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Controlled assemble of erythrosine B/layered double hydroxide ultrathin film: Preparation, fluorescence properties, and photo-response to bovine serum albumin

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ABSTRACT

The ultrathin films (UTFs) based on erythrosine B/layered double hydroxide have been prepared by a layer-by-layer assembly technique. UV–vis, fluorescence spectroscopy, XRD, SEM and AFM have been adopted to monitor the assembly process. The UTFs display a uniform morphology and a periodical layered structure. Fluorescence spectra demonstrated that the $(ER/LDH)_{26}$ UTF exhibited the optimal luminescent intensity. Moreover, the fluorescence-response of $(ER/LDH)_{26}$ UTF to bovine serum albumin (BSA) was investigated. The films have a good selectivity and reusable ability. The specific fluorescence response of the UTF is attributed to a strong interaction between ER and BSA. Circular dichroism (CD) revealed that the secondary conformation of BSA has been changed from α-helical structure to β-sheet after adsorbed on $(ER/LDH)_{26}$ UTF, further confirmed the interaction between BSA and ER/LDH film. These results demonstrate that ER/LDH system can serve as a good candidate for the solid-sate luminescence and sensor materials for BSA.

1. Introduction

There has been a growing interest in the use of xanthene dyes and their related compounds as labeling and sensing biomolecules, because of the high extinction coefficients, the excellent quantum yields, and their ability to attach to biomolecules [1–3]. For example, a new fluorescent chemosensor based on xanthene complex for nucleoside polyphosphates such as ATP has been reported [4]. Disodium-2,4,5,7-tetraiodofluorescein (erythrosine B, ER), which the hydrogen atoms in xanthene are substituted by halogen atoms, has been used as an efficient laser dye, food coloring in food industry or as a diagnostic tool in medicine [5]. Soedjak was the first to show the effectiveness of using ER in the spectrophotometric determination of protein in aqueous solution [6]. The spectroscopic and photochemical feature of ER dye was studied in aqueous solution in the presence of BSA in a large concentration range [7]. At present, the preferential protein binding and inherent photoluminescence of ER are getting established, making it an attractive tool for the quantitative measurement of proteins in biological samples. Several reports were also published on the interactions of ER as a probe to detect the oxygen content [8], Vitamin B6 [9] and urinary protein [10].

Although much progress has been made in researching the performance of ER dye, there are still existed some drawbacks, such as poor stability, the reduced fluorescence intensity due to molecular aggregation and the small stokes shifts. It is well known that the aggregation of ER dye in the solid state usually leads to fluorescence quenching, which greatly restricts its application in solid-state devices. In order to circumvent these problems and increase both the fluorescence property and photo stability of ER dye, the design of hybrid materials containing an inorganic host represents a valid solution [11,12]. At present, fabrication of the guest molecule with the host material such as silica, montmorillonite, and layered double hydroxides have being largely exploited for potential uses in optoelectronic and biosensing devices [13–16]. In this regard, layered double hydroxides (LDHs) represent suitable hosts, because of the presence of arrays of uniform structure, high surface area and a good biocompatibility. As the important 2-dimensional clay with anion-exchange properties, LDHs have been widely used in the fields of separation, catalysis, biology, and optical materials [17–19]. Recently, the delamination of LDHs into monolayers which can be used as building blocks for the construction of functional ultrathin films has been widely investigated [20,21]. This inspires us to challenge the goal of fabricating ER dye and LDHs film by the

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layer-by-layer (LBL) technique, which is biocompatible and functional in the complex biological milieu.

In this paper, we design and characterize an effective system for the immobilization of ER on LDHs, and explore the consequence of ER/LDH thin film on the interaction with BSA. The obtained nanocomposite films display a uniform morphology with a long-range ordered structure, and can be utilized as a fluorescence chemosensor for the detection of BSA with high selectivity. Furthermore, the ER/LDH UTFs show the advantages of easy regeneration and recycle ability for long-term employment. It demonstrates that our novel strategy is rapid and will efficiently provide the fluorescent sensor in protein detection yields. Through engineering the ER/LDH system, the ultrathin film nanocomposites with tailorable thickness may be created for selective applications, such as enrichment, bioseparation and drug delivery.

2. Experimental section

2.1. Materials

Erythrosin B sodium salt was purchased from Sigma–Aldrich Company. BSA, Glucose, Cysteine, Leucine, Serine, Sodium oleate, and PBS buffer solution were purchased from Sangon Biotech Ltd. Shanghai (China). The analytical grade chemicals including $Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, NaOH, and other nitrate salts of metal ion were used without further purification. The deionized and decarbonated water was used in the preparation experimental processes. The ultrapure water was used in the measurement experiment processes.

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

The $Mg_2Al–NO_3$ LDH precursor was synthesized by the hydrothermal method reported previously [22]. 0.1 g of $Mg_2Al–NO_3$ LDH was shaken in 100 mL of formamide solution for 48 h to obtain a colloidal suspension of exfoliated Mg_2Al-LDH nanosheets. The quartz glass substrate was cleaned in concentrated NH_3:H_2O_2 (v/v 7:3) and concentrated H_2SO_4 for 30 min, respectively. Thereafter, the surface of substrates was hydrophilic and negatively charged. The quartz substrate was rinsed and washed thoroughly with deionized water before use. The multilayer films composed of LDH nanosheets and ER molecule were fabricated on the pretreated quartz glass substrate through the LBL technique. The substrate was dipped in a colloidal suspension (0.1 g/mL) of LDH nanosheets for 10 min and washed thoroughly with deionized water. Then the substrate was immersed into an aqueous solution of ER (10^{-5} mol/L) for another 10 min followed by washing. Subsequently, the deposition operation for LDH nanosheets and ER was repeated n times to obtain a multilayer film of $(ER/LDH)_n$. The resulting films were dried with a nitrogen gas flow for 2 min at 25 °C.

2.3. The response of BSA measurement

The BSA solutions with the different concentrations were prepared by dissolving the BSA in PBS buffer solution (pH 7.0). The fluorescence chemosensor of ER/LDH UTF was immersed into a quartz cell with BSA solution, and its response was recorded by a RF-5301PC fluorophotometer with a liquid holder based on the fluorescence quenching as a function of the BSA concentration. All experiments were conducted at 25 °C.

2.4. Characterization

The UV–vis absorption measurements were performed on a Shimadzu UV-2501PC spectrometer. Fluorescence emission spectra were recorded on a RF-5301PC fluorophotometer in the range 400–700 nm with the excitation wavelength of 500 nm and a slit width of 5 nm. 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). X-ray diffraction patterns (XRD) measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu K_α radiation ($\lambda = 0.15418$ nm) at 40 kV, 30 mA, with a scanning rate of 10 min^{-1}, and the 2θ angle ranging from 2° to 10°. Circular dichroism (CD) measurements were performed on a Jasco J810 spectropolarimeter at 25 °C, cover the wavelength range 190–260 nm. The scan speed was 20 nm/min with 0.2 nm resolution.

3. Results and discussion

3.1. Assembly of the $(ER/LDH)_n$ UTFs

The assembling process of the $(ER/LDH)_n$ UTFs was monitored by UV–vis absorption spectra of quartz substrates coated with $(ER/MgAl\text{-}LDH)_n$ (Fig. 1A, n varies from 2 to 30). The inset in Fig. 1A shows that the intensities of the absorption bands at ~545 nm attributed to ER increase linearly as a function of bilayer number n, indicating a regular and uniform growth of the UTFs, which was further confirmed by the gradual color enhancement with the

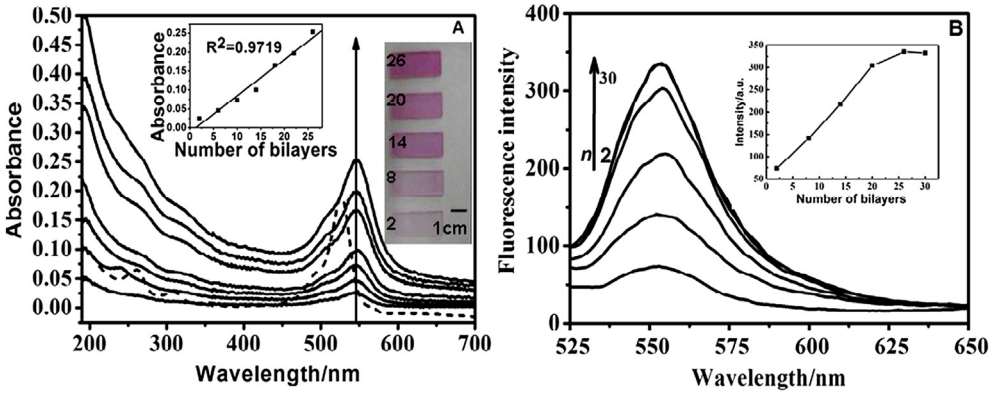

Fig. 1. (A) UV–vis absorption spectra of the $(ER/LDH)_n$ UTFs assembled on quartz substrates (The dashed line shows the absorption of ER in aqueous solution. Inset: the linear relationship between absorbance at 545 nm and bilayer number n, and photographs with different n under daylight). (B) Fluorescence emission spectra of the $(ER/LDH)_n$ UTFs assembled on quartz substrates ($n = 2$, 8, 14, 20, 26 and 30, respectively. The inset is the fluorescence intensity at the maximum emission peak varying with the increase of bilayer number n).