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A ratiometric fluorescence sensor for Be^{2+} based on Beryllon II/layered double hydroxide ultrathin films

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ABSTRACT

A ratiometric fluorescence sensor for Be^{2+} has been fabricated *via* alternate assembly of 2-(3,6-disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (Beryllon II) and MgAl-LDH nanosheets on quartz substrates using the layer-by-layer (LBL) deposition technique. UV–vis absorption and the fluorescence emission spectroscopy indicate a stepwise and regular growth of the Beryllon II/LDH UTFs upon increasing deposition cycle. The film of Beryllon II/LDH possesses a periodic layered structure perpendicular to the substrate revealed by X-ray diffraction and scanning electron microscopy. Atomic force microscopy images show that the film surface is continuous and uniform. The Beryllon II/LDH UTFs display ratiometric fluorescence response for Be^{2+} with a linear response range in 1.0×10^{-7}–1.9×10^{-6} mol L^{-1} and a detection limit of 4.2×10^{-9} mol L^{-1}. Furthermore, the ratiometric sensor exhibits good repeatability, high stability (thermal, storage and mechanical) as well as excellent selectivity toward Be^{2+}. XPS and Raman measurements demonstrate that the specific response of the sensor is attributed to the coordination between Be^{2+} and Beryllon II in the UTF. The Beryllon II/LDH UTFs in this work can be potentially used as a chemosensor for the detection of Be^{2+} in the environmental and biomedical field.

1. Introduction

Recently, the existence of beryllium in soil, water and food has attracted much attention due to its high toxicity and debated carcinogenicity. Therefore, detection of this element is of considerable significance in their disposal sites as well as in the industry using beryllium products [1,2]. The determination of beryllium has been generally carried out based on atomic absorption spectrometry [3–5], fluorometry [6,7], voltammetry [8–10] and high-performance liquid chromatography (HPLC) [11]. Fluorescence spectroscopy is a powerful method to detect ions and neutral molecules because of its high sensitivity, selectivity, fast-response and low cost [12–17]. However, a key disadvantage of fluorescence determination is that the fluorescence indicators generally suffer from changeable fluorescence intensity upon the agitation of external environment (pH, polarity, temperature, photobleaching). Compared with intensity-based systems, ratiometric fluorescence sensors are preferred in bioimaging applications because this measurement involves the change of intensity ratio of absorption or emission at two wavelengths, which effectively eliminates most or all interferences from environment and thus increases the selectivity and sensitivity [18–25]. Up to now, considerable efforts have been focused on the development of fluorescence sensors for Zn^{2+} [26–30], Ag^{+} [31–33], and Pb^{2+} [34,35] *etc.*, based on the ratiometric fluorescence method.

Organic fluorescence indicators are normally prone to be thermally or optically unstable, which limits their practical application. One effective solution to this problem is the incorporation of indicator molecules into solid supports. Recently, the fabrication of organic chromophore–inorganic matrix composite materials has attracted much attention owing to their novel functionalities which are not present in the individual components [36–40]. Layered double hydroxides (LDHs) are one type of 2D inorganic materials whose general formula can be expressed as $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{z+}A^{n-}_{z/n}\cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metals respectively; A^{n-} is the anion to compensate for the positive charge of the hydroxide layers [41,42]. LDH materials have been widely used in the fields of catalysis [43,44], separation process [45] and drug delivery [46–48] based on their specific intercalation property. Recently, the delamination of LDH into nanosheets as building blocks and preparation of inorganic/organic fluorophore ultrathin films (UTFs) have been reported [49,50]. This inspires us to challenge the goal of fabricating fluorescence chemosensors *via* alternate assembly of positively charged LDH nanosheets and negatively charged fluorophore indicators with the layer-by-layer (LBL) technique. The resulting UTFs

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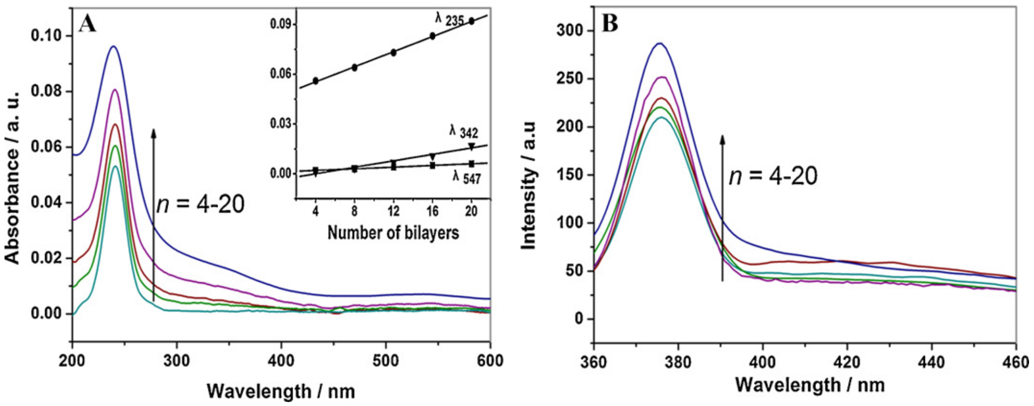

Fig. 1. (A) UV–vis absorption spectra of the (Beryllon II/LDH)$_n$ UTFs (n = 4–20) (inset: plots of the absorbance at 235, 342 and 547 nm *vs.* n); (B) the emission spectra of the (Beryllon II/LDH)$_n$ UTFs (n = 4–20).

would exhibit the following advantages: firstly, the LDH matrix would enhance the optical and thermal stability of the chromophore due to the ordered stacking of the LDH nanosheets; secondly, the molecular level control of the assembly will result in a high dispersion of fluorophore molecules with uniform orientation, which can suppress aggregation and reduce fluorescence quenching effectively.

2-(3,6-Disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (Beryllon II) is one of the most promising indicators in chemical sensor application, which has been used as a chromogenic reagent to determine cations and proteins under different conditions [51–54]. Its absorption and fluorescence emission strongly depend on pH value owing to the presence of cationic, neutral and anionic forms in aqueous solution. In this work, fluorophore Beryllon II and MgAl-LDH nanosheets were alternately assembled on quartz substrates using the LBL method, which was demonstrated as a ratiometric fluorescence chemosensor for Be^{2+}. The Beryllon II/LDH UTF chemosensor shows a linear response range (1.0×10^{-7}–1.9×10^{-6} mol L^{-1}) and a low detection limit (4.2×10^{-9} mol L^{-1}) at the optimal working pH (11.0). In addition, its thermal- and storage stability, repeatability as well as excellent selectivity toward Be^{2+} have been demonstrated. The regeneration of the chemosensor was also achieved, which induced reversible changes in surface morphology and fluorescence anisotropy. Therefore, the strategy in this work provides a successfully paradigm for the fabrication of highly oriented luminescence UTFs based on an organic indicator immobilized within an inorganic matrix, which can be potentially applied as chemosensors in environmental and biological fields.

2. Experimental

2.1. Materials

2-(3,6-Disulfo-8-hydroxynaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (Beryllon II, biochemistry grade) was purchased from Sigma–Aldrich Company. Analytical grade chemicals including $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, $Ca(NO_3)_2$, $Cd(NO_3)_2$, $NaNO_3$, $Hg(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, NH_4VO_3, $Pb(NO_3)_2$, $Fe(NO_3)_3$, KNO_3, $Mn(NO_3)_2$, $Ni(NO_3)_2$, $BeSO_4$ and KF were used without further purification. The deionized and decarbonated water was used in all the experimental processes.

2.2. Fabrication of the (Beryllon II/LDH)$_n$ UTFs

The $Mg_2Al–NO_3$ LDH precursor was synthesized by a hydrothermal method reported previously [55] and its XRD pattern is shown in Fig. S1. A 0.1 g of $Mg_2Al–NO_3$ LDH was shaken in 100 mL of formamide solution for 24 h to obtain a colloidal suspension of exfoliated $Mg_2Al–NO_3$ LDH nanosheets. The quartz glass substrate was cleaned in concentrated NH_3/30% H_2O_2 (7:3, v/v) and concentrated H_2SO_4 for 30 min each. After each procedure, the quartz substrate was rinsed and washed thoroughly with deionized water. The substrate was dipped in a colloidal suspension (0.1 g mL^{-1}) of LDH nanosheets for 10 min followed by washing thoroughly, and then the substrate was treated with a 100 mL of Beryllon II aqueous solution (0.025 wt%) for another 10 min followed by washing. Multilayer films of (Beryllon II/LDH)$_n$ were fabricated by alternate deposition of LDH nanosheets suspension and Beryllon II solution for n cycles. The resulting films were dried with a nitrogen gas flow at 25 °C for 2 min.

2.3. The response of the UTF toward Be^{2+}

The Be^{2+} solutions with different concentrations were prepared by dissolving $BeSO_4$ in deionized water. The fluorescence chemosensor was immersed into a quartz cell with $BeSO_4$ solution, and its response was recorded by a RF-5301PC fluorophotometer with a liquid holder.

2.4. Characterization techniques

The UV–vis absorption spectra were collected in the range from 280 to 550 nm on a Shimadzu T-9201 spectrophotometer, with the slit width of 1.0 nm. The fluorescence spectra were performed on a RF-5301PC fluorospectrophotometer with the excitation wavelength of 333 nm. The fluorescence emission spectra range in 350–600 nm, and both the excitation and emission slits were set to 5 nm. Steady-state polarized photoluminescence measurements of the Beryllon II/LDH UTFs were recorded with an Edinburgh Instruments' FLS 920 fluorospectrophotometer. X-ray diffraction patterns (XRD) were recorded using a Rigaku 2500 VB2 + PC diffractometer under the conditions: 40 kV, 50 mA, Cu Kα radiation (λ = 0.154 nm) step-scanned with a scanning rate of 0.5° min^{-1}, and a 2θ angle ranging from 0.5° to 10°. The morphology of thin films was investigated by using a scanning electron microscope (SEM ZEISS), and the accelerating voltage applied was 20 kV. The surface roughness and thickness data were obtained by using the atomic force microscopy (AFM) software (Digital Instruments,