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Visual Detection of Thiocyanate Based on Fabry–Perot Etalons with a Responsive Polymer Brush as the Transducer

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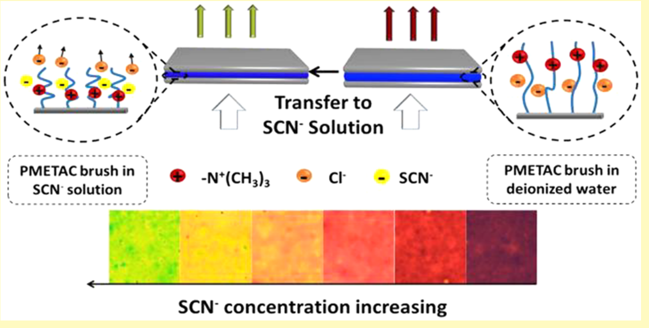
ABSTRACT: The detection of thiocyanate (SCN^-) is particularly important in industrial effluents and biological fluids because of the toxic nature of SCN^-. Herein, a metal–insulator–metal (MIM) resonator for visual detection of SCN^- is presented based on a poly[(2-(methacryloyloxy)ethyl) trimethylammonium chloride] (PMETAC) brush. The MIM resonator exhibits obvious color change as the concentration of SCN^- changes, which can be easily distinguished by the naked eyes. In addition, the as-prepared MIM resonator also shows the advantages of good anti-interference, excellent reusability, and fast response rate. Combining the above advantages, the proposed MIM resonator may provide a broad perspective for a wide variety of visible-light applications.



KEYWORDS: *Fabry–Perot etalons, polymer brush, SCN^- sensor, naked eye detection, MIM resonator*

It is of great significance to detect SCN^-, since it is harmful to human health. SCN^- exists widely in industry waste, and it is also considered to be a biomarker for distinguishing smokers from nonsmokers.[1,2] So far, various methods, such as chromatography,[3] spectroscopy,[4] and electrochemistry,[5] have been used to detect SCN^-. However, all these testing methods require expensive instruments and complicated preparation processes. This not only increases the overall cost, but also is time-consuming. Meanwhile, some testing methods may also use toxic substances, causing secondary pollution. Therefore, it is quite desirable to develop a simple, economical, rapid, and environmentally friendly method for detecting SCN^-.

For decades, visual detection has drawn great attention because it does not require complex instruments and cumbersome means to achieve detection.[6−9] Recently, metal microstructures have been considered as potential candidates for visual detection, owing to their excellent capability to confine and manipulate electromagnetic waves at the nanoscale.[7,10] However, most of these microstructures require electron beam lithography, for which the manufacturing steps are complicated. The lithography-free metal–insulator–metal (MIM) resonator[3,11−13] based on the Fabry–Perot etalon is an excellent structure in metal microstructures because its manufacturing process is simple and time-saving. In particular, the optical properties of the MIM resonator can be easily manipulated by adjusting the physical parameter of the intermediate layer.[4,14] Therefore, it would be a feasible strategy to achieve visual detection for SCN^- by introducing an intermediate layer with a specific response for SCN^- to the MIM cavity.

Herein, a novel MIM resonator with an anion responsive layer (poly[2-(methacryloyloxy)ethyl] trimethylammonium chloride, PMETAC) as an intermediate layer was reported for visual detection of SCN^-. The as-prepared MIM resonator displays evident color change in different concentrations of SCN^- solutions, which can be observed by the naked eye. Furthermore, the as-prepared MIM resonator also shows various advantages such as good anti-interference, excellent repeatability, and rapid response rate. Together with these outstanding features, the proposed detection strategy may provide new insights for visually detecting SCN^- and also help further explore optical devices based on MIM resonators and other species of polymer brush.

A schematic diagram of the preparation processes and the detection principle of the as-prepared MIM resonator are shown in Figure 1. Briefly, a layer of silver is first deposited on the glass substrate. Subsequently, the PMETAC brush was then prepared on the bottom silver layer via surface-initiated Cu(0)-mediated controlled radical polymerization (SI-CuCRP), and the thickness of PMETAC could be well controlled.[15,16] Finally, another layer of silver was evaporated

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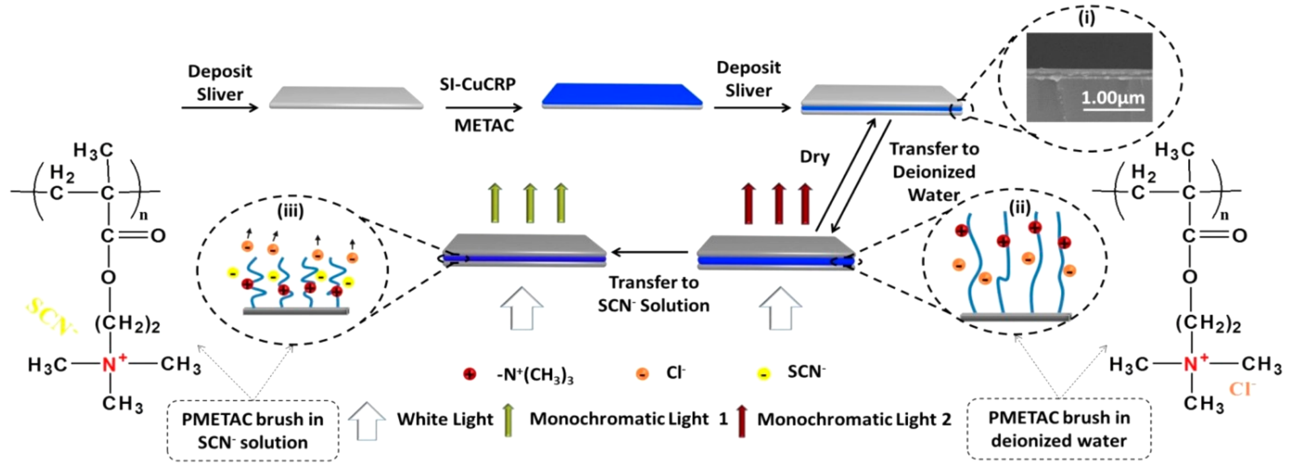

Figure 1. Schematic diagram of the preparation process and the detection principle of the as-prepared MIM resonator. Insets show the cross-sectional SEM image of the MIM resonator (i) and the conformation of PMETAC chain in deionized water (ii) and electrolyte solution (iii).

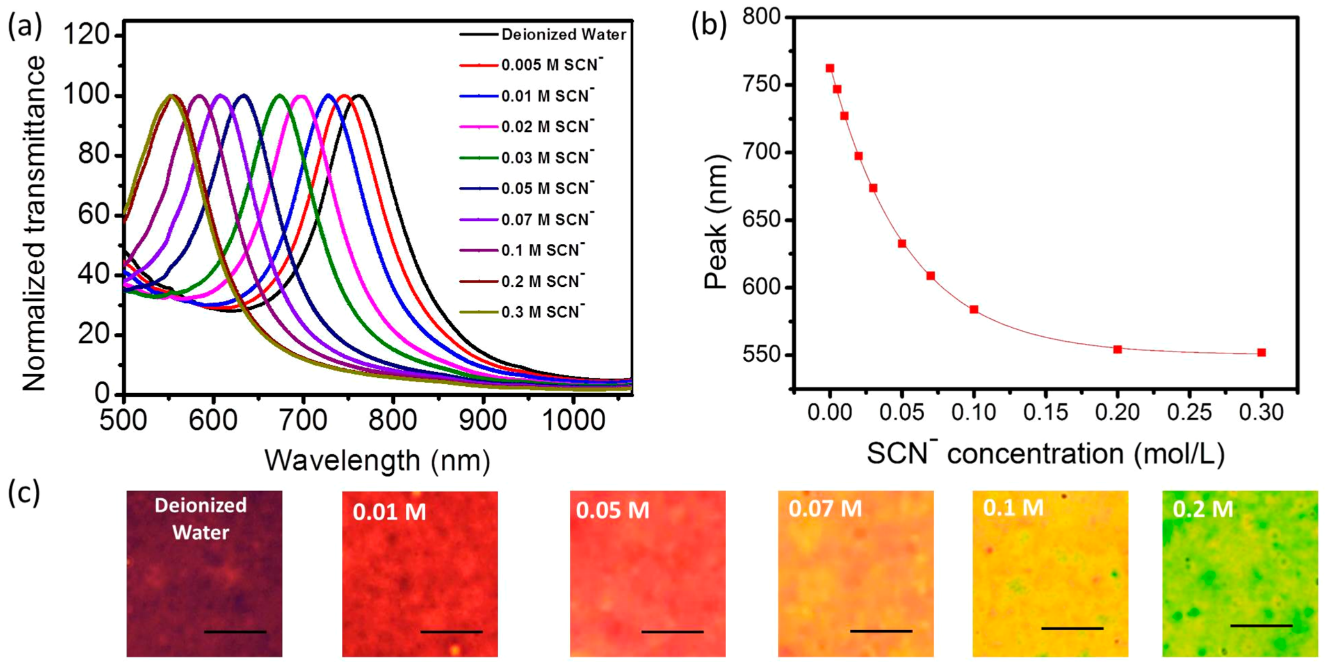

Figure 2. (a) Transmittance spectra of the as-prepared MIM resonator in different solutions. (b) Relation curve between the shift of the peak and the concentration of the SCN^- solutions. (c) Optical photographs of the as-prepared MIM resonator in different concentrations of SCN^- solutions (the bar is 10 μm).

onto the polymer brush to construct the MIM resonator. Consequently, the as-prepared MIM resonator is obtained with sandwich construction, which is clearly shown in its cross-sectional SEM image (Figure 1, inset (i)). Since the optical property of MIM resonator depends closely on the physical parameter of the intermediate layer, the optical appearance of the as-prepared MIM resonator will undergo a corresponding evolution as the refractive index and physical volume of PMETAC brush change during the conformation transition under different conditions.[14,17−21] In general, the chemical nature of the counterions shows great influence on the conformation of PMATAC. When the MIM is placed in deionized water, the PMETAC chains containing Cl^- as counterions exhibit a strongly stretched conformation because of the force of electrostatic repulsion and volume exclusion effects.[22] Other counterions like Br^-, CO_3^{2-}, NO_3^-, and SCN^- can exchange with Cl^- anions to form hydrophobic ion pairs. Among all of these hydrophobic ion pairs, only the SCN^--based ion pairs exhibit a greatly strong hydrophobic character. Hence, the conformation of PMETAC chains will show a greater collapse when the as-prepared MIM resonator is put into the SCN^- solution compared with that in solution of other ions. Consequently, the as-prepared MIM shows different optical performance against SCN^-, and the naked eye detection of SCN^- can be achieved.

Quantitative detections were performed by recording the transmission spectra of the as-prepared MIM resonator. As shown in Figure 2a, the transmission peak blue shifted from 756 to 560 nm when the concentration of SCN^- increased from 0.005 to 0.3 M. It is worth noting that only a slight peak shift was observed as the concentration of SCN^- increased from 0.2 to 0.3 M, implying the maximum detection limit for

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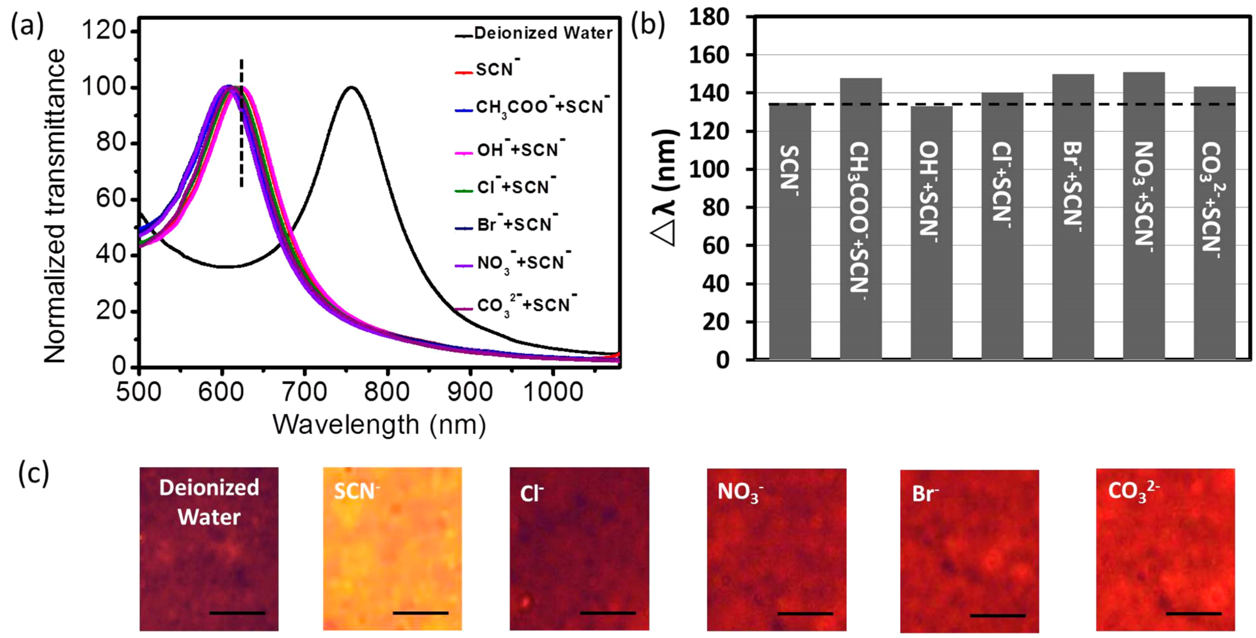

Figure 3. (a) Transmittance spectra of the as-prepared MIM resonator in water, SCN^-, and mixtures of SCN^- and disturbing anions. (b) {eak of the as-prepared MIM resonator for detecting SCN^- in different solutions and water. (c) Photographs of the as-prepared MIM resonator in different anion solutions (the bar is 10 μm).

SCN^- is 0.2 M. This is because the combination of SCN^- and the positively charged trimethylammonium chloride group is saturated, so excessive SCN^- cannot make the PMETAC brush continue to collapse. The relation curve between the shift value of the peak and the concentration of SCN^- solutions is shown in Figure 2b: the peak position shift value changes significantly from 0.005 to 0.2 M while it becomes less significant from 0.2 to 0.3 M. As the transmission peak blue shifts for ~200 nm in visible region, the as-prepared MIM resonator shows different colors simultaneously in different concentrations of SCN^- solutions; a few representative optical photographs are shown in Figure 2c. The color of the resonator changes from fuchsia to yellow-green, which can be distinguished by the naked eye directly, indicating that the MIM resonator can act as a sensor for visual detection of SCN^-.

As an ion sensor, anti-interference is an important parameter to evaluate the applicability of the as-prepared MIM resonator in deionized water, SCN^- solution, and mixtures with other disturbing anions. The transmission spectra measured in all the other mixed solutions almost overlap with that measured in the SCN^- solution as shown in Figure 3a. There is no significant difference in the peak value between these transmission spectra, indicating that other disturbing anions show little influence for the detection of SCN^-. The peak shift ($\Delta\lambda$) in different solutions with respect to water is shown in the histogram in Figure 3b. It could be seen that the values of the peak shifts are close, intuitively indicating good anti-interference performance of the as-prepared MIM resonator for detecting SCN^-. In order to further demonstrate the anti-interference of the as-prepared MIM resonator for detecting SCN^-, the resonator is separately immersed in different solutions containing only one kind of anion. The optical photographs were captured and are shown in Figure 3c. The resonator displays as orange in SCN^- solution and can be easily distinguished by the naked eye from deionized water. By contrast, the resonator shows negligible color change in other anion solutions. The color changes in SCN^- solution with different concentrations are obvious compared with those in other anion solutions with different concentrations (Figure S1), once again demonstrating the excellent anti-interference performance of the as-prepared MIM resonator relative to other anions.

Besides the anti-interference performance, the repeatability and response rate are also very important for detection application. The repeatability of the as-prepared MIM resonator is evaluated by alternately immersing it in SCN^- solution and deionized water. As shown in Figure 4a, the transmission peak position of the as-prepared MIM resonator shows a reversible conversion with little offset during 50 cycles, suggesting that the resonator possesses good repeatability. The main reason behind it is due to the unique structure of the middle polymer brush layer. Compared with a cross-linked film, the PMETAC brush is firmly grafted onto the Ag layer through covalent bonds, which is beneficial to improve the repeatability of the MIM resonator. The response time is another important factor to evaluate the performance of the as-prepared MIM resonator. As shown in Figure 4b, as the external environment changes, the transmission peak shifts and reaches a balanced and steady state after no more than 1 s (260 ms from deionized water to SCN^- solution and 200 ms from SCN^- solution to deionized water). The response rate and recovery rate are also faster than those of other responsive materials based on a bulk cross-linked polymer film because the movement of polymer brush chains is more flexible and the conformation change is much easier without the limitation of cross-linked networks, which causes the PMETAC brush to respond rapidly against external environmental change.

In conclusion, a sensitive MIM resonator based on a PMETAC brush for visual detection of SCN^- was successfully constructed. First of all, the as-prepared MIM resonator shows various colors in different concentrations of SCN^- solution which can be observed by naked eyes. In addition, it exhibits

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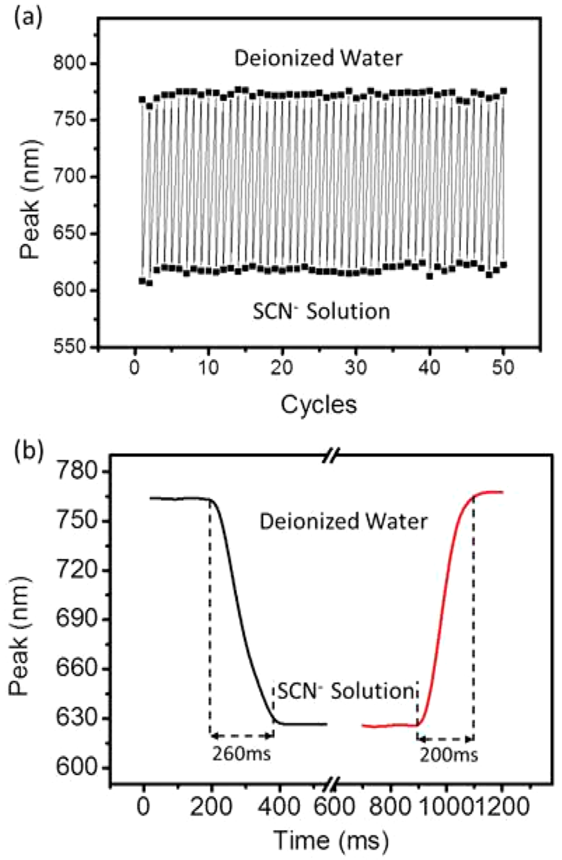

Figure 4. (a) Detecting cycles of the resonator between deionized water and SCN^- solution. (b) Peak position against time of the as-prepared MIM resonator as the external environment changes.

excellent anti-interference and selectivity in the presence of disturbing ions. The detection process is fast, and repeatability is perfect. Considering the visible read-out, outstanding optical properties, and easy detection process, the as-prepared MIM resonator for detecting SCN^- will show enormous potential for sensing applications in the chemical and biological fields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssensors.9b02270.

Materials; preparation of the poly[2-(methacryloyloxy)-ethyl] trimethylammonium chloride (PMETAC) brush metal−insulator−metal (MIM) resonator; characterization and optical measurement (PDF)

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Notes

The authors declare no competing financial interest.

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