wt% PVC, 62.8 wt% DOS, 1% wt% Cu^{2+} ionophore I and 4.8 wt% BTDT-TFPB were prepared. The common Cu^{2+} -selective membranes contained 32.6 wt% PVC, 65.5 wt% DOS, 1.0% wt% Cu^{2+} ionophore I and 0.89 wt% NaTFPB. 100 mg of the membrane components were dissolved in 1.0 mL of tetrahydrofuran. By applying a 0.014 mA current for 714 s in aqueous solution containing 0.1 M NaPSS and 0.01 M EDOT, the poly(3,4-ethylenedioxythio phene)-poly(styrenesulfonate) (PEDOT/PSS) film was electrodeposited on the glassy carbon electrode (GC) as described before [37]. Solid-contact ISEs were prepared by drop-casting 80 μL of the membrane cocktail on the GC/PEDOT-PSS electrodes. After being dried for 12 h at room temperature, the ISEs (with a membrane thickness of ca 100 μm) were conditioned in 1.0×10^{-3} M NaCl solution overnight. For comparison, the light-sensitive ion-selective membranes for Cu^{2+} were conditioned in the 10^{-3} M primary ions overnight.

2.3. Fluorescence microscopy imaging

For fluorescence microscopy imaging, a pH indicator dye CH 1 was incorporated into the sensing membrane to verify the generation of protons. The sensing membranes contains 30.6 wt% PVC, 61.0 wt% DOS, 1% Cu^{2+} ionophore I, 4.8 wt% BTDT-TFPB and 2.6 wt% CH 1. Membranes were obtained by casting a solution of 50 mg of the membrane components dissolved in 1.0 mL of THF into a glass ring of 2.0 mm diameter fixed on a glass plate and letting the solvent evaporate overnight. Fluorescence images of the polymeric membranes with and without light illumination at 375 nm for 30 s were recorded. Fluorescence images were constructed from fluorescence collection (620–670 nm, $\lambda_{\text{ex}} = 480$ nm) and using Fluoview FV1000 system (Tokyo, Japan). To verify the Cu^{2+} uptake by the membrane, a small piece of membrane was cut with sharp edges and placed in contact with a 10^{-4} M CuCl_2 solution containing 10^{-4} M calcein in a 0.001 M NaCl. The fluorescence of the polymeric membrane with and without light illumination at 375 nm for 30 s was recorded.

2.4. Potentiometric and coulometric measurements

All measurements were carried out at room temperature using a CHI 760D electrochemical work-station (Shanghai Chenhua Apparatus Corporation, Shanghai, China). A conventional three-electrode cell with the membrane electrode as the working electrode, a platinum wire as auxiliary electrode, and Ag/AgCl (3.0 M KCl) as reference electrode was used [7]. A home-made setup for light illumination is illustrated in Fig. S2. The source of UV light irradiation was a 375 nm LED array (10 W, 10.8 mm \times 10.8 mm, 5.0 lm/W) with 9 LEDs (Taiwan Guanghong Chip co., Ltd.). The sample was irradiated through the bottom of a beaker using the LED array. The irradiation time was controlled by an electromagnetic relay. Previous research shows that the EMF of the PVC membrane-coated electrode was satisfactorily stable under UV or visible light illumination [22]. For electromotive force (EMF) measurements, the response of the sensing membrane (ON and OFF state) over CuCl_2 concentrations ranging from 10^{-1} to 10^{-6} M was obtained in 1.0×10^{-3} M NaCl solution. For constant potential coulometric sensing mode, a constant potential at 0 V in 1.0×10^{-3} M NaCl solution was applied. The current-time trace of the electrode was recorded.



Scheme 1. Schematic illustration of the extraction of cations into the polymeric membrane before (A) and after (B) light illumination at 375 nm. (C) Conventional potentiometric sensing mode and (D) Constant potential coulometric sensing mode. R^+ , R^- , R , and L are bis(4-tert-butylphenyl)iodonium, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, neutral organic fragments and Cu^{2+} ionophore, respectively. (E) Protons and neutral residues generation from bis(4-tert-butylphenyl)iodoniumtriflate with light illumination at 375 nm.

3. Results and discussion

The operation principle of the ISE is illustrated in Scheme 1. Without light illumination, the electrode membrane with the lipophilic salt BTDT-TFPB possesses no ion-exchange properties. The BTDT can decompose to yield protons and neutral residues with light illumination at 375 nm (Scheme 1E), thus leaving the anion

exchanger TFPB⁻ and H⁺ as counterion [29]. Indeed, fluorescence images reveal that acid production inside the membrane can occur within 30 s (Fig. 1). The generation is observed not only on the surface exposed to light but also in the bulk of the membrane. It should be noted that while the surface is active (with fluorescence) even without illumination, the emission intensity will increase with illumination. Meanwhile, the exchange of the photogenerated

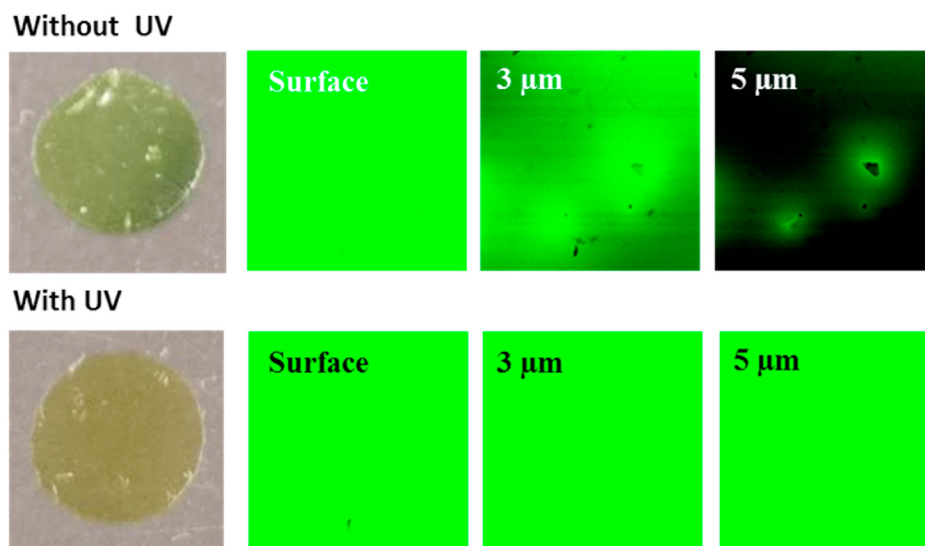


Fig. 1. Photography (Left picture) and fluorescence microscopy images (Right 3 pictures) of the sensing membrane containing the pH indicator dye CH 1 without and with light illumination at 375 nm. The fluorescence of the membrane with different depth was recorded.

protons with the analyte ions should occur to maintain the electroneutrality in the membrane. In the presence of the ionophore, a selective exchange process can be obtained due to the favorable ion-ligand interaction. The target ions (A^+) extracted from the sample solution into the membrane phase can produce a detectable signal, which can be read in the open-circuit potential (zero-current potentiometry mode) or in the coulometric current (constant potential coulometry mode).

For the potentiometric measurement, the light-driven ion extraction can result in a change in the potential of the polymeric membrane electrode. For the constant potential coulometry measurement, the potential of the whole electrode is kept constant during the measurement process. Therefore, the light-controlled potential change can be converted to a current that can be measured. In this way, the constant potential coulometry can be operated in a direct detection mode. It should be noted that since the photolysis of the photoacid generator is an irreversible process [29], the proposed sensor was used only once for coulometric measurement. Reversible sensors can be designed by the replacement of photoacid generator with spiropyran derivatives or metastable photoacid, which are reversible upon UV and visible light irradiation [27,30]. Copper, as an essential trace element for humans and also one kind of toxic heavy metal, was selected as a model analyte [38]. Preliminary experiments using copper ISEs reveal that BTDT cannot react with Cu(II) ions.

The sensor's characteristics using light as a non-invasive stimulus was first evaluated. The typical dynamic potentiometric

response characteristics are shown in Fig. 2. While there is TFPB in the membrane, the counter cation is too hydrophobic to allow for cation exchange with the target ion. Without UV light irradiation, the electrode possesses no ion-exchange properties and cannot induce a Nernstian response for different concentrations of Cu^{2+} . The total voltage change is less than 8 mV from 10^{-6} to 10^{-3} M Cu^{2+} , which may be due to the presence of the anionic impurities. These impurities can work as ion exchangers. Indeed, previous research shows that neutral-carrier-based membranes can show cationic responses in the presence of anionic impurities present in the membrane [39]. Moreover, the co-extraction of Cu^{2+} and anions should result in an obvious potential change at high concentrations (Fig. S3 in the supporting information). Upon irradiation at 375 nm, BTDT can produce hydrophilic protons and neutral fragments. In this case, its ion-exchange properties are restored, resulting in the ISE transform from passive to active states. Indeed, the proposed electrode shows a near-Nernstian response with a slope of 23.1 mV/decade in the range from 10^{-5} to 10^{-3} M. A detection limit calculated as the intersection of the two slope lines is $10^{-5.5}$ M. The non-equilibrium responses may lead to the different magnitudes of potential changes between different concentrations of Cu^{2+} .

Having shown that we can activate the electrode through light-induced ion-exchanger restoration, the light-triggered potentiometric response traces of the ISE were measured in different concentrations of Cu^{2+} . As shown in Fig. 3, a relatively stable OCP can be obtained for different concentrations of Cu^{2+} . The potential-generating mechanism involves perturbation of the surface potential by charge-density changes at the membrane/solution interfaces originating from the release of protons and free counter anion $TFPB^-$ in the membrane. Meanwhile, a gradual exchange of H^+ ions for Cu^{2+} occurred in the presence of the ionophore. Under UV irradiation, there is an obvious potential decrease. When the UV irradiation was turned off, the extraction process, which was driven by the complexation reaction between the ionophore and the target ions, can lead to a potential increase. More importantly, the potential increase is concentration dependent. Indeed, the extraction of Cu^{2+} was verified by fluorescence microscopy using calcein as an indicator. The extraction of Cu^{2+} into the polymeric membrane leads to the decrease of the fluorescence intensity of calcein in the sample solution (Fig. S4 in the supporting information). It should be noted that light intensity could influence the potential stability. Previous report has shown that PEDOT (PSS) is insensitive to room light (~ 150 lx), but were light-sensitive under illumination with intensive light ($\geq 5 \times 10^4$ lx) [40].

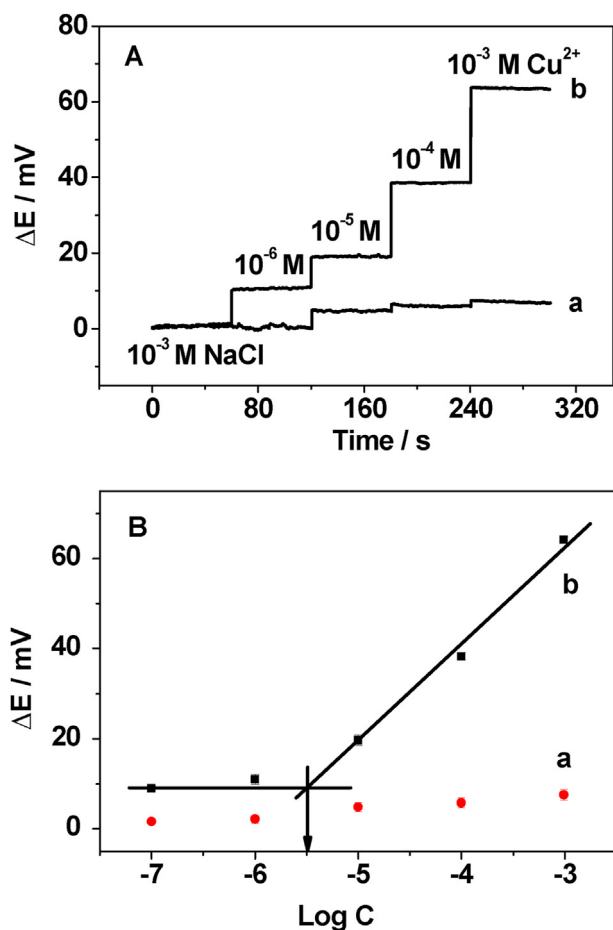


Fig. 2. (A) Potentiometric responses of the light-controlled electrode to varying concentrations of Cu^{2+} before (a) and after (b) light illumination at 375 nm for 30 s. (B) Calibration curves obtained from Fig. 2A. The background solution was 10^{-3} M NaCl.

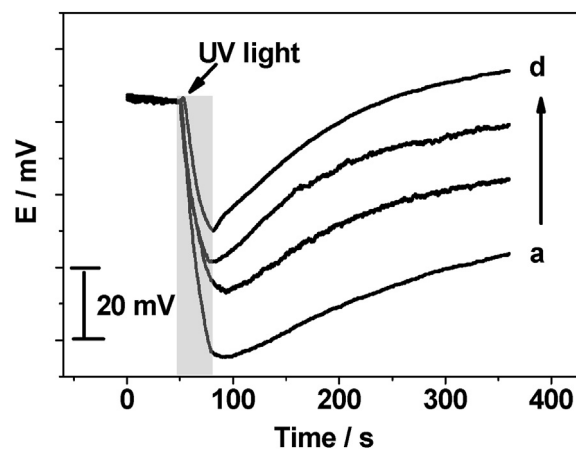


Fig. 3. Time trace of the electrode for (a) 0, (b) 10^{-5} , (c) 10^{-4} , and (d) 10^{-3} M of Cu^{2+} . Light illumination at 375 nm for 30 s. The background solution was 10^{-3} M NaCl. The duration of the UV illumination was highlighted.

While the differences of the OCP before and after the UV illumination could be used as the analytical signal, a sub-Nernstian response with a slope of 15 mV/decade was obtained in the range from 10^{-5} to 10^{-3} M (Fig. 3). For higher concentrations, a suppression of the potential will be observed. Similar phenomenon has been observed in previous research, which may be due to the enhancement of the complex formation between Cu^{2+} and ionophore on the irradiated surface of the membrane [20]. Since the irradiation time determines both the amount of released protons and the ionic sites. An increase in the photoreleased protons favors the exchange of protons with the Cu^{2+} [31]. To eliminate the interference from protons and avoid the deterioration of the selectivity of the electrode, 30 s was selected for the measurements. To avoid sample acidification by H^+ produced within the membrane, the pH of the aqueous phase can be buffered.

These findings, as well as the light-based nature of the potentiometric technique, prompted us to explore its applications for ion sensing based on constant potential coulometry. Previous reports have shown that the changes in ion concentrations (activities) at the sample/membrane interface are required for the constant potential coulometry, which would make the direct determination of target ions virtually impossible with the traditional solid-contact ISEs [35]. Utilizing the light-driven ion extraction of polymeric membranes, direct determination of target ions based on constant potential coulometry can be expected. In this work, the potential was held constant at zero volts. Meanwhile, current-time traces were recorded. Without UV light irradiation, the ion sensor holds in a passive state. Since there is no change in ion concentrations at the sample/membrane interface, the measured current was stable and close to zero. Upon 375 nm irradiation, light-triggered ion extraction leads to the change in ion concentrations at the sample/membrane interface and subsequently the boundary potential between the ion-selective membrane and the sample solution. Indeed, as illustrated above, light-triggered activation of the electrode can result in changes in the membrane potential. Since the potential of the solid-contact ISE is instrumentally kept constant, the boundary potential change will be counterbalanced by the redox conducting polymer-PEDOT/PSS [41]. The transient redox current during the adjustment process can be used as a signal for ion sensing.

As shown in Fig. 4, illumination of the system with UV light resulted in a current increase. The transient current will be observed until a new equilibrium is reached. In the presence of the Cu^{2+} , Cu^{2+} will be extracted into the active membrane to produce a potential increase (as shown in Fig. 3). The transient redox current will decrease due to the smaller potential change. When the concentration of Cu^{2+} is increased, the peak current will decrease (Fig. 4). A linear dependence of charge on logarithm of analyte concentration is observed in the range of 10^{-6} to 10^{-3} M (Coulometric charge = $-4.89 - 2.45 \log C$, $R^2 = 0.981$, the cut time for coulometry is 300 s). In principle, both the coulometric signal and peak current can be used as readout [41]. However, during transition from one equilibrium state to another, the diffusion potential inside the conducting polymer layer and the ion-selective membrane partially make contributions to the transient current. In addition, any electrochemical side reaction taking place at the ISE may contribute to the measured signal. At longer times, oxidation/reduction of the conducting polymer accompanied by the ion transport start to play a role. Moreover, when the UV irradiation is turned off, the current will decrease due to the return of the boundary potential to its initial value. Therefore, a variation of the linear range between the peak current and the Cu^{2+} in the sample solution can be observed. While the detection limit for Cu^{2+} is relatively modest, the proposed electrode shows promise for on-demand sensing or biosensing. Light-triggered ion concentration

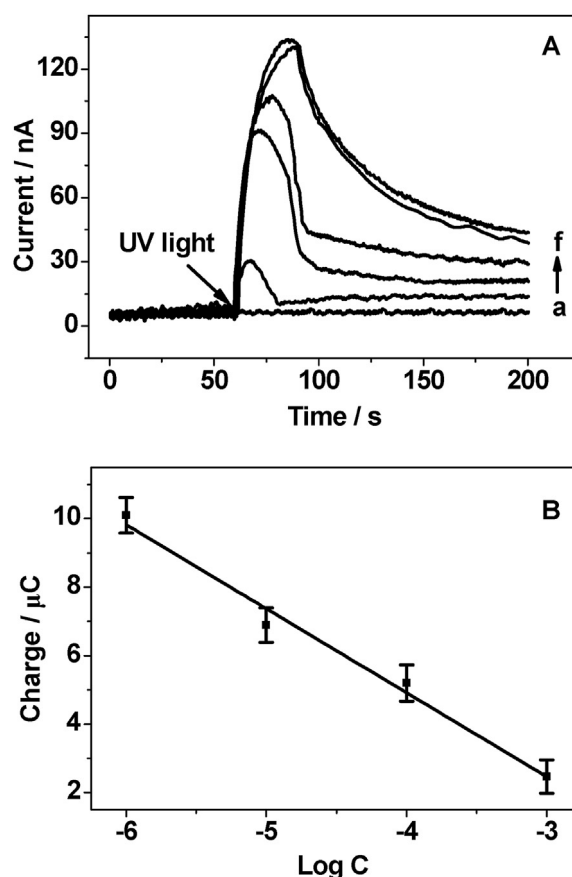


Fig. 4. (A) Current-time trace of the electrode in the absence (a) and presence of light illumination for (b) 10^{-3} , (c) 10^{-4} , (d) 10^{-5} , (e) 10^{-6} , and (f) 0 M of Cu^{2+} . (B) The corresponding calibration curve. Light illumination at 375 nm for 30 s. A constant potential of 0 V was applied on the electrode. Error bars represent one standard deviation of three measurements.

perturbation or modulation may allow one not only to stimulate cellular chemistry but also to measure the processes [42]. Moreover, by selecting new ion-to-electron transducers and optimizing the parameters include the intensity of the UV light and the amount of BTDT-TFPB in the membrane, dynamic ion sensors with improved performance can be expected. The practical applications may include personal health monitoring, environmental monitoring in seawater [43–45].

In order to verify the selectivity of the ion sensor, current-time trace of the electrode for the interfering Ca^{2+} was also investigated. Experiments reveal that the presence of Ca^{2+} cannot lead to a peak current change, which is due to the presence of the highly selective ionophore for Cu^{2+} (Fig. S5 in the supporting information). Indeed, previous research has shown that the selectivity of the polymeric membrane ISE can be enhanced for dynamic sensors [46]. The potential responses of the electrode in different matrixes were investigated. In principle, no obvious potential changes were observed for different matrixes, which may be due to the stable phase boundary potential depending on the lipophilic electrolyte BTDT-TFPB [47]. Experiments reveal that the presence of the anionic impurities can lead to a slight potential shift (data are not shown here).

4. Conclusions

In summary, we have demonstrated that the ion-extraction can be controlled and activated by light illumination at 375 nm. The

light-triggered polymeric membrane ion-selective sensor can be designed for determination of ions with dual-modes sensing. Especially, one may achieve a direct measurement based on the coulometric readout. By incorporation of reversible light sensitive molecules or nanomaterials and using visible light, the proposed dynamic ion sensors show promise for constant potential coulometry. While the selection of proper materials and the optimization of the analytical procedures would be required to achieve measurements with high accuracy, reversibility and reproducibility, the result is encouraging for on-demand ion sensing and ion concentration perturbation.

CRediT authorship contribution statement

Han Zhang: Methodology, Investigation, Data curation, Writing – review & editing. **Lining Liu:** Methodology, Investigation, Data curation. **Longbin Qi:** Investigation, Data curation. **Jiawang Ding:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Wei Qin:** Supervision, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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