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# Self-assembly film of azobenzene and layered double hydroxide and its application as a light-controlled reversible sensor for the detection of $Be^{2+}$

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ABSTRACT

This paper reports the fabrication of optical chemosensors based on the self-assembly of Azobenzene (2-(3,6-disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate) and layered double hydroxides (LDHs) nanosheet, which demonstrates sensory property for $Be^{2+}$ and reversible response to UV and visible light. The fluorescence intensity of the UTF is linear proportional to $Be^{2+}$ concentration in the range 0.1–1.2 μM. The absolute detection limit is 3 nM (S/N = 3). Moreover, the UTF shows reversibly optical behavior through alternate irradiating by UV and visible light. Combining sensory and light response property, the light-controlled reversible sensor for detection of $Be^{2+}$ was realized. The chemosensor displays a good repeatability (RSD less than 1.1% in 5 consecutive measurements). Study on the mechanism shows the light-controlled reversible behavior leads to reversible change of elements, structure and morphology of the UTF confirmed by XPS, Raman, XRD, and AFM. Therefore, we provided a high efficient, clean and environmental-friendly method to achieve reversibility of optical chemosensor by employing light as controlled condition, which open a new avenue to design the advanced optical sensors and switches.

## 1. Introduction

The development of optical chemosensors for the determination of trace metal elements in living systems and environment has attracted considerable interests [1–5]. In particular, fluorescence chemosensor has witnessed speedy growth in a short span of time because of its sensitive, fast, and low-cost instrumentation [6,7]. For the purpose of recognizing and sensing, it is indispensable to a fluorophore to provide a suitable binding site with high complexing capacity and matched space for metal ion. To realize reusability and reversibility which is necessary for sensor, an external stimulus is generally employed. Complexing agent and pH are the most common external inputs. However, both methods have inevitably led to contamination of the analyte solution and producing of much waste-water. Among variety of external stimulus, light has its competitive advantages: (i) it provides a high level of temporal and spatial resolution with precisely controlled irradiation wavelength and emission intensity, (ii) no chemical contaminants are introduced, and (iii) the closed systems can be actuated [8–14]. Thus the sensor using light as input to realize reversibility will arouse novel applications in advanced switch and sensor fields. For organic fluorescence sensor unit, however, the great challenge using light as input lies in how to improve optical stability due to its nature photobleaching property. Recently, our work group has been addressing ourselves to enhance optical character of organic fluorescence molecules by combining inorganic layered double hydroxide (LDH) nanosheet and fluorophore [15–18]. The resulting materials show huge improvement in the aspects of stability of light, heat, storage, mechanics, *etc.* Motivated by this, we hypothesized the assembly of LDH nanosheets and fluorescence molecule may be used as light-controlled reversible sensor.

Beryllium is considered as the most toxic element in non-radioactivity materials, but it is still widely applied due to its distinct performance [19]. Water-soluble $Be^{2+}$ may cause a serious and fatal threat to human health because it is accumulated in the skin and soft tissue through food and

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water in one's daily diet [20]. Thus, it is essential to detect the trace of $Be^{2+}$ in water (less than 0.1 $\mu M L^{-1}$ required by World Health Organization) [21,22]. In this work, $Be^{2+}$ and Azobenzene dye (2-(3,6-disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate) were chose as model analyte and fluorescence indicator, respectively. Azobenzene dye was used to assemble with LDH nanosheet by layer-by-layer (LBL) method owing to its photo-isomerization property and associated wide application in the field of information storage [23–25], switching [26–28], sensors [29–31], variable wettability [32–34], and nonlinear devices [35–37]. The optical chemosensors based on the self-assembly of azobenzene dye and LDH nanosheet were fabricated, which demonstrates sensory property for $Be^{2+}$ with high sensitivity, wide linear range, low detection limit, as well as reversible response to UV and visible light. Thus, the light-controlled reversible sensor for the detection of $Be^{2+}$ was obtained based on both ion sensory and light response behaviors. The mechanism of detection for $Be^{2+}$ and light triggered reversible and reusable performance was systematically studied through XPS, Raman, XRD, and AFM. The results display the process of light-controlled reversible sensor causes reversible change of elements, structure and morphology of the ultrathin film (UTF). Therefore, this work provide a novel method to realize the reversibility of chemosensor by employing light as external input, which not only provide a new idea for design reversible sensor, but propel economic and environmental-friendly development of optical chemosensor.

## 2. Experimental

### 2.1. Materials

2-(3,6-disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (Azobenzene dye, biochemistry grade) was purchased from Sigma–Aldrich Company. Analytical grade chemicals including $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, $C_2H_5OH$, $NH_3$, $H_2O_2$, $H_2SO_4$, and $BeCl_2$ were used without further purification. The deionized and decarbonated water was used in all the experimental processes.

### 2.2. Fabrication of the (Azobenzene/LDH)$_n$ UTFs

The $Zn_2Al–NO_3$ LDH precursor was synthesized by the hydrothermal method reported previously [38]. A 0.1 g of ZnAl–LDH was shaken in 100 mL of formamide solution for 24 h to obtain a colloidal suspension of exfoliated ZnAl–LDH nanosheets. The quartz glass substrate was cleaned in concentrated $NH_3$/30% $H_2O_2$ (7:3) and concentrated $H_2SO_4$ for 30 min each. After each procedure, the quartz substrate was rinsed and washed thoroughly with deionic water. The substrate was dipped in a colloidal suspension (1 $g L^{-1}$) of LDH nanosheets for 10 min followed by washing thoroughly and drying with nitrogen gas, and then the substrate was treated with a 100 mL of Azobenzene aqueous solution (0.025 wt %) for another 10 min followed by washing and drying. Multilayer films of (Azobenzene/LDH)$_n$ were fabricated by alternate deposition of LDH nanosheets suspension and Azobenzene solution for $n$ cycles. The resulting films were dried with a nitrogen gas flow for 2 min at 25 °C.

### 2.3. The response of $Be^{2+}$ measurement

A standard solution of $Be^{2+}$ (1 mM) was prepared from $BeCl_2$ in deionized and decarbonated water with pH = 11, which was further diluted to obtain the required different concentrations of $Be^{2+}$. Fifteen different concentrations of $Be^{2+}$ ranging from 0.1 to 1.6 $\mu M$ were prepared and subsequently used for studying the sensing performance of the proposed sensors. The detection limit was calculated based on S/N = 3. The (Azobenzene/LDH)$_{20}$ UTF was fixed in a quartz cell, and the $BeCl_2$ solution was injected into quartz cell. Then the fluorescence response was recorded by a RF-5301PC fluorophotometer. Between two different concentration measurements the chemosensor was washed thoroughly with deionized and decarbonated water.

### 2.4. The response to UV and visible light

The film was irradiated by UV light with different times (0, 5, 10, and 15 min) at room temperature, and then the irradiated film by UV light was put in visible light environment. The response of film to light was recorded by fluorescence spectra with a liquid holder.

### 2.5. The reversible operation process

Firstly, the film was immersed in $Be^{2+}$ solution, and fluorescence intensity was recorded. Then, the film treated by $Be^{2+}$ was put in deionized and decarbonated water, and UV light was used as external stimulus to irradiate, followed by recording fluorescence intensity. Thirdly, the film irradiated by UV light was rising in deionized and decarbonated water for three times. Finally, visible light was applied to irradiate the film followed by recording fluorescence intensity.

### 2.6. Characterization techniques

UV–vis absorption spectra were collected in the range from 200 to 500 nm on a Shimadzu T–9201 spectrophotometer, with the slit width of 2.0 nm. Fluorescence spectra were performed on a RF–5301PC fluorospectrophotometer with the excitation wavelength of 330 nm. Fluorescence emission spectra range in 350–650 nm, and both the excitation and emission slits were set to 2.0 nm. X-ray diffraction (XRD) patterns were recorded using a Rigaku 2500 VB2+PC diffractometer under the conditions: 40 kV, 50 mA, Cu K$\alpha$ radiation ($\lambda$ = 0.154 nm) step-scanned with a scanning rate of 0.5°/min, and a $2\theta$ angle ranging from 1.5 to 9°. The morphology of the UTF was investigated by using a scanning electron microscope (SEM ZEISS), and the accelerating voltage applied was 20 kV. The surface roughness data were obtained by using the atomic force microscopy (AFM) software (Digital Instruments, version 6.12). X-ray photoelectron spectroscopy (XPS) measurement was performed with monochromatized A1-K$\alpha$ exciting X-radiation (PHI Quantera SXM). Raman spectra were obtained with 785 nm of excitation by using a confocal Raman microspectrometer (Renishaw Instruments Co. Ltd., RM2000) in the range 1100–1800 $cm^{-1}$. Metallic elemental analysis was performed by atomic emission spectroscopy with a Shimadzu ICPS-7500 instrument.

## 3. Results and discussion

### 3.1. Assembly of the Azobenzene/LDH UTF

Fig. 1A shows the UV–vis absorption spectra of the (Azobenzene/LDH)$_n$ UTFs with various bilayer numbers ($n$) deposited on quartz substrates. It is observed that the absorption bands of Azobenzene at ~235, 335 ($\pi$–$\pi^*$) and 547 nm ($n$–$\pi^*$) correlate linearly with $n$ (Fig. 1B), indicating a stepwise and regular film growth procedure, which is further confirmed by the gradual color enhancement with the increase of bilayer number (inset in Fig. 1A). Compared with the absorption spectrum of Azobenzene solution sample (Fig. S1(A)), the absorption band of the (Azobenzene/LDH)$_n$ UTFs becomes broader and unresolved,