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Hydro gel light-guiding conjunction for absorptive type multi-ions detection

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ABSTRACT

We present a novel miniaturized solid state sensor produced by embedding two optical fibers in a sensing hydro gel conjunction. The conjunction is a poly (2-hydroxyethyl methacrylate) (poly HEMA) hydro gel mixed with two kinds of selective fluorescent probes. Meso-2,6-Dichlorophenyltripyrrinone (TPN-Cl2) is used to react with zinc ion (Zn^{2+}) and the synthesized "Chemosensor **1**" is used to detect ferric ion (Fe^{3+}). This hydro gel conjunction can serve as a light-guiding waveguide that allows light signals to transfer between two fibers. By using a multi-wavelength excitation light, a mixed solution that contains Zn^{2+} and Fe^{3+} can be detected in real-time. This miniaturized sensor develops an image for real-time monitoring of Zn^{2+} and Fe^{3+} ions *in vivo*.

1. Introduction

A transition metal is an indispensable element to regulate normal physiological functions. In the last few decades, considerable effort has been given to developing various methods to detect these metal ions. Despite the fact that the field-effect transistor (FET) has attracted considerable attention in the electrical biosensing field [1–3], using fluorescent characteristics of specific materials is the most common means of detecting metal ions [4–6]. These probes absorb light signals with specific wavelengths and emit fluorescent light. Most of these fluorescent sensors have not been applied to solid state devices. Despite photoluminescence or absorption spectrometers being indispensable in analyzing light signals, solid state sensors require a minimum size for applications *in vivo*. Simultaneously, light signals should also be adequate to stimulate a sufficiently large sensing signal to be collected by the analyzer. To overcome this challenge, some solid state sensors that employ light guiding functions have been demonstrated [7–9]. However, a sensor that can detect different metal ions simultaneously has not been demonstrated. In this study, we propose a multiple metal ion sensing system with a light-guiding structure. The light-guiding conjunction that serves as a waveguide is produced by a hydro gel sensing film and double fibers. The excitation light signal is guided into the sensing film and absorbed by probes that are sensitive to metal ions. With a higher concentration of metal ions, the probe absorption becomes stronger and the output sensing signal becomes lower. Among all transition elements, ferric ion (Fe^{3+}) and zinc ion (Zn^{2+}) are both essential to many biological and biochemical processes in humans. Fe^{3+} not only plays a major role in many biochemical processes at the cellular level but also acts as a potential catalyst in many chemical reactions [10,11]. Irregular concentration of Fe^{3+} has also been associated with many diseases [12–14]. Zn^{2+} also plays a vital role in physiology functions and is a structural component of proteins [15,16]. Irregular Zn^{2+} metabolism is associated with many brain diseases [17,18]. To detect Fe^{3+} and Zn^{2+}, synthesized *meso*-2,6-Dichlorophenyltripyrrinone (TPN-Cl_2) and Chemosensor **1** are used as sensing probes [9,19]. In addition, we develop a structure to

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provide different wavelength light sources to the sensing system. By combining the hydro gel light-guiding conjunction and multi-wavelength excitation light, we can detect multiple metal ions simultaneously. This real-time sensing system is portable, cheap, and has the potential to detect multiple ions inside the living body in future.

2. Experiments

2.1. Hydro gel solid film

The Fe^{3+} ion sensing probe was designed and synthesized by the reaction of 2-(N-methylpiperazinylimino)acetaldehyde and rhodamine B, and named Chemosensor **1** [19]. Meso-2,6-Dichlorophenyltripyrrinone (TPN-Cl_2) was chosen as the fluorescent zinc ion probe [9]. Poly (2-hydroxyethyl methacrylate) (300 kDa, poly HEMA, Sigma-Aldrich) was dissolved in dimethylformamide (DMF, SigmaAldrich) with a mass ratio of 3:7. TPN-Cl_2 or Chemosensor **1** was mixed with poly HEMA solution with a mass ratio of 1:2000. The mixed solution was stirred and annealed at 80 °C for 12 h. To form a solid film, the solution was annealed on a Teflon mold at 80 °C for 12 h.

2.2. Double fiber system

For the double fiber sensing system, a special Teflon mold with two small holes on the opposite sidewalls was applied as shown in Fig. S1(a). The solid sensing film served as a waveguide connecting two glass fibers, which are the excitation and collection fibers, respectively. The silica core diameter of two fibers is 300 μm, the doped silica cladding thickness is 30 μm, and the polyimide coating thickness is 70 μm. The mixed DMF solution is dropped on the Teflon mold that covers the tips of fibers, followed by annealing at 80 °C for 12 h.

The setup of the double fiber system is shown in Fig. S1(b). We used semiconductor laser having a 532 nm wavelength with a power of 10 mW as the light source for our sensing system. The excitation fiber was fixed by means of a fiber coupler. The laser beams were first focused by means of a focusing lens and attenuated by an intensity attenuator. The laser light was collected by the excitation fiber and transmitted by the solid hydrogel film, which served as a waveguide. The light signal was collected by the collection fiber and analyzed by a charge-coupled device (CCD) spectrometer.

3. Results and discussion

3.1. Absorptive reaction of the sensing film

3.1.1. Individual film

To demonstrate the sensing ability of the sensing film containing the sensing probe, the solid sensing film was studied first. The designed Chemosensor **1** and TPN-Cl_2 were individually mixed with hydrogel polymer poly HEMA to form the solid sensing film as shown in Fig. 1. The absorption spectra of the sensing film containing the Chemosensor **1** and TPN-Cl_2 are shown in Fig. 1(a) and 1(b), respectively. To test the sensing ability of Fe^{3+}, the sensing film containing Chemosensor **1** was first immersed in deionized water (DI water) for 30 min. After stabilizing the sensing film, we added Fe^{3+} at a concentration between 10^{-5} and 10^{-3} M to the sensing film. As shown in Fig. 1(a), the absorption spectrum shows a strong absorption band at 564 nm and a secondary band at approximately 532 nm. With the increasing concentration of Fe^{3+}, the peak intensity of the spectrum increased. For the film containing TPN-Cl_2, as shown in Fig. 1(b), the absorption spectrum was measured by adding Zn^{2+} with a concentration varied from 10^{-5} to 10^{-3} M

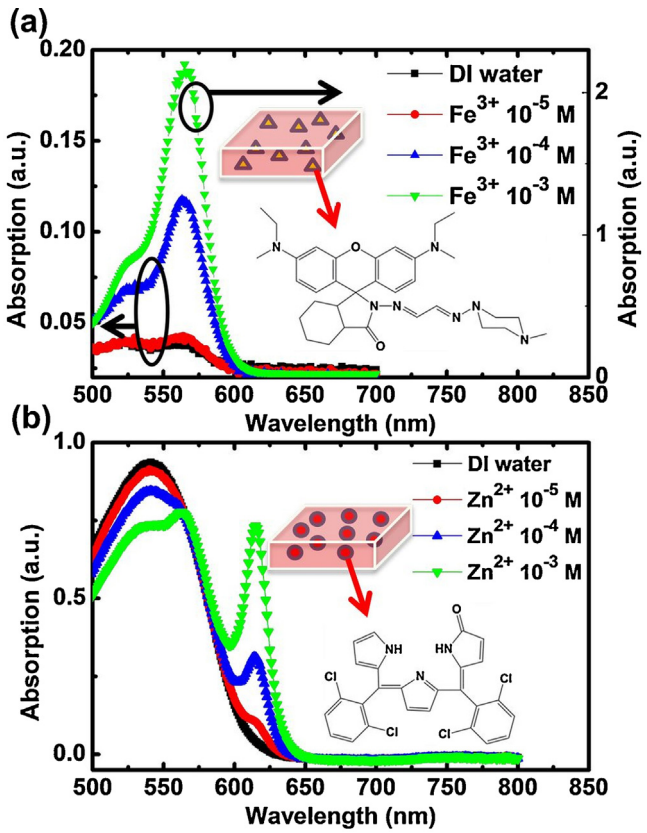

Fig. 1. Absorption spectra of the solid sensing film containing: (a) Chemosensor **1** and (b) TPN-Cl_2.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with a DI water background. The spectrum showed a strong absorption band at 550 and 620 nm. With the increasing concentration of Zn^{2+}, the peak intensity near 620 nm increased. To summarize, the absorption intensity of the sensing films became stronger with the higher concentration of metal ions.

Although TPN-Cl_2 reacted not only with Zn^{2+} but also other metal ions such as Cu^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, and Cr^{3+} [9], its sensitivity to Zn^{2+} was the strongest. The selectivity of Chemosensor **1** was also tested by reacting with these metal ions [19]. The Fe^{3+} ion produced a strong red fluorescence. Although Cu^{2+} also caused an emission peak, the intensity of Fe^{3+} was much higher. Therefore, TPN-Cl_2 and Chemosensor **1** are both effective at detecting Zn^{2+} and Fe^{3+}, respectively. Furthermore, Chemosensor **1** did not react with Zn^{2+} and TPN-Cl_2 did not react with Fe^{3+} (not shown).

3.1.2. Mixed film

After confirming the sensing ability of the hydro gel sensing film containing different probes individually, Chemosensor **1** and TPN-Cl_2 were mixed and added to the same sensing film shown in Fig. 2(a). The mixed film contained both Chemosensor **1** and TPN-Cl_2, and was used to test sensing ability by adding Fe^{3+} or Zn^{2+}. As shown in Fig. 2(b), various levels of concentration of Fe^{3+} were added. Although the absorption intensity did not change with as low a concentration as 10^{-5} M, the intensity difference between 10^{-4} and 10^{-3} M Fe^{3+} remained recognizable. Here, we defined the region between 530 and 580 nm is able to detect Fe^{3+} in the absorptive sensing system. By contrast, Zn^{2+} with concentration that varied from 10^{-5} to 10^{-3} M were added to the mixed film shown in Fig. 2(c). For Zn^{2+} sensing, the waveform of the mixed film was the same as that of the film containing only TPN—Cl_2. With the increasing Zn^{2+} concentration, the peak intensity at 530 nm dimin-