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Study of Rhodamine-Derivated Thin Films by a Modern and Simple Process of Deposition

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ABSTRACT

The dye Sulphorhodamine (SR) belongs to the a family of organic dye. This dye can interact electrostatically with fibrinogen protein (Fib) to form organic-organic hybrid layer-by-layer (LbL) self-assembled film onto a poly(allylamine hydrochloride) coated quartz substrate. The degree of dye aggregations in LbL films was found to depend on concentrations of both, as evidenced by UV–vis absorption spectroscopic technique.

Keywords : Hybrid Layer-By-Layer, Sulphorhodamine, UV–Vis Absorption Spectroscopic Technique

I. INTRODUCTION

As new thin-film manufacturing technologies emerge, surfaces that enable localized and precise controlled re- lease of active therapeutics can be fabricated [1- 8]. Strat- egies for the fabrication of ultrathin film devices include the Langmuir–Blodgett method [9, 10], self-assembled monolayer techniques [11, 12], and layer-by-layer (LbL) assembly [13–22]. LbL assembly is most suited for the fabrication of films used for drug delivery because it imposes no bindings to the size and shape of the film and does not require high pressure or temperature. In the LbL assembly process, multilayer films are deposited onto the surface of the substrate via alternate adsorption of the interacting materials. A variety of materials, including polyelectrolytes, micelles, graphene oxide (GO), nanoparticles, and proteins can be used as building blocks for LbL-assembled multilayer films [23–26]. The materials interact with each other via driving forces such as electrostatic interactions, hydrogen bonds, covalent bonds, and bio-specific interactions. These properties allow the controlled release of the drug, depending on the materials used in the particular multi- layer film, containing the drug. Thus, the LbL technique can be considered as the most appropriate method for preparing nano-multilayer films incorporated with therapeutic molecules [27, 28].

The dye Sulphorhodamine (SR) can interact electrostatically with fibrinogen protein (Fib) to form organic-organic hybrid layer-by-layer (LbL) self-assembled film onto a poly(allylamine hydrochloride) coated quartz substrate. In this paper, we have tried to show that the degree of dye aggregations in LbL films was found to depend on concentrations of both, as evidenced by UV–vis absorption spectroscopic technique.

Fabrication :

For fabrication of alternate LbL self-assembled film of Sulpho-Rhodamine (SR) and fibrinogen (Fib) protein, electrolytic deposition bath was prepared by triple distilled deionized Milli-Q water. Quartz substrates were first dipped into PAH solution (concentration of 0.5 mg/ml) for 15 min followed by subsequent rinsing

in deionized water for 2 min and drying in N2 air. The dipping of the substrates was done by a commercial computer controlled dipcoating unit (Model: Xdip-SV1, Make: Apex Instrument Co, India). Both electrostatic and van der Waals interactions are responsible for adsorption of PAH layer onto the quartz substrates and attains entropically a favorable conformation in the solid substrate. The substrates were then dipped into aqueous dispersion of MMT of desired concentrations for 15 min followed by same rinsing and drying procedure. Thus SR/Fib LbL film was prepared. The substrate containing SR/Fib was then emerged into the solution of cationic dye SR for 15 min to adsorb the dye molecules in the top of SR/Fib LbL films. Finally the substrate was rinsed with deionized water and subsequently dried. The purpose of rinsing after each deposition is to remove any surplus cations or anions loosely bound to the terminal layer of LbL film as this can affect the local electrostatic environment as well as the homogeneity of the surface of LbL film. Thus organic-inorganic hybrid LbL film (SR/Fib) was fabricated. For preparing multilayered LbL film, one layer SR/Fib LbL film was alternately dipped into SR and Fib solutions for the same dipping time followed by subsequent rinsing and drying steps. The whole adsorption procedure was performed at a constant room temperature (25 °C). The LbL films were also deposited at different pH and different dipping time for the dye solution as discussed in the present work.

Results and Discussions:

Figure-1 shows the UV–vis absorption spectra of pure SR in aqueous solution (concentration of 10-5 M) along with SR/Fib mixed aqueous solution for different varying concentration of Fib colloidal suspension in the mixture. Pure SR shows a strong monomeric absorption band with peak at around 664 nm and is attributed to a π π^* transition and a shoulder at around 610 nm which is possibly associated with a vibronic transition of the main 0–1 transition of isolated dye molecules . However, it is well known that with increasing solution concentration, dimers of SR start to form and the corresponding absorption band is observed at around 605 nm. Also at very high concentration SR or more higher order dye aggregates are formed because of increased intermolecular vibrational coupling of their electronic states.

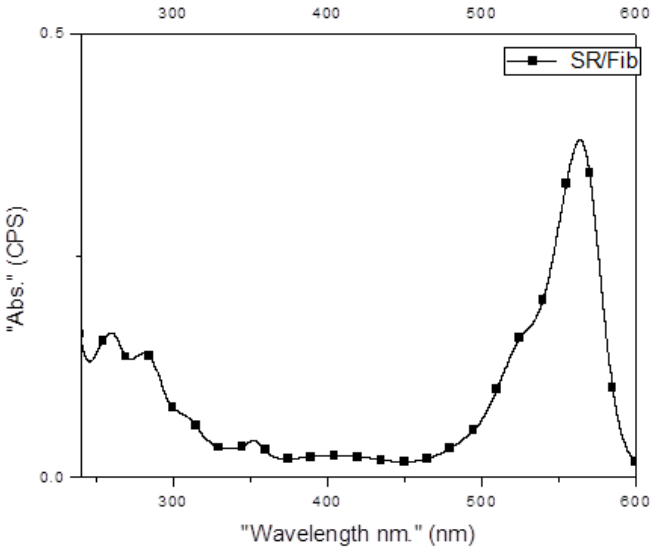

Figure-1

On the other hand, in the SR/Fib mixed solution absorption spectrum it is interestingly observed that with increasing Fib concentration, the intensity of monomeric band of SR systematically decreases and the vibronic shoulder (at 610 nm) is more prominent up to the Fib concentration of 0.02 mg/ml because the dimers of SR are formed gradually. However, their concentration is relatively low. On further increase in Fib concentration up to 0.03 mg/ml, the 610 nm band shifted to 605 nm i.e. the number of SR dimers increases sufficiently for higher dye loading at the Fib surfaces. Some fractions of the dye dimers are also formed due to intercalation between clay nanosheets. The appearance of blue shifted band observed at 605 nm is definitely due to increased number of SR dimers which are generally referred to as the H-dimers or aggregates.

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