Specific Visual-volumetric Sensor for Mercury Ion Based on Smart Hydrogel

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Abstract

On the bases of “seeing is believing” concept and the existing theory of coordination chemistry, we innovatively designed and synthesized a visual-volumetric sensor platform with fluorescein and uracil functionalized polyacrylamide hydrogel for the first time. Without the aid of complicated instruments and any power sources, the sensor enables quantitative detection μM level by reading graduation on a pipette with the naked-eye. The sensor undergoes volumetric response and shows a wide linear response range to (1.0 × 10⁻⁶—5.0 × 10⁻⁵) mol·L⁻¹ of the detection limit. The high selective (easily distinguished from other common metal ions), rapid response (ʒ30min) and acceptable reproducibility (RSD<5% in all cases) demonstrated that the developed sensor is suitable for practical use onsite for the determination of Hg²⁺ while conveniently being low cost, simple and portable. The design principles of the obtained materials and the construction techniques and methods of the sensors in our work provide a new idea for the research and development of smart materials and series of visual-volumetric sensors for other analytes.

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Keywords
Hydrogel|Visual-volumetric| Sensor| Mercury Ion|Coordination

Comprehensive Summary

On the bases of ”seeing is believing” concept and the existing theory of Hg²⁺coordination chemistry, we innovatively designed and synthesized a visual-volumetric sensor platform with fluorescein and uracil functionalized polyacrylamide hydrogel for the first time. Without the aid of complicated instruments and any power sources, the sensor enables quantitative detection μM level by reading graduation on a pipette with the naked-eye. The sensor undergoes volumetric response and shows a wide linear response range to (1.0 × 10⁻⁶—5.0 × 10⁻⁵) mol·L⁻¹ of the detection limit. The high selective (easily distinguished from other common metal ions), rapid response (ʒ30min) and acceptable reproducibility (RSD<5% in all cases) demonstrated that the developed sensor is suitable for practical use onsite for the determination of Hg²⁺ while conveniently being low cost, simple and portable. The design principles of the obtained materials and the construction techniques and methods of the sensors in our work provide a new idea for the research and development of smart materials and series of visual-volumetric sensors for other analytes.

Background and Originality Content

Polymer hydrogel with three dimensional networks that contain a large amount of water in the matrix and possess many specific functional groups in the molecular chains. Similar to the living creatures responding
to environmental changes, polymer hydrogel can undergo multifarious changes such as volume, mechanical, and electrical properties, etc. in response to external stimuli, showing great promise in developing smart materials. Based on the interesting structure and excellent performance, such as remarkable flexibility, softness, superior absorption capacity in their swollen state, nontoxicity, biocompatibility, biodegradability and tunable mechanical properties, polymer hydrogels have been used as superabsorbent materials, for industrial wastewater treatment, to build various of intelligent apparatus and actuators, to control drugs delivery and release, to engineer artificial muscles and tissue. Hydrogels characterized by recognizing and responding specific analytes such as human metabolites, heavy metal ions, anionic species, etc. are promising in the development of multifarious sensors.

Mercury is the only highly toxic heavy metal that can completely circulate in the ecosystem. It can be transferred and transformed in water, soil, atmosphere and biosphere through various ways. Inorganic mercury ions (Hg$^{2+}$) can easily pass through biofilms and may cause damage to the brain, kidney, liver, central nervous system, immune system and endocrine system. More seriously, some lower organisms can also convert Hg$^{2+}$ into more toxic central neurotoxin methylmercury, which accumulates in the human body through the food chain transmission, and causes permanent and irreversible acute or chronic toxic brain damage. Due to the serious harm of Hg$^{2+}$ to the environment and human health, as well as its persistent toxicity and high bioaccumulation and bioamplification effect, even very low concentration of Hg$^{2+}$ will pose a great threat to the environment and human health. Therefore, it is of great significance to develop a mercuric ion detection method with high sensitivity, good selectivity, rapid accuracy and simple operation.

Many reported classical instrumental analysis methods such as atomic fluorescence spectrometry (FL), atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), electrochemical method and inductively coupled plasma mass spectrometry (ICP-MS), etc., have the advantages of high accuracy, wide measurement range and less interference, etc. However, the expensive instruments, professional operators and complex sample pretreatment processes extremely increased the analysis cost and seriously restricts the application of these methods to detect Hg$^{2+}$ in actual samples. In recent years, sensors taken chem-/biomolecules as recognizer to detect Hg$^{2+}$ have attracted wide attention due to their high sensitivity, good specificity, fast response, excellent accuracy and easy operation. A series of chem-/biological sensors on the basis of strong coordination between Hg$^{2+}$ and thymine to form "thymine-Hg$^{2+}$-thymine" (T-Hg$^{2+}$-T) structure showed unique advantages such as high selectivity, good water solubility, and fast response under neutral pH or physiological conditions. Optical sensor and electrochemical sensor are two of the most important of this kind. Although electrochemical biosensors generally have high sensitivity and fast response speed to detect Hg$^{2+}$, usually need to be fixed DNA probe on the electrodes, which increases the complexity of sensor preparation. In addition, non-specific adsorption on the electrode surface may also affect the determination results. On the contrary, visual biosensors are in line with human perception instinct of "seeing is believing", and can conduct direct and reliable qualitative and quantitative analysis of the analytes through "visual" signal changes. Fluorescence sensors with high sensitivity, fast response speed, wide linear range, and short time are the most commonly used optical biosensor, but it is not suitable for field detection of Hg$^{2+}$. Colorimetric sensors based on color changes is another kind of optical biosensor, which has great potential in naked-eye and field detection of Hg$^{2+}$. However, relatively low sensitivity limited by color vision difference usually make it is difficult to accurately quantify and generally be used for qualitative or semi-quantitative analysis. Compared with fluorescence sensor and colorimetric sensor, volume sensor, another type of visual sensor, is more in line with human’s perception nature of "seeing is believing", and can detect specific analytes by measuring the volume changes. However, there is no specific visual-volumetric sensor for Hg$^{2+}$ has been reported until now.

Here we present a promising, sophisticated hydrogel-based visual-volumetric sensor, capable of detecting Hg$^{2+}$ with naked-eye readout based on our previous work and the basis of strong coordination between Hg$^{2+}$ and uracil to form "U-Hg$^{2+}$-U" complex structure that similar with "T-Hg$^{2+}$-T". The working principle of our hydrogel sensor is shown in Scheme 1.
**Scheme 1** Schematic diagram of the visual-volumetric response principle of the fluorescein and uracil functionalized polyacrylamide hydrogel to Hg$^{2+}$ in 0.01 mol $\cdot$ L$^{-1}$ pH=7.4 PBS buffer solution (A), and Photographic images of the hydrogel sensor and its responses to Hg$^{2+}$ ranging from 0 to 50 μM in 0.01mol $\cdot$ L$^{-1}$ pH=7.4 PBS buffer solution(figures in red), which can be quantitatively distinguished by the naked eye (B).

Results and Discussion

**Composition and characteristics of the stimuli-responsive hydrogel**

In the 3D network of the designed polyacrylamide hydrogel, there are a certain amount of fluorescein and uracil units covalent-bonded to the molecular chains acted as dyes for indicator and specific recognizer for Hg$^{2+}$, respectively (see Fig. S1). The dry hydrogel powder (80~120 mesh) was light yellow under natural light and bright yellow under ultraviolet light (Fig.1A). The fully swelled hydrogel in water was also different colour under natural and UV light (Fig. 1B). The excitation and emission spectra of the dry hydrogel and that of the fully swelled hydrogel shows a maximal excitation and emission wavelength at 472 nm/537 nm (Fig.2A) and 467 nm/534 nm (Fig.2B), respectively. The good color and fluorescence properties providing the excellent indication capability for the volume change of the obtained hydrogel.
Fig. 1: Dry hydrogel (up) under natural (left) and 365 nm ultraviolet light (right) (A), and Fully swelled hydrogel (down) under natural (left) and 365 nm ultraviolet light (right) (B)

Fig. 2: Excitation and emission spectra of the dry hydrogel (A) and, and Excitation and emission spectra of the fully swelled hydrogel (B)

The 3D network structure confers the capability of absorbing and storing water, which provide the swelling and shrinkage performance of the designed polyacrylamide hydrogel. The average volumetric swelling rate is 3933 %, which demonstrated sufficient swelling and shrinkage capacities, one of the key to fabricate our visual-volumetric sensor (Table 1)

<table>
<thead>
<tr>
<th>Test number</th>
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<th>2</th>
<th>3</th>
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<td>Volume of the dry hydrogel /V_0 (μL)</td>
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<td>100</td>
<td>100</td>
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<tr>
<td>Volume of the swelling hydrogel /V_1 (μL)</td>
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<td>4030</td>
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<tr>
<td>Swelling rate / S_R (%)</td>
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<td>3950</td>
<td>3930</td>
</tr>
<tr>
<td>Average swelling rate / S_R (%)</td>
<td>3933</td>
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Bisection of the fully swelling fluorescent hydrogel particles are filled into two 10 mL measuring cylinders. A clear interface between hydrogel and water is formed after standing for a while and then take the photographs under ultraviolet light at 365 nm. Transferring the mixture in the measuring cylinders to two beakers, respectively. Thereafter, 10 mL 0.0 × 10^{-4} mol L^{-1} NaCl solution and 10 mL 2.0 × 10^{-4} mol L^{-1} Hg(NO_3)_2 solution was added. After 30 min stirring followed by standing, all the hydrogel particles and parts of the salt solution was transferred into the original measuring cylinders with the aid of a drip pipe and syringe. Take the photographs under ultraviolet light at 365 nm again (Fig. S4). The experimental results show that the hydrogel's macroscopic volume shrinkage has nothing to do with ionic strength but caused by Hg^{2+} indeed.

Sensing mechanism

There are a lot of uracil covalently linked to the molecular chains of the obtained fluorescent hydrogel by an amide bond. The similar molecular structure makes a strong coordination between Hg^{2+} and uracil to form "U-Hg^{2+}-U" complex like the reported "T-Hg^{2+}-T" structure[92], which leads to microscopic curl of the molecular chains to aggregation, subsequent macroscopic volume shrinkage coupled with water drainage. The assumption verified by SEM investigations on the hydrogel micromorphology in the absence and presence of Hg^{2+}. The SEM photos of the water swelled and freeze-dried hydrogel display a discontinuous porous structure with an average pore size of about 10 μm (Fig. 3A). After interaction with 1.0 × 10^{-4} mol L^{-1} Hg^{2+}, the hydrogel dramatically shrinks its porous network and displays a stacking structure (Fig. 3B). The "U-Hg^{2+}-U" coordination complex formation is the enabler for the volume shrinkage that linear correlated with the Hg^{2+} concentration, which lays a foundation for the construction of our visual-volumetric sensor.
Fig. 3 SEM plots of the freeze-dried fully swelled hydrogel (A), and the hydrogel that immersed in $1.0 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$ $\text{Hg(NO}_3\text{)}_2$ solution for 20 min (B)

Construction of the sensor

Take the good materials in hand, a similar visual-volumetric sensor as reported in our previous work is built, all the procedures for sensor preparation and detection are the same as before. The volume changes were also recorded with the aid of the green fluorescent colour and pipette graduation marks. Similar construction makes the similar visual errors and acceptable precision for quantitative analysis, which offers the possibility of detecting $\text{Hg}^{2+}$ without external or other power sources.

Analytical characteristics index of the sensor

It is the common pursuit of general analytical methods in excellent selectivity, high sensitivity, good reproducibility and wide linear range. The selectivity of our visual-volumetric sensor toward $\text{Hg}^{2+}$ and other common metal ion solutions of the same concentration include $\text{Ag}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, $\text{Mn}^{2+}$, $\text{Ni}^{2+}$, $\text{Cd}^{2+}$, $\text{Al}^{3+}$, $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$ is shown in Fig. 4. In comparison to the volume response for $\text{Hg}^{2+}$, other common metal ions caused only slight or negligible volume responses. That is to say, with the help of our sensor, $\text{Hg}^{2+}$ can be distinguished from other common metal ions by naked-eye observation. Such selectivity towards $\text{Hg}^{2+}$ matches that of reported "T-Hg-T" sensors.

Fig. 4 Selectivity properties of the sensor. The concentration of all the metal ions are $5.0 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$

In addition to the excellent selectivity, our sensor can also sensitively detect $\text{Hg}^{2+}$ by measuring the hydrogel volume decrease in a wide range of concentrations with the linear range from $1.0 \times 10^{-6} \text{mol} \cdot \text{L}^{-1}$ to $5.0 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$ and $2.8 \times 10^{-7} \text{mol} \cdot \text{L}^{-1}$ of the detection limit according to the IUPAC recommendation (Fig. 5).

Fig.5 The response curve of the sensor to $\text{Hg}^{2+}$ (0.5 ~ 500 μM). The inner illustration shows the linear relationship between hydrogel volume decrease value and $\text{Hg}^{2+}$ concentration.

With regard to sensor reproducibility, three concentrations of $\text{Hg}^{2+}$ the linear range showed less than 5% relative standard deviation ($n=7$) that is typically acceptable for quantitative detection (Fig. 6).

Fig.6 The reproducibility of the sensor for $\text{Hg}^{2+}$ determination

Conclusions

Here, we developed a specific visual-volumetric sensor for quantitative detection of $\text{Hg}^{2+}$ that is convenient, elegant, and power-free. The sensor was developed from a macroporous fluorescent hydrogel with a designed recognition group and fluorescence indicator in the 3D networks, which assured the high selective, sensitive and proportional volume response to $\text{Hg}^{2+}$. Experiments demonstrated the analytical characteristics including excellent selectivity, high sensitivity, good reproducibility, and acceptable linear range of
our sensor. Our design for the first time offered direct volumetric quantification of Hg^{2+} without the aid of instruments. The selectivity for Hg^{2+} springs from design rather than the results of screening, which opened an avenue of stars for consciously developing more analytes stimuli-responsive materials. With more analytes stimuli-responsive materials in hand, together with the platform established here, series cheap portable visual-volumetric sensors can be expected in the future.

Experimental

Apparatus

Identification of the mentioned chemical is conducted by an electrospray ionization mass spectrometer (ESI-MS, MAXIS, Bruker). The morphology of the hydrogel is evaluated by a emission scanning electron microscopy (SEM, Quanta 200, FEI Company) operated at 200 kV. FL spectra were measured with a fluorescence spectrometer (FL-960, Tianmei Instrument Co., Ltd., China). Photographs are taken by a mobile phone camera.

Materials

Acrylamide (99.5%) were purchased from Shanghai Rhawn Reagent Co. Ltd. Methylene diacrylamide (99.5%) were purchased from Shanghai Yuanye Bio-Technology Co. Ltd. Sodium sulfide hydrate (Na_{2}S \cdot 9H_{2}O) were purchased from Tianjin Tianli Chemical Reagent Co. Ltd. Resorcinol, 4-nitrophthalic acid (98%), acryloyl chloride (96%, with 200 ppm MEHQ stabilizer), 6-amino-uracil(98%), polyethylene glycol-6000 (PEG-6000), etc. raw materials and auxiliaries, hydrochloric acid (HCl), acetic acid (HAc), sodium hydroxide (NaOH), sodium hydrosulfide hydrate (NaHS \cdot xH_{2}O, 68-72%), zinc chloride (ZnCl_{2}), potassium persulfate (K_{2}S_{2}O_{8}), mercuric nitrate [Hg(NO_{3})_{2}], sodium bicarbonate (NaHCO_{3}), and sodium chloride (NaCl), etc. conventional acid, base and salt were analytical reagents and purchased from Shanghai Macklin Biochemical Co., Ltd. N, N-dimethylformamide (DMF, 99.5%), ethanol (EtOH, 99.5%), etc. organic solvent were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were used without any further purification and all water was deionized water.

Synthesis of the fluorescent hydrogel

Synthesis of the hydrogel include two steps: (1) Preparation of the functional monomers 5-acrylamido-fluorescein and 6-acrylamino-uracil[63]; (2) Preparation of the fluorescein and uracil functionalized polyacrylamide hydrogel via atom transfer radical polymerization (ATRP):

Preparation of 5-acrylamide fluorescein: To a 50 mL flask, 1.39 g (4.0 mmol) home-made 5-amino-fluorescein (synthesized according to the literature[64], M=347.33 g.mol^{-1}) was dissolved in 8 mL anhydrous DMF, and then 0.50 g NaHCO_{3} (6.0 mmol, M=84.01 g.mol^{-1}) solid was added into the solution under vigorous stirring in ice bath. After cooling the mixture to 0-5 , 0.4 mL acryloyl chloride (4.8 mmol; 96%, containing 200 ppm MEHQ stabilizer, ρ=1.12 g.mL^{-1}, c=11.9 mol.L^{-1}, M=90.5 g.mol^{-1}) was added drop by drop (finished about 30 minutes) under stirring, then, removing the ice bath and stirring the reaction mixture at room temperature for another 1h. Finally, poured the reaction mixture into 40 mL 0.1 mol.L^{-1} HCl solution, filtering under reduced pressure, washing the filter cake with a small amount of ice water and drying it in vacuum to constant weight, 1.26 g 5-acrylamide fluorescein was obtained as a reddish-brown solid in 78.6% yield. MS(ESI^+): m/z[C_{25}H_{16}NO_{6}^+] = 402.0969 [M+H], cal. m/z[C_{25}H_{16}NO_{6}^+] = 402.0972 (Fig. S3)

Preparation of 6-acrylamino-uracil: To a ceramic mortar ( =9 cm), 1.30g 6-amino-uracil (10.0 mmol, Mr=127.10), 1.30 g NaHCO_{3} (15.0 mmol) and 10.0 mL anhydrous DMF was added. After fully grinding, the mixture was transferred into a 100 mL dry round-bottomed flask. The mixture was cooled in ice bath to 0-5 under vigorous stirring, and then, 1.0 mL of acryloyl chloride (12.0 mmol; 96%, containing 200 ppm MEHQ stabilizer, ρ=1.12 g.mL^{-1}, c=11.9 mol.L^{-1}, M=90.5 g.mol^{-1}) was added drop by drop (finished about 30 minutes). Thereafter, removing the ice bath and stirring the reaction mixture at room temperature for another 1h. Finally, poured the reaction mixture into 40 mL 0.1mol.L^{-1} HCl solution and stewed the obtained mixture for 30 min, and then filtered under reduced pressure. Washing the filter cake with a small
amount of ice water and drying it in vacuum to constant weight, 1.0 g of pale yellow solid was obtained in 55% yield. The product was directly used for further synthesis without separation.

Preparation of the fluorescein and uracil functionalized polyacrylamide hydrogel: The synthetic method based on our previous work but slightly modification[3,4]. Typically, acrylamide 7.10 g (0.1 mol), 5-acrylamido-fluorescein 0.04 g (0.1 mmol), 6-amino-uracil 0.15 g (0.83 mmol), N, N'- methylenediacrylamide 0.09 g (0.6 mmol), potassium persulfate (KPS) 0.14 g (0.5 mmol) and 0.94 g PEG-6000 were added to 150 mL water in 250 mL clean beaker, fully stirring followed by a water bath of 65 for 2 h, a hydrogel with strong fluorescence was obtained. Thereafter, soaking the hydrogel in 600 mL of anhydrous ethanol and when its volume completely shrinking, pouring the upper clear liquid away. After that, 150 mL water was added to the obtained solid, which completely swelling to hydrogel again. The the newly formed hydrogel was precipitated and rinsed again with 600 mL ethanol. The above operations were alternatively conducted for 2~3 times in order to remove the unreacted impurities until the supernatant was colourless. Finally, cleaned the shriveled hydrogel with anhydrous ethanol for 3~4 times and then dried it in vacuum oven at 50 to constant weight, 6.93 g orange solid product in 92.4% yield was obtained, which was used to constructed the sensor after grinding to proper size.

The synthetic route and structure of the smart fluorescent hydrogel are listed as Fig. S1 and Fig. S2 in supporting information.

Characterization assays

The dry hydrogel powder (80˜120 mesh) and the fully swelled hydrogel were photographed under natural and ultraviolet light to show its fluorescence properties. The morphologic structure of the obtained hydrogel particles were analysed with scanning electron microscope (SEM). Swelling rate is directly related to the sensing properties of the obtained hydrogel. To test the volume swelling rate, the initial volume of a certain quality of dry hydrogel particles ($V_0$) was determined by extruding anhydrous ethanol in a calibrated graduated pipette, and then immersed the above dry hydrogel in 0.01 mol • L$^{-1}$ pH=7.4 PBS buffer solution to the full swelling. Absorbed the excessive water by filter paper and measured the volume again ($V_1$) to calculate the swelling rate ($S_R$) with the following formula:

$$S_R = \frac{V_1 - V_0}{V_0} \times 100\%$$

Construction of the sensor

The sensor is constructed by a 5.0 mL calibrated graduated pipette that 80 holes (0.8 mm in diameter) were uniformly sculpted in the wall using a laser and with a minimum graduation of 50 μL. To prevent the leakage of the hydrogel from the bottom, a piece of cotton was placed at the pipette mouth. As a result, fully swelled hydrogel particles remain in the pipette and water could easily penetrate in or out of the holes.

Sensor preparation and sample measure procedures

According to the method reported in the literature[3,4], the sensor preparation and sample measure procedures are described as follows: the dried hydrogel was ground into 80˜120 mesh particles and immersed it in 0.01 mol • L$^{-1}$ pH=7.4 PBS buffer to the full swelling. With the aid of a drip pipe, the swelled hydrogel was transferred into a 5.0 mL calibrated graduated pipette that described above. By vibrating the pipettes up and down continuously to ensure the swelled hydrogel particles were closely packed until the initial volume readout was 0.00 mL. In this process, filter paper is used to remove the water drained from the micropores in the pipette wall. The prepared sensor was immersed in 100 mL PBS buffer solution for 30 min, and the same operation was repeated to ensure that the hydrogel volume was restored to 0.00 mL, and the preparation of the sensor was completed. When measuring the actual sample, it is only necessary to place the prepared sensor in the measuring cylinder containing 100 mL sample solution (volume 100 mL) for 30 min, then take out the sensor and vibrate slightly up and down as described above and remove the discharged water in the pipette wall with filter paper. After 10 min of vibration, the volume shrinkage can be clearly seen by
naked-eye and record the contraction volume of the hydrogel. Different concentrations of Hg$^{2+}$ solution were tested following the same procedure.

**Selectivity, sensitivity and reproducibility of the sensor**

To evaluate the selectivity of our volumetric sensor towards Hg$^{2+}$, several pieces of 80~120 mesh dry hydrogel particles of the same weight were fully swelled with 0.01 mol $\cdot$ L$^{-1}$ pH=7.4 PBS buffer and fabricated to series of hydrogel sensors as described in section 2.4. Thereafter, soak these sensors in the 100 mL Hg$^{2+}$ solution and other common metal ion solutions of the same concentration include Ag$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Al$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$, respectively for the same time in a certain temperature. After no liquid oozing, the volume shrinkage of the hydrogel in the sensors were read out with naked-eye to evaluate the selectivity of the prepared sensor.

To investigate the sensitivity of our sensor towards Hg$^{2+}$, soak the prepared sensors in the 100 mL Hg$^{2+}$ solutions of various concentration and read out the volume shrinkage of the hydrogel in the same way.

To examine the reproducibility of the prepared sensor, replicate measurements were performed with $1.0 \times 10^{-6}$ mol $\cdot$ L$^{-1}$, $1.0 \times 10^{-5}$ mol $\cdot$ L$^{-1}$ and $5.0 \times 10^{-5}$ mol $\cdot$ L$^{-1}$ of Hg$^{2+}$.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2023xxxx.

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iso-luminol-SCN

Other Metal ions + H₂O₂ \rightarrow \text{Weak Chemiluminescence}

Fe^{2+} + H₂O₂ \rightarrow \text{Strong Chemiluminescence}
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