



Assembly of 8-aminonaphthalene-1,3,6-trisulfonate intercalated layered double hydroxide film for the selective detection of Mg^{2+}

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ARTICLE INFO

Article history:

Received 2 September 2011

Received in revised form 1 November 2011

Accepted 7 November 2011

Available online 17 November 2011

Keywords:

Layered double hydroxide

ANTS

Thin film

Chemosensor

Mg^{2+}

ABSTRACT

A novel fluorescent film based on 8-aminonaphthalene-1,3,6-trisulfonate/layered double hydroxide composite (ANTS/LDH) has been synthesized by the electrophoretic deposition (EPD) method, and its application as an optical sensor for Mg^{2+} is demonstrated. The ANTS/LDH film with a thickness of $2\ \mu\text{m}$ exhibits a good *c*-orientation of LDH platelets, which is confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The ANTS/LDH film shows a good fluorescent response for Mg^{2+} ion. Meanwhile, a linear correlation between the fluorescence intensity of the ANTS/LDH film and the concentration of Mg^{2+} is obtained ($I = 0.496 + 0.0708 \log c(\text{Mg}^{2+})$, $R^2 = 0.996$), with a detection limit of $2.37 \times 10^{-7}\ \text{M}$. The results indicate that ANTS/LDH film has a high fluorescence selectivity for Mg^{2+} ions, with no significant response to other metal ions, including Ca^{2+} , Na^+ , K^+ , Fe^{3+} , Co^{2+} , Ni^{2+} , or Cu^{2+} . Furthermore, the ANTS/LDH thin film shows a good reusable ability for Mg^{2+} by alternately changing the solution of Mg^{2+} ($5.0 \times 10^{-3}\ \text{M}$) and EDTA ($8.0 \times 10^{-2}\ \text{M}$), and the relative standard deviation of 8 cycles is calculated as 1.7% (EDTA) and 0.14% (Mg^{2+}). The specific fluorescence response of the film sensor is attributed to the complexation between ANTS and Mg^{2+} , which is verified by ^{13}C solid state NMR spectroscopy. In addition, density functional theory (DFT) calculation confirms that a strong interaction occurs between Mg^{2+} and ANTS molecule, which is responsible for the significant fluorescence quenching of the ANTS/LDH film. The results indicate that the ANTS/LDH thin film in this work can be used as a chemosensor for the quantitative detection of Mg^{2+} .

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1. Introduction

Sensing of a metal ion with selective reagents has received considerable attention because of its important application in biological and environmental systems [1]. Magnesium ion, being the most abundant intracellular divalent cation, plays a major role in many cellular processes including stabilization of DNA conformation, ion transport through the membrane and signal transduction. Additionally, the activity of magnesium in blood and serum is an important clinical parameter that needs to be monitored in different situations. All these provide sufficient impetus to fabricate chemical sensors for the detection of magnesium. Owing to the spectroscopic silence of Mg, the development of fluorescent chemosensors with high selectivity toward Mg^{2+} represents an important challenge, especially in the discrimination of calcium for many applications [2]. Recently, Farruggia et al. reported the 8-hydroxyquinoline derivatives as effective Mg^{2+} indicators [3]. Naruta and coworkers synthesized a porphyrin analogue with an embedded 1,10-phenanthroline moiety, and found that this

complex could be exploited as a Mg^{2+} -responsive fluorescent sensor [4]. A new multifunctional ferrocenophane derivative has been reported to selective recognition of Mg^{2+} [5]. Although much progress has been made in designing chemosensors for magnesium ion, some problems associated with their application remain unresolved, which include interference from other metal ions, irreversible response, and need to work in organic or aqueous solution.

It is known that organic indicator in solution generally suffer from the leaching or degradation of active species over a long period of application. In this regard, a supramolecular assembly based on the immobilization of organic indicator in an inorganic matrix would be a good resolution with the following advantages: the improved stability, higher fluorescence emission and can be used conveniently to achieve real-time and real-space measurements. However, the investigation on solid film chemosensors for magnesium which meets the requirements of high stability, sensitive detection as well as facile manipulation has been rarely studied and remains a challenging goal.

Recently, metallic nanoparticles, quantum dots, silica nanoparticles and layered double hydroxides have been used as the matrix of various chemosensors [6–10]. Among these solid matrices, layered double hydroxides (LDHs) have been reported as attractive supports for many applications because of its simple synthetic

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procedure, good biocompatibility and low toxicity. LDHs are layered inorganic materials which can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are di- and tri-valent metal cations, respectively, and (A^{n-}) is the interlayer charge-balancing anion. Numerous studies show that LDHs have been widely used in the fields of catalysis [11,12], separation technology [13], biology and medicine [14,15]. Some fluorescence films based on fluorophore/LDH composites have also been successfully prepared [16–18].

8-Aminonaphthalene-1,3,6-trisulfonate (ANTS) is a fluorescence dye that has been generally used for labeling the protein in electrophoresis [19–21]. Taking into account the affinity of ANTS to Mg^{2+} in solution [22], herein we fabricate a thin film of ANTS assembled with LDH by the electrophoretic deposition method, which can signal Mg^{2+} specifically. The molecule of ANTS in this composite film serves as the metal ion receptor. This composite film can be utilized as a chemosensor specific for detection of Mg^{2+} by monitoring the changes in luminescence spectrum, with no significant response to other metal ions, especially Ca^{2+} . Furthermore, the ANTS/LDH composite shows a good regeneration ability for Mg^{2+} by alternately changing the solution of Mg^{2+} (5.0×10^{-3} M) and EDTA (8.0×10^{-2} M). The ANTS/LDH thin film exhibits the following advantages: ease in handling, short analysis time and low cost. Additionally, few or no organic liquid reagents are required. Therefore, this work demonstrates a successful paradigm for the fabrication of composite film based on organic indicator immobilized within an inorganic matrix, which can be potentially applied in the field of optical sensors.

2. Experimental

2.1. Materials

8-Aminonaphthalene-1,3,6-trisulfonate acid (ANTS) was purchased from J&K Scientific Ltd. The analytical grade chemicals including $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, disodium ethylenediamine tetraacetate (Na_2EDTA) and other nitrate salts of metal ion were used without further purification. The deionized and decarbonated water was used in all these experimental processes.

2.2. Synthesis of ANTS/LDH colloidal suspension

NO_3 -ZnAl-LDH (Zn/Al molar ratio 2:1) precursor was synthesized by the hydrothermal method reported previously [23]. Subsequently, the ANTS intercalated LDH composite was prepared following the ion-exchange method. ANTS (3.5×10^{-3} mol) were dissolved in 150 mL of deionized and decarbonated water. The solution was adjusted to pH 7.0 with a NaOH (0.2 M) solution. A freshly prepared NO_3 -ZnAl-LDH (1 g) was dispersed in the solution thoroughly. The suspension was stirred at room temperature under a N_2 atmosphere for 48 h. The resulting product ANTS/LDH was washed extensively with water. Then the ANTS/LDH colloidal suspension (5×10^{-2} M) was obtained by dispersion in methanol. Element analysis results: Zn 63.14%, Al 14.41%, C 11.28%, N 0.71%, H 3.09%. The chemical composition of the ANTS/LDH composite was found to be $Zn_{0.66}Al_{0.34}(OH)_2(ANTS)_{0.093}(NO_3)_{0.0066}(CO_3)_{0.013} \cdot 0.32H_2O$.

2.3. Fabrications of the ANTS/LDH thin films

Firstly, the substrates of fluoride-doped tin oxide (FTO) were cleaned in deionized water and ethanol (1:1, v/v) in an ultrasonic bath for 30 min each. The thin film of ANTS/LDH was fabricated by the electrophoretic deposition (EPD) method. Two FTO substrates were used as the working and counter electrodes, respectively, which were placed parallel to each other with a separation of 1 cm

in a 10 mL of ANTS/LDH colloidal suspension. The voltage between the two electrodes was 30 V and the thickness of the film can be precisely controlled by changing the electrophoretic time.

2.4. The measurement for Mg^{2+}

The Mg^{2+} solutions with different concentration were prepared by dissolving $Mg(NO_3)_2$ in deionized water. The ANTS/LDH film fluorescent sensor was immersed in a quartz cell with Mg^{2+} aqueous solutions ($[Mg^{2+}] = 1.0 \times 10^{-6}$, 5.0×10^{-6} , 1.0×10^{-5} , 5.0×10^{-5} , 1.0×10^{-4} , 5.0×10^{-4} , 1.0×10^{-3} , 5.0×10^{-3} and 1.0×10^{-2} M, respectively) with pH = 7.0. The fluorescence response was recorded by a RF-5301PC fluorophotometer with a liquid holder based on the fluorescence quenching as a function of Mg^{2+} concentration.

2.5. Techniques of characterization

The powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using $Cu K\alpha$ radiation ($\lambda = 0.15418$ nm) at 40 kV, 30 mA, with a scanning rate of $10^\circ/\text{min}$, and a 2θ angle ranging from 3° to 70° . The morphology and thickness of the thin film were investigated by using a ZEISS scanning electron microscope (SEM). The surface roughness data were obtained by using the atomic force microscopy (AFM) software (Digital Instruments, Version 6.12). Zn and Al elemental analysis were performed by atomic emission spectroscopy with a Shimadzu ICPS-7500 instrument. C, H, and N contents were determined using an Elementar vario elemental analysis instrument. Fluorescence emission spectra were recorded on a RF-5301PC fluorophotometer in the range 400–650 nm with the excitation wavelength of 365 nm and a slit width of 10 nm. Solid-state ^{13}C cross polarization/magic angle spinning (CP/MAS) NMR was recorded by Bruker BioSpin AV 300 MHz spectrometer (frequency: 75.48 MHz; srelaxation delay: 5 s; temperature: $20^\circ C$). Glycine was used as the external standards (carbonyl $\delta = 176.03$ ppm for ^{13}C).

2.6. Computational details

The structure of ANTS- Mg^{2+} was fully optimized by using Gaussian03 package [24] with B3PW91 functionals [25], which has been proven to produce a more reliable performance where weak interactions are involved than other functionals such as the most popular B3LYP [26]. All calculations were carried out in combination with 6-31G** [27] basis set for H, C, N, O, S atoms and LANL2DZ [28] basis set for Mg atom. Bond orders were characterized by the Wiberg's bond index (WBI) [29] and calculated with the natural bond orbital (NBO) methods, which has been demonstrated as a useful tool to provide quantitative description of interatomic and intermolecular interactions [30].

3. Results and discussion

3.1. Structural and morphological study of the ANTS/LDH film

The XRD patterns of the NO_3 -ZnAl-LDH precursor, the ANTS/LDH powder and the ANTS/LDH thin film are shown in Fig. 1. From Fig. 1, it can be seen that the reflections can be indexed to a hexagonal lattice with $R\bar{3}m$ rhombohedral symmetry, which is often used for the description of LDH structure. Compared with NO_3 -ZnAl-LDH (Fig. 1a, $2\theta = 10.0^\circ$, $d_{003} = 0.88$ nm), the basal reflection (003) of ANTS/LDH powder (Fig. 1b, $2\theta = 6.5^\circ$, $d_{003} = 1.17$ nm) shifts to a lower 2θ angle, and the expansion of interlayer distance was observed. The results indicate that ANTS anions have been intercalated into the LDH lamellar. For the ANTS/LDH thin film (Fig. 1c), the XRD profiles only reveal (00l) reflections, indicating

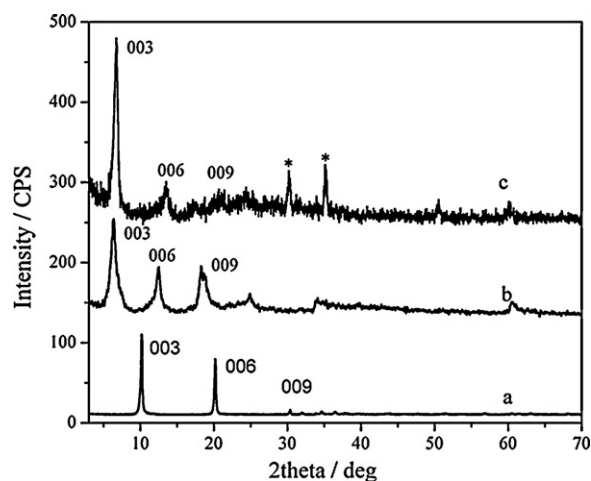


Fig. 1. XRD patterns of (a) NO_3 -ZnAl-LDH, (b) ANTS/LDH powder and (c) ANTS/LDH thin film. (The * symbol indicates peaks from the FTO substrate.)

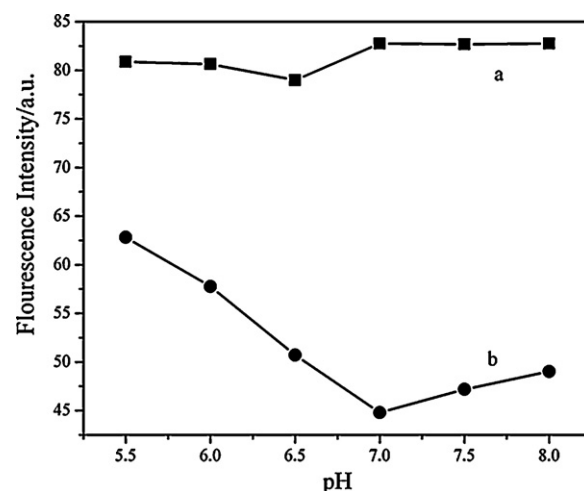
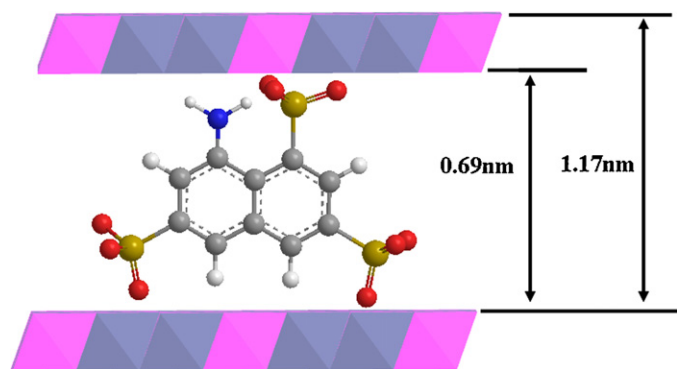


Fig. 3. Fluorescence intensity of (a) ANTS/LDH film and (b) ANTS/LDH film in the presence of Mg^{2+} as a function of pH.



Scheme 1. A schematic representation for the structure of ANTS/LDH composite. (C grey, H white, S brown, O red, and N blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a highly ordered stacking of the LDH layers in the c -direction normal to the supporting surface. Taking into account the dimensions of ANTS molecule and the basal spacing of ANTS/LDH composite, it is concluded that ANTS adopt a monolayer arrangement in the interlayer region of LDH. The schematic structures of ANTS/LDH composite were tentatively proposed and presented in Scheme 1.

SEM images of the ANTS/LDH samples are displayed in Fig. 2A and B. It can be seen that the ANTS/LDH lamellar crystallites are stacked with ab -plane parallel to the substrate, which is consistent with the XRD result. The thin film is continuous and uniform in the top view (Fig. 2A), with the average film thickness of ca. $2\ \mu\text{m}$ observed from its side-view of SEM image (Fig. 2B). The AFM image of the thin film is shown in Fig. 2C. The average root-mean-square

(rms) roughness for the film is ca. $9.40\ \text{nm}$, indicating a relatively smooth surface of the film.

The FT-IR spectra of NO_3 -ZnAl-LDH precursor, ANTS and ANTS/LDH film are shown in Fig. S1. For the sake of clarity, only the main absorption bands were listed. The spectrum of NO_3 -ZnAl-LDH (Fig. S1a) shows a strong absorption band at $1384\ \text{cm}^{-1}$ and a weak one at $825\ \text{cm}^{-1}$, which can be assigned to the stretching vibration of interlayer NO_3^- . In the spectrum of ANTS (Fig. S1b), the strong absorption bands at 1200 and $1047\ \text{cm}^{-1}$ are due to the $\text{O}=\text{S}=\text{O}$ stretching vibration of the sulfonate group [31]; the band at $1380\ \text{cm}^{-1}$ is assigned to the C–N stretching vibration of aromatic amine. The spectrum of the ANTS/LDH composite (Fig. S1c) displays characteristic bands of $-\text{SO}_3^-$ group at 1200 and $1047\ \text{cm}^{-1}$, and C–N at $1386\ \text{cm}^{-1}$ with a little shift compared with pristine ANTS, as a result of host-guest interactions between ANTS and LDH matrix [32]. Compared with the NO_3 -ZnAl-LDH precursor (Fig. S1a), the intensity of absorption band at $1384\ \text{cm}^{-1}$ attributed to NO_3^- decreases significantly for the ANTS/LDH composite, confirming the coexistence of ANTS anion and NO_3^- in the galleries of LDH. This is in agreement with the chemical composition of the ANTS/LDH composite.

3.2. The response of ANTS/LDH film for Mg^{2+}

3.2.1. Effect of pH

For many biological applications, it is very important that the sensor can be suitable for measuring specific cation in the physiological pH range. Therefore, we measured the fluorescence intensity of ANTS/LDH composite film in the absence and presence of Mg^{2+} at various pH values. As can be seen from Fig. 3, the emission

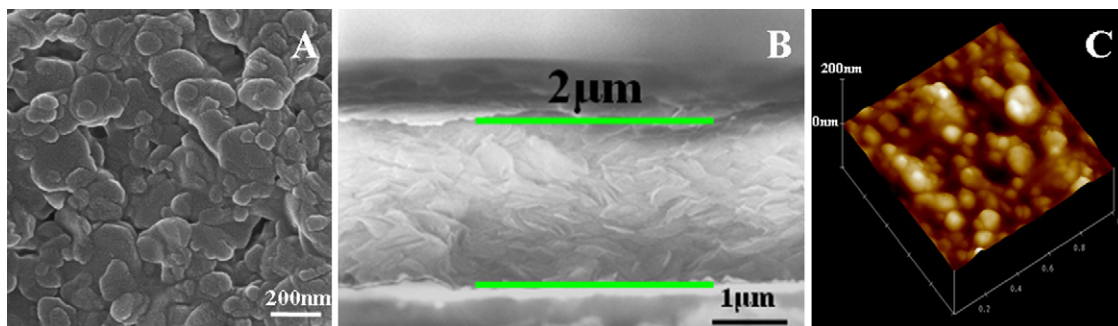


Fig. 2. (A and B) Top view and side view of SEM images of the ANTS/LDH thin film; (C) AFM images of the ANTS/LDH thin film.

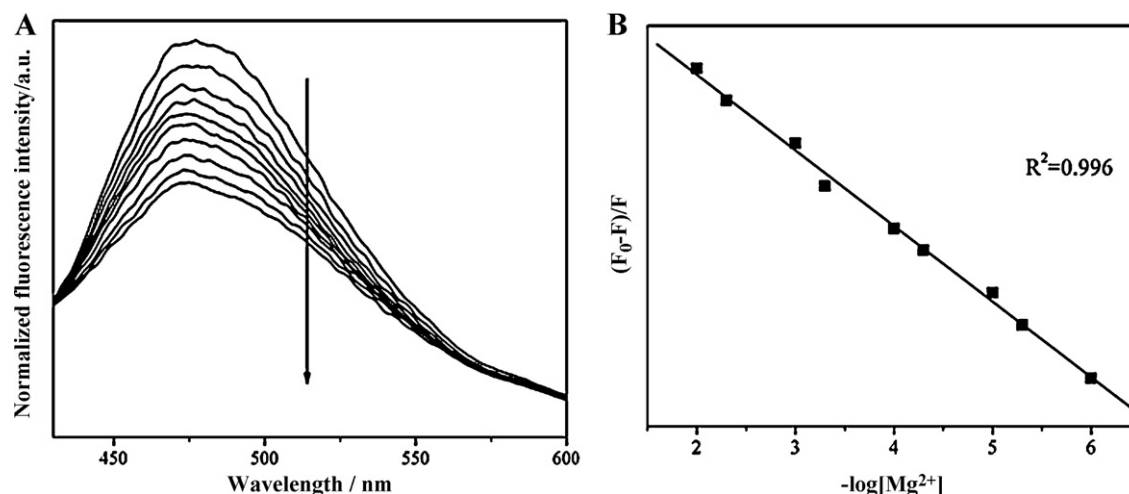


Fig. 4. (A) Fluorescence spectra of the ANTS/LDH film upon addition of different Mg^{2+} concentrations in aqueous solution. (B) Plot of fluorescence intensity as a function of Mg^{2+} concentration ($\lambda_{\text{ex}} = 365 \text{ nm}$).

intensity (477 nm) of ANTS/LDH film remains essentially constant over a broad pH range 5.5–8 (Fig. 3a). After the film being immersed into Mg^{2+} aqueous solution, the response is slightly affected by pH, and the fluorescence intensity gradually decreased from pH 5.5 to 7.0, then increased at pH 8.0 (Fig. 3b). So a large variation in fluorescence intensity was observed at pH 7.0 for the ANTS/LDH film upon the addition of Mg^{2+} . The results indicate that the ANTS/LDH film maintains a good fluorescence sensing ability toward Mg^{2+} over a wide pH range, which is feasible for its biological usage. Taking into account the most significant change in fluorescence intensity, the pH value of 7.0 was chosen in the following study.

3.2.2. Sensor response to Mg^{2+}

To investigate the optical response of the ANTS/LDH film sensor toward Mg^{2+} , the fluorescence spectra of ANTS/LDH film before and after the addition of Mg^{2+} solutions (concentration range from 1.0×10^{-6} to 10^{-2} M) are shown in Fig. 4. From Fig. 4A, a significant decrease in fluorescence intensity of the ANTS/LDH film was observed upon increasing Mg^{2+} concentration in this range. A linear relationship between fluorescence intensity and Mg^{2+} concentration was obtained from 1.0×10^{-6} to 10^{-2} M , with the following linear regression equation: $I = 0.496 + 0.0708 \log c(\text{Mg}^{2+})$, $R^2 = 0.996$ (Fig. 4B). The absolute detection limit is $2.4 \times 10^{-7} \text{ M}$. It meets the requirement for Mg^{2+} detection in intracellular free Mg^{2+} concentration levels (0.1–10 mM) [3]. The change of the fluorescence may originate from the following: ANTS is a naphthalene derivative which the 8-amino is an electron-donating group and 1,3,6-sulfonic group is an electron-acceptor, therefore ANTS is a donor–acceptor conjugated π -electron system and can undergo intramolecular charge transfer upon excitation [33]. Upon coordinated Mg^{2+} with the donor or acceptor moiety, the photo-physical properties of ANTS will be changed. This was confirmed quantitatively by the DFT calculation results, which will be further discussed in the next section.

3.2.3. Selectivity studies

An important feature of the chemosensor is its high selectivity toward analyte over other competitive species. The fluorescence intensity of the ANTS/LDH film was carried out against several biologically relevant alkali, alkaline earth ions and transition metal ions (Na^+ , K^+ , Ca^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} ; $5.0 \times 10^{-3} \text{ M}$, respectively). Fig. 5 illustrates the change of the fluorescence intensity of the ANTS/LDH film at 477 nm for various metal ions. Remarkably, no optical intensity change was observed before or after the

addition of the ions except Mg^{2+} . The results demonstrated that the ANTS/LDH thin film can be useful as a chemosensor for selective detection of Mg^{2+} over a range of other metal ions.

In addition, the fluorescence response of the film toward Mg^{2+} ion in the presence of other metal ion was investigated as well. Among these metal ions, Ca^{2+} is known to be a serious competitor of Mg^{2+} for many proposed Mg^{2+} sensors. Fig. 6 shows the fluorescence intensity change of ANTS/LDH film in detecting Mg^{2+} ($5.0 \times 10^{-3} \text{ M}$) in the presence of Ca^{2+} ($5.0 \times 10^{-3} \text{ M}$). From Fig. 6, no significant variation in fluorescence intensity was found by comparison with that without Ca^{2+} ions (curves c and d). This means that ANTS/LDH composite film has a high selectivity for Mg^{2+} .

3.2.4. The regeneration and reversibility

An important advantage of the detection method is the low-carbon recycling yield and facile regeneration. So the regeneration of fluorescence chemosensor was performed by immersing the quenched ANTS/LDH film into EDTA (a strong metal ion chelator) solution. Fig. 7 displays the reversibility (reusability) of the film sensor for Mg^{2+} . The film was alternately exposed to the magnesium ion aqueous solution ($5.0 \times 10^{-3} \text{ M}$) and EDTA aqueous solution ($8.0 \times 10^{-2} \text{ M}$), and the corresponding fluorescence emission at 477 nm was measured every 2 min. It was found the ANTS/LDH thin

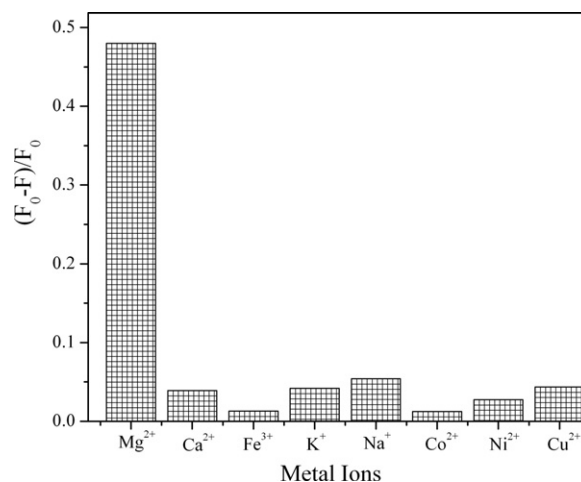


Fig. 5. Fluorescence intensity changes ($(F_0 - F)/F_0$) of ANTS/LDH film before and after addition of Mg^{2+} , Ca^{2+} , Fe^{3+} , K^+ , Na^+ , Co^{2+} , Ni^{2+} and Cu^{2+} aqueous solutions, respectively (the concentration of metal ions is $5.0 \times 10^{-3} \text{ M}$) ($\lambda_{\text{ex}} = 365 \text{ nm}$).

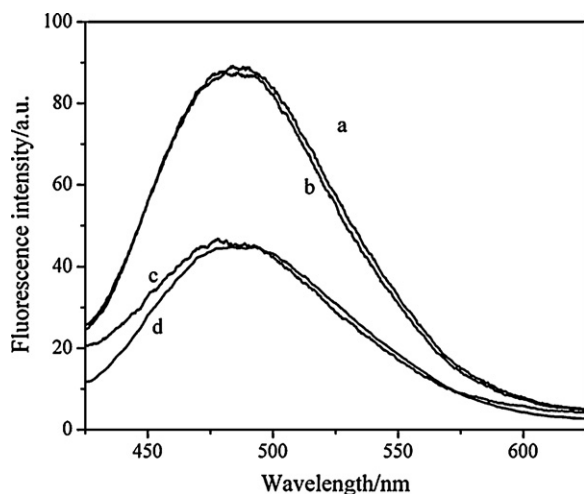


Fig. 6. Fluorescent spectrum of (a) ANTS/LDH film, (b) ANTS/LDH film in the presence of Ca^{2+} , (c) ANTS/LDH film in Mg^{2+} solution with the presence of Ca^{2+} and (d) ANTS/LDH film in Mg^{2+} solution with the absence of Ca^{2+} .

film shows a good reusable ability for Mg^{2+} , and the relative standard deviation of 8 cycles was calculated as 1.7% (EDTA) and 0.14% (Mg^{2+}). However, when the quenched ANTS/LDH film was washed with just pure water, the emission could not be restored. This result may indicate that Mg^{2+} was not simply adsorbed in the ANTS/LDH film, but complexed by the ANTS recognition in the film. The reason for the reversibility is that, EDTA has a stronger complexation capability with Mg^{2+} than ANTS dye, and upon being treated by EDTA, the ANTS molecule turns back. Therefore, the regeneration and reversibility of the ANTS/LDH film create new opportunities for the design and application in optical chemosensors.

To examine the structure stability of the ANTS/LDH film, we have also conducted XRD of the ANTS/LDH film after the quenching experiments and the subsequent washing or recovering (Fig. S2, Supporting Information). It can be seen that the X-ray diffraction pattern is almost identical to that of the original ANTS–LDH film (Fig. 1c), and there is no change occurred in interlayer distance and the host layers of LDH. It is indicated that ANTS molecules exist in the interlayer of LDH, and do not lose during the quenching experiments and the subsequent washing

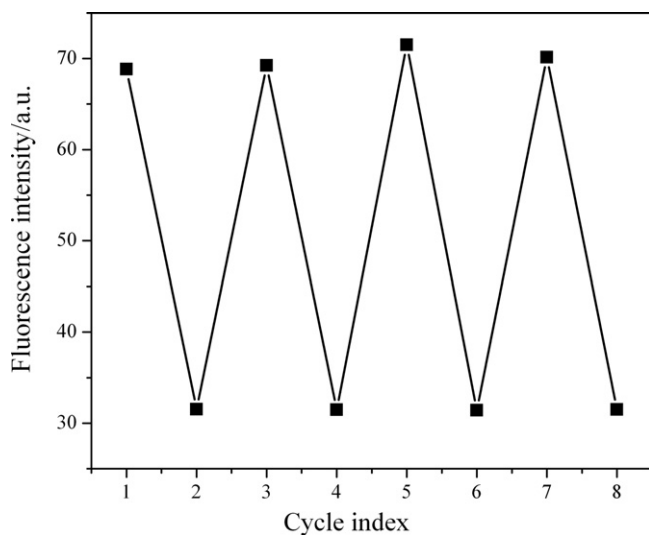


Fig. 7. Fluorescence intensity for the ANTS/LDH film chemosensor after alternate treatment by aqueous solution of Mg^{2+} (5.0×10^{-3} M) and EDTA (8.0×10^{-2} M) ($\lambda_{\text{ex}} = 365$ nm).

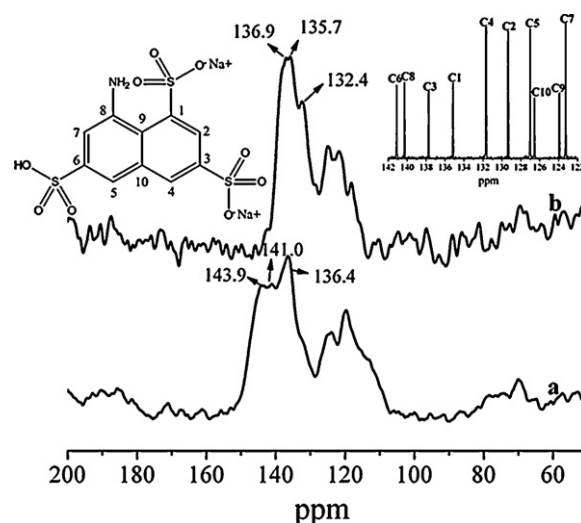


Fig. 8. ^{13}C solid state NMR spectrum for (a) ANTS/LDH composite and (b) ANTS/LDH after the determination of Mg^{2+} . The inset shows the assignments of carbon atoms in ANTS anion and its ^{13}C NMR in $\text{DMSO}-d_6$ solution.

or recovering. Therefore, the ANTS/LDH thin film possesses high structure stability for sensor in Mg^{2+} ion.

3.3. Mechanism of the detection of Mg^{2+}

To gain insights into the sensing mechanism of ANTS/LDH for Mg^{2+} , ^{13}C solid state NMR were performed to obtain more information about the interaction between ANTS and Mg^{2+} . ^{13}C CP-MAS NMR observations were carried out for pristine ANTS in $\text{DMSO}-d_6$ solution and ANTS/LDH film before and after detection of Mg^{2+} , respectively (Fig. 8). Firstly, a assignment of ^{13}C NMR resonances was performed for pristine ANTS, and the results were shown in the inset of Fig. 8 (ten signals: C7 123.2, C9 123.9, C10 126.5, C5 127.0, C2 129.3, C4 131.6, C1 135.1, C3 137.7, C8 140.2, and C6 141.1 ppm). Compared with pristine ANTS in solution medium, the observed ^{13}C resonances for the ANTS/LDH film were rather broad (Fig. 8a) owing to the superimposed resonances. The peak at 136.4 ppm (curve a) is deemed to contain the C1 and C3 line, and the resonance peaks at 141.0 and 143.9 ppm are assigned to the C8 and C6 of ANTS moiety, respectively. After determination of Mg^{2+} (curve b), a regular upshift of the peaks can be found. The peak corresponding to the C1 moved from 136.4 to 132.4 ppm, with a shift of ~ 4 ppm compared with curve a. Meanwhile, the peak corresponding to C8 and C6 shifted to 136.9 and 135.7 ppm, respectively. It indicates that the coordination may occur among Mg^{2+} , O atoms of sulfonic group and N atom of amino linked to C1 and C8 in the ANTS moiety, accounting for the fluorescence quenching of the ANTS/LDH thin film.

DFT calculations have been performed to obtain more information about the structure of the complex between ANTS and Mg^{2+} (see Supplementary data). The structure for the ANTS– Mg^{2+} complex was calculated, based on the previous report of stoichiometric between Mg^{2+} and ANTS [22]. In view of the participation of possible anions, the optimized structure (ANTS– Mg^{2+}) (Fig. 9) shows that one Mg^{2+} ion essentially coordinated with two oxygen atoms of one sulfonic group ($d_{\text{Mg}\cdots\text{O}} = 2.062$ and 2.056 Å, $\text{WBI}_{\text{Mg}\cdots\text{O}} = 0.1025$ and 0.0965), one nitrogen atom of amino ($d_{\text{Mg}\cdots\text{N}} = 2.197$ Å, $\text{WBI}_{\text{Mg}\cdots\text{N}} = 0.0812$), and two oxygen atoms of nitrate anion ($d_{\text{Mg}\cdots\text{O}} = 2.022$ and 2.122 Å, $\text{WBI}_{\text{Mg}\cdots\text{O}} = 0.897$ and 0.0636). It means that Mg^{2+} has a square pyramidal geometry with an axially coordinated with nitrogen from amino. Therefore, the computational results further confirm that the complexation occurs between ANTS and Mg^{2+} , which is responsible for the

Table 1Data for Mg^{2+} concentration determined in real samples by ICP-AES and the ANTS-LDH film sensor.

| Sample | Mg^{2+} concentration as determined by the ANTS-LDH sensor (ppm) | Mg^{2+} concentration as determined by ICP-AES (ppm) |
|--|---|---|
| Commercially drinking water | 54.4 ± 0.2 | 54.1 ± 0.1 |
| Simulated physiological Solution of Mg^{2+} (100 ppm) | 92.2 ± 0.1 | 92.4 ± 0.2 |

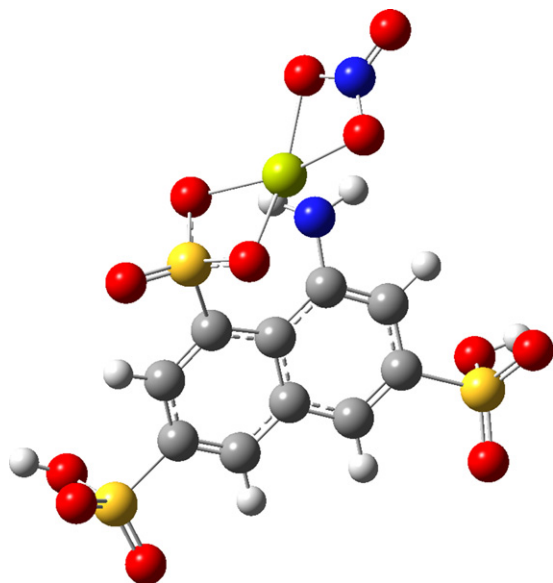


Fig. 9. Calculated structure for the complex $[(\text{ANTS})\text{-Mg}(\text{NO}_3)]$ by Gaussian03 (C grey, H white, O red, N blue, S yellow, and Mg yellow green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

significant fluorescence quenching of ANTS/LDH film. These results are in agreement with the conclusion from ^{13}C NMR spectroscopy.

3.4. Analytical application

To investigate practical application of the ANTS-LDH thin film, two samples (the commercially drinking water and the simulated physiological solution of Mg^{2+} , pH 7.0) were used for Mg^{2+} determination. The simulated physiological solution is a phosphate buffered solution (PBS) with 100 mM NaCl to keep constant ionic strength. The results presented in Table 1 indicate very good correspondence between the results obtained by ICP-AES and the ANTS-LDH film sensor. This indicates that the ANTS-LDH film can be potentially used as a chemosensor for the detection of Mg^{2+} ion.

4. Conclusions

In this work, we have successfully designed and synthesized a thin film of ANTS assembled with LDH to develop a new fluorescent sensor toward Mg^{2+} ion. The ANTS/LDH thin film with thickness of $2\ \mu\text{m}$ exhibits a good *c*-orientation of LDH platelets, which are confirmed by XRD and SEM. It was found that the ANTS/LDH thin film can be used for Mg^{2+} sensing in the concentration range of 1.0×10^{-6} – 10^{-2} M, and the detection limit of 2.37×10^{-7} M is obtained. Good selectivity toward Mg^{2+} over some other metal ions including Ca^{2+} has also been demonstrated. In addition, the mechanism of the ANTS/LDH thin film for determination of Mg^{2+} was revealed by a combination study based on ^{13}C NMR spectroscopy and density functional theory (DFT) calculation, from which the coordination between Mg^{2+} and ANTS immobilized in the LDH matrix occurs and is responsible for the significant fluorescence quenching of the ANTS/LDH film. Furthermore, the ANTS/LDH thin

film shows a good reusable ability for Mg^{2+} . Therefore, this work provides a facile and efficient strategy for the immobilization of organic indicator into an inorganic matrix, which can be potentially applied for the selective detection of Mg^{2+} ion.

Acknowledgments

This project was supported by the 973 Program (Grant No. 2011CBA00504), the National Natural Science Foundation of China, the 111 Project (Grant No. B07004), the Collaboration Project from the Beijing Education Committee and the Cooperative Special Program of Beijing.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2011.11.018.

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