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Concentration-dependent dye aggregation in the LbL-assembly of fluorescein isothicyanate labeled poly(allylamine hydrochloride) and poly(acrylic acid) on cotton fabrics

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ABSTRACT

In this work, we prepared layer-by-layer (LbL) assembled films of fluorescein isothicyanate labeled poly(allylamine hydrochloride) (PAH-FITC) and poly(acrylic acid) (PAA) on cotton fabrics, and researched the influence of the PAH-FITC concentration on the FTIC aggregation. With the LbL assembly, the ratio of FITC dimers to monomers in films approached a constant that was decided by the deposition situation of PAH-FITC on cotton. The concentration increase of the PAH-FITC solution induced more FTIC dyes to deposit on fabrics, thus generating a higher degree of H-aggregation. Interestingly, as the PAH-FITC concentration decreased, a high content of FITC dimers was obtained in LbL-assembled films as well. The possible reason is the excessive PAA in LbL films made the counter PAH-FITC chains coil overlap, increasing the aggregation degree. Additionally, the H-aggregates with weak fluorescence were effectively inhibited in PAH-FITC films, which were prepared by a multi-immersion in the PAH-FITC solution. This work shows the concentration-dependent dye aggregation in LbL-assembly, providing a new strategy for the applications of dye molecules on fabrics.

1. Introduction

Dye molecules, which possess conjugated chromophores, can easily form the aggregates (*i.e.* H-aggregates and J-aggregates) and thus significantly convert their photophysical properties in the applications of sensors, metal ion detection, protein detection, diagnostic imaging, photodynamic therapy, dye-sensitized solar cells, and organic photovoltaic cells [1–4]. With the development of wearable computing, the control of dye aggregation on textiles have attract more and more attention for practical applications. H-aggregates (face-to-face stacking), with a higher lowest excited level, are characterized by the blue-shifted absorption band and the weak fluorescence [5–7]. In contrast, the head-to-tail stacked J-aggregates have a lower energy, which provides the strong, narrow and red-shifted absorption band and the high quantum yield for emission. To optimize the performance of the final devices of dyes, many efforts have been devoted to the dye aggregation, including the formation of aggregates and the transformation between H-aggregates and J-aggregates [8–11]. Compared with the chemical methods for improving molecular structures of dyes, one practical strategy to change the dye aggregation is the physical methods including the adjustment of solvents, ionic strengths, pH values, fabrication temperatures and procedures [12–17]. Self-assembled procedures have been proven to be useful to change dye aggregates, by the assist of non-covalent interactions [18–20].

LbL-assembly as a versatile tool is suitable to various materials and controllable by the concentration, pH value, temperature and even the number of assembly cycles [21–27]. Layer-by-layer (LbL) assembly technique has been used to realize the dye aggregation for various applications of membrane materials [28–34]. In our previous work, the dye aggregation behaviors in LbL-assembled coatings on cotton fabrics was researched [35]. The results indicated that LbL-assembly technique played a significant role in the applications of dyes on textiles. Conditioning the parameters of LbL-assembly is a promising strategy for changing the dye aggregation. However, to date, little attention has been paid on the dye aggregation in LbL-assembly. Herein, we reported the

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concentration-dependent of dye aggregation in LbL-assembly. Fluorescein isothicyanate labeled poly(allylamine hydrochloride) (PAH-FITC) was LbL-assembled with poly(acrylic acid) (PAA) on cotton fabrics. With the LbL assembly, the ratio of FITC dimers to monomers in films approached a constant that was decided by the deposition situation of PAH-FITC on cotton. The concentration increase of the PAH-FITC solution induced more FTIC dyes to deposit on fabrics, thus generating a higher degree of H-aggregation. Interestingly, as the PAH-FITC concentration decreased, a high content of FITC dimers was obtained in LbL-assembled films as well. This possibly attributed to the excessive PAA in LbL films made the counter PAH-FITC chains coil overlap, increasing the aggregation degree. Additionally, the weak-fluorescent H-aggregates in the PAH-FITC film, which was constructed by multi-immersing cotton fabrics in the PAH-FITC solution, can be effectively inhibited. This work shows the concentration-dependent dye aggregation in LbL-assembly, providing a new strategy for the applications of dye molecules on fabrics.

2. Experimental section

2.1. Materials

100% previously scoured and bleached cotton plain woven fabric (72 ends × 60 picks, 80 g/m^2) was used as substrates. 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHP$_3$MAC, 65% w/v) was obtained from Tokyo Chemical Industry Co. Ltd. Fluorescein isothicyanate (FITC), poly(allylamine hydrochloride) (PAH, *Mw*~15000) and poly(acrylic acid) (PAA, *Mw*~1800) were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was procured from Shanghai Lingfeng Chemical Reagent Co. Ltd. Sodium bicarbonate and sodium carbonate were bought from Shanghai Titanchem Co. Ltd. Dialysis tube with molecular weight cut-off 7000 was purchased from Shanghai Yuan Ye Shengwu Co. Ltd. All chemicals were used as received without further purification and all experiments used Milli-Q water.

2.2. Synthesis of PAH-FITC

Fluorescein isothicyanate labeled poly(allylamine hydrochloride) (PAH-FITC) was prepared by a protein labeling technique [36]. First, 25 mL, 4.0 mg/mL PAH aqueous solution was added into a 500 mL sodium carbonate buffer (pH = 9.0). Then, 10 mg FITC was solved into 10 mL DMSO solvent, followed by ultra-sonicating for 10 min. Afterwards these two solutions were mixed together and gently stirred for 6 h. The obtained PAH-FITC solution (1% labeling degree) was purified by Millipore water in darkness for 48 h.

2.3. Coating fabrication

Cotton fabric was first pretreated to produce enough positive charges for the subsequent LbL-assembly, which was reported in our previous works [28]. Using the LbL-assembly technique, PAA/PAH-FITC films were deposited on the pretreated cotton, as depicted in Fig. 1. A cotton fabric was repeatedly immersed into the PAA and PAH-FITC solutions for 15 min and then three distilled water baths for 1 min. The alternate immersion steps of cotton fabric were conducted for preparing PAA/PAH-FITC films. Additionally, we also prepared PAH-FITC films by repeatedly immersing the fabric into the PAH-FITC solution. In this research, to clarify the influence of concentration on the aggregation, we changed the concentration of PAH-FITC solution from 0.1 to 1.0 and 4.0 mg/mL while keeping PAA at 1.0 mg/mL. The obtained films were denoted as (PAA/PAH-FITC$_{0.1}$)*n, (PAA/PAH-FITC$_{1.0}$)*n, (PAA/PAH-FITC$_{4.0}$)*n, (PAH-FITC$_{0.1}$)*n, (PAH-FITC$_{1.0}$)*n, and (PAH-FITC$_{4.0}$)*n, where n is the number of assembly cycles. It is noted that all immersion and rising steps were carried out on shaking table at 25 °C with 100 rpm for homogeneous deposition.

2.4. Characterization

The surface morphologies of fabric samples were observed by optical microscopy (Nikon, Japan) and scanning electron microscopy (SEM, TM 3000, Hitachi, Germany). The absorption spectra were obtained by a UV-visible-near infra-red (UV-VIS-NIR) spectrophotometer (U-4100, Hitachi, Japan). Emission fluorescence spectra were determined using a fluorescence spectrometer (Quant Master 40, Photon Technology International Inc., USA). The fluorescent images were captured by a confocal laser scanning microscope (CLSM, Carl Zeiss LSM 700, Jena, Germany) using 488 nm excitation.

3. Results and discussion

The fluorescein isothicyanate labeled poly(allylamine hydrochloride) (PAH-FITC) was prepared for the LbL assembly on cotton fabrics, as shown in Fig. 1. Because of the labeled FITC dye, the orange PAH-FITC solution showed a UV-Vis absorption characteristic peak of 497 nm and can be excited to emit a yellowish-green fluorescence under a 365 nm UV-light. Using the electrostatic interaction between the amine groups of PAH-FITC and the carboxylate groups of poly(acrylic acid) (PAA), the LbL-assembled PAA/PAH film was constructed on cotton fabrics, as depicted in Fig. 1. To view the deposition of different concentration PAH-FITC on cotton fabric, the uncoated and coated fabrics were characterized by optical microscopy and scanning electron microscopy (SEM). In Fig. 2, different from the white color of raw cotton, the PAA/PAH-FITC coated cotton fabrics exhibited the orange of PAH-FITC. With the increase of PAH-FITC concentration from 0.1 to 1.0 and 4.0 mg/mL, the orange color was darker obviously, and the films became thicker and even filled up the gaps among fibers.

In Fig. 3a–c, the UV-Vis absorption spectra of (PAA/PAH-FITC$_{0.1}$)*n, (PAA/PAH-FITC$_{1.0}$)*n and (PAA/PAH-FITC$_{4.0}$)*n (n = 2, 4, 6, 8, 10) on cotton exhibited two strong peaks of FITC monomers and dimers [35,37], obviously changing in the wavelength and the maximum absorption. For the (PAA/PAH-FITC$_{1.0}$)*n cotton, the wavelength of FITC monomer peak went into a blue-shift 503 to 485 nm during the LbL assembly, whereas the emerging dimer peak was fixed at 461 nm. Furthermore, considering of the growth of FITC dimers at 461 nm, we confirmed the H-aggregation of fluorescent agent FITC by $\pi-\pi^*$ interactions between the benzene rings of FITC. For the higher concentration (4.0 mg/mL) of PAH-FITC, the fast blue-shift of monomer peak and the rapid growth of dimer peak indicated that the dense dye was contributed to a higher degree of H-aggregation. Interestingly, for the lower concentration of (PAA/PAH-FITC$_{0.1}$)*n, the monomer and dimer peaks both maintained at 485 nm and 461 nm, respectively. Furthermore, the dimer peaks of the (PAA/PAH-FITC$_{0.1}$)*n at the initial LbL-assembly were obviously stronger than that of the (PAA/PAH-FITC$_{1.0}$)*n and (PAA/PAH-FITC$_{4.0}$)*n. The majority of dimer peaks in (PAA/PAH-FITC$_{0.1}$)*n reached and maintained at the maximum absorption in all detected spectra. These results illustrated that the PAH-FITC in a dilute solution absorbed with a high content FITC dimers, possibly resulting from the coil of PAH-FITC polymer chains induced by the excessive PAA on the cotton surface.

To further understand the adsorption growth behavior, Fig. 3d represents the monomer absorption with respect to the number of deposition cycles. It can be seen that, with the increase of PAH-FITC concentration from 0.1 to 1.0 and 4.0 mg/mL, the higher concentration play positive effect on the deposition of polyelectrolyte. The