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Layer-by-layer self-assembled multilayer of cationic spiroxazine and polystyrenesulfonate

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Abstract

Novel spiroxazine (SO) bearing two positive charges has been synthesized via an improved synthetic route. Alternate multilayer films of an SO and anionic polystyrenesulfonate (PSS) are prepared by self-assembly based on layer-by-layer (LBL) deposition using electrostatic attraction between oppositely charged ions. The build up of the multilayer films is followed by UV–vis spectroscopy and atomic force microscopy (AFM). Photoinduced ionic conductivity response and salt effect of SO/PSS multilayer have been also studied.

Keywords: Spiroxazine; Layer-by-layer deposition; Photochromism; Ionic conductivity; Multilayer

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1. Introduction

Ultrathin organic films are of considerable interest because of their potential technological applications in the fields of surface coatings, sensors and optoelectronics [1]. These films are commonly formed using Langmuir–Blodgette (LB) deposition or self-assembly techniques based on chemisorption.

Recently developed electrostatic layer-by-layer deposition has been shown to be a simple and versatile method for assembling thin films [2]. Alternate adsorption of a polycation and a polyanion is readily achieved by excessive adsorption of polyelectrolytes on oppositely charged surfaces. LBL method developed by Decher et al. has also proved to be a simple and effective technique for fabricating ultrathin organic multilayer films. This technique provides a way to control the construction of ultrathin films at nanoscale and a long-term stability of the film can be obtained easily. This approach has been extended to various other materials, including inorganic nanoparticles [3–5], dyes [6–9] and biological macromolecules such as DNA [10,11] and proteins [12,13].

Spiroxazines are photochromic compounds analogous to spiropyrans. These two classes of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring results in spiroxazine having the advantage of greatly improved resistance to prolonged UV irradiation, which confers a much more commercial importance to them [14]. On UV irradiation the C–O bond of the colorless spiroxazine is cleaved and the colored merocyanine form is obtained. Thus, the interconversion of spiro (SP)-merocyanine (MC) systems, SP-MC, has been extensively investigated due to their potential applications in molecular devices and uses in biotechnology [15].

We have previously reported the synthesis and self-assembly of the spiroxazine containing alkanethiol with an amide group incorporated into the backbone [16–18]. Also reported has been the photoinduced thickness change of a self-assembled spiroxazine monolayer based on surface plasmon resonance spectroscopy [19]. Here we report the synthesis of a new spiroxazine containing two quaternary ammonium

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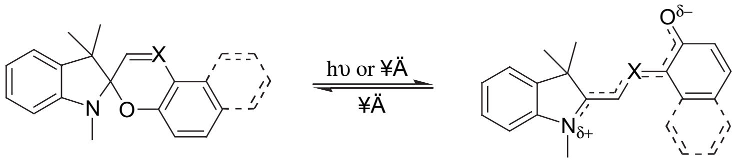


(colorless, closed form) (colored, open merocyanine form)

X = CH : spiropyran
X = N : spiroxazine

groups. The cationic spiroxazine synthesized was soluble in a mixture of dimethylsulfoxide (DMSO) and water and used as cationic electrolyte to fabricate thin films by means of an LBL deposition process driven by the electrostatic attractions developed between positively charged SO and negatively charged PSS. The preparation, characterization, and LBL multilayer fabrication of the newly synthesized SO were described.

2. Experimental

2.1. Materials

1,3,3-Trimethyl-2-methyleneindolin, 1-nitroso-2,7-dihydroxynaphthalene, 1,6-dibromohexane, *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine (TMPDA), and polystyrenesulfonate (sodium salt, $M_w = 70,000$) (PSS) were purchased from Aldrich. The analytical grade solvents were dried with an appropriate drying agent and distilled.

2.2. Synthesis of spiroxazine **4**

1,3,3-Trimethyl-6′-hydroxyspiro[2*H*]-indol-2,3′-[3*H*]-naphth[2,1-*b*][1,4]oxazine **3** was prepared from 1,3,3-trimethyl-2-methyleneindoline **1** and 1-nitroso-2,7-dihydroxynaphthalene **2** according to the method described in Refs. [20,21]. Yield 50%; mp 212–214 °C; Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.89; H, 4.97; N, 8.59.

A stirred solution of **3** (1 g, 2.9 mmol) and 1,6-dibromohexane (1.47 g, 2.9 mmol) in acetone (150 ml) containing suspended powdered potassium carbonate (0.32 g) was refluxed for 24 h. The solution was filtered and then the filtrate was evaporated under reduced pressure. The product obtained was washed with methanol several times and recrystallized from hexane. Yield 63%; mp 147 °C; MS *m*/*z* M^+ 507; ^1H NMR ($CDCl_3$, δ ppm): 1.35 (s, 6H), 1.57 (m, 5H), 1.91 (m, 4H), 3.44(t, $J = 6.52$ Hz, 2H), 4.18 (t, $J = 6.52$ Hz, 2H), 6.57 (d, $J = 7.52$ Hz, 1H), 6.84 (d, $J = 9$ Hz, 1H), 6.89 (t, $J = 8.04$ Hz, 1H), 7.03 d, $J = 9.1$ Hz, 1H), 7.08 (d, $J = 6.52$ Hz, 1H), 7.20 (t, $J = 7.16$ Hz, 1H), 7.56 (d, $J = 9.04$ Hz, 1H), 7.63 (d, $J = 9.04$ Hz, 1H), 7.71 (s, 1H), 7.84 (s, 1H); Anal. Calcd for $C_{28}H_{31}N_2O_2Br$: C, 66.27; H, 6.16; N, 5.52; O, 6.31. Found: C, 66.95; H, 6.43; N, 6.07; O, 6.27.

2.3. Synthesis of dye **6** (SO)

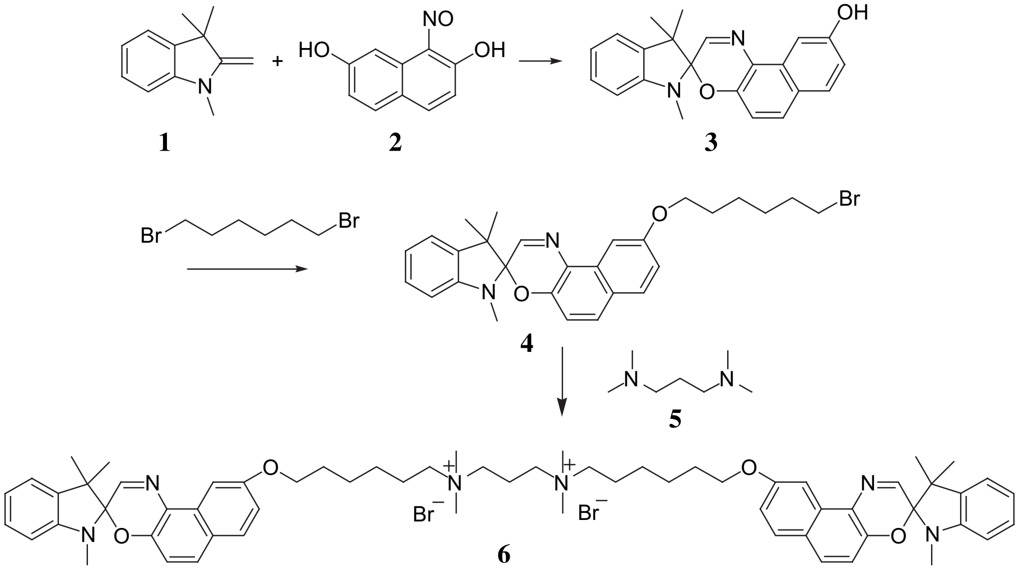
Dye **4** (4.9 mmol) and 0.32 g (2.46 mmol) *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine **5** were refluxed in 150 ml 2-methoxyethanol for 48 h. The reaction mixture was cooled to room temperature and 2 l diethyl ether was added. The precipitated dye was suction filtered, washed with ether, methanol and dried. Yield 40%; mp 193 °C; ^1H NMR (DMSO-d_6, δ ppm): 7.84 (s, 2H), 7.82 (s, 2H), 7.76 (d, $J = 9.04$ Hz, 2H), 7.70 (d, $J = 9.04$ Hz, 2H), 7.15 (m, 4H), 7.05 (d, $J = 4.56$ Hz, 2H), 6.91 (d, $J = 9.04$ Hz, 2H), 6.83 (t, $J = 8.04$ Hz, 2H), 6.66 (d, $J = 7.52$ Hz, 2H), 4.14 (t, $J = 6.04$ Hz, 4H), 3.29 (m, 8H), 3.02 (s, 12H), 2.69 (s, 6H), 1.81 (m, 6H), 1.71 (m, 4H), 1.55 (m, 4H), 1.38 (m, 4H), 1.28 (s, 6H), 1.25 (s, 6H).

2.4. Substrate cleaning and multilayer preparation

The glass slides (20 × 10 × 1 mm) were used as substrates for UV–vis spectroscopy. The surface of the glass is pretreated to render a net negative surface charge by placing it in 2% KOH aqueous solution under sonication for 1 h. A negatively charged glass slide was first immersed into a solution containing 0.16 g SO in a mixture of 14 ml Milli-Q water and 6 ml DMSO for 20 min. After rinsing three times in Milli-Q water, the modified substrate was dried with gentle stream of nitrogen. The layered support is then transferred into a solution containing 0.21 g PSS in 20 ml Milli-Q water. This process is repeated until the desired number of bilayers of SO/PSS is obtained. All adsorption procedures were carried out at room temperature.

2.5. Measurement

Melting points were determined using an Electrothermal IA 900 and are uncorrected. A multichannel photodiode detector (MCPD, Otsuka Electronics, Co., Japan) was used to obtain visible absorption spectra and CHN analyses were carried out with a Carlo Elba model 1106 analyzer. ^1H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Atomic force microscopy (AFM) of the sample surface morphology in air by using a Nanoscope IV Multimode. The photographic images were recorded in the conventional height mode (tapping mode, normal AFM). For the measurement of photoinduced ionic conductivity, the device comprised with



Scheme 1. Synthesis of spiroxazine **6** (SO).

two ITO glass (3 cm × 3 cm) separated by a 0.1 mm thickness spacer of PET film was prepared and placed so as to face each other on the side of the cell, and the edges of the cell were sealed with insulating epoxide resin. The multilayer assemblies of SO/PSS were deposited on the surface of only one ITO glass. Prior to final sealing, the space between the electrodes was filled with 1 mmol tetra-*n*-butylammonium perchlorate, $[CH_3(CH_2)_3]_4NClO_4$, as electrolyte. A high pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm. In order to investigate the photochromic properties of the multilayer, the UV light source was switched and radiated the multilayer.

3. Results and discussion

A functional alkyl bromide, spiroxazine **4**, was prepared by the reaction of 1,3,3-trimethyl-6′-hydroxyspiro[2*H*]-indol-2,3′-[3*H*]-naphth[2,1-*b*][1,4] oxazine **3** and 1,6-dibromohexane as described in Scheme 1. 1,3,3-Trimethyl-6′-hydroxyspiro[2*H*]-indol-2,3′-[3*H*]-naphth[2,1-*b*][1,4] oxazine **3** was prepared from 1,3,3-trimethyl-2-methyleneindoline **1** and 1-nitroso-2,7-dihydroxynaphthalene **2** according to the method described in Refs. [20,21]. Then spiroxazine **4** was reacted in 2-methoxyethanol with *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine **5** to yield bisquaternized compound **6**. Fig. 1 shows a schematic illustration of a self-assembled film fabricated with alternating layers of two compounds. In step A, a substrate with a negative charged surface is immersed in the solution of the positively charged SO. In step B, the substrate is dipped into the solution containing the negatively charged PSS.

The growth of SO/PSS multilayer films formed by the sequential adsorption of SO and PSS was examined by using UV–vis spectroscopy. In Fig. 2, the adsorption spectra upon UV irradiation in self-assembled multilayer containing SO and PSS are shown. The regularity of the LBL adsorption is demonstrated in the plot of the absorbance of SO in its

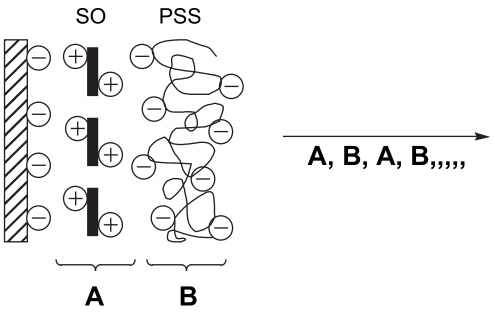


Fig. 1. Schematic view of a self-assembled alternating multilayer film composed of a cationic spiroxazine and polystyrenesulfonate.

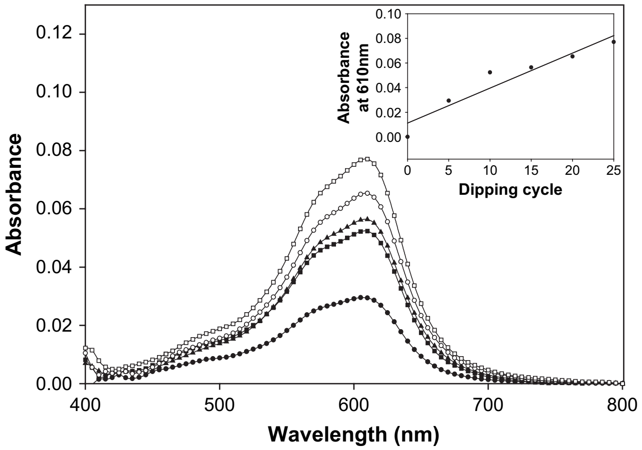
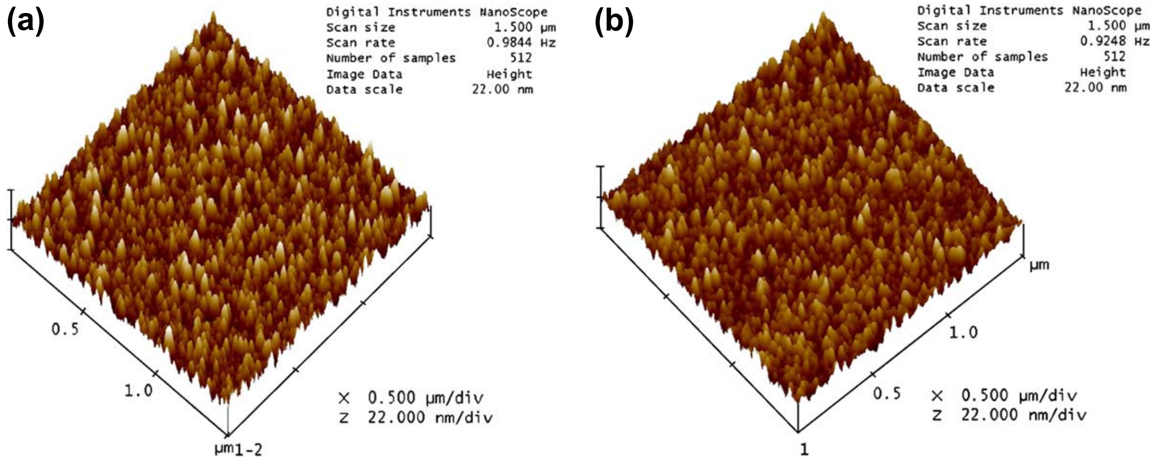
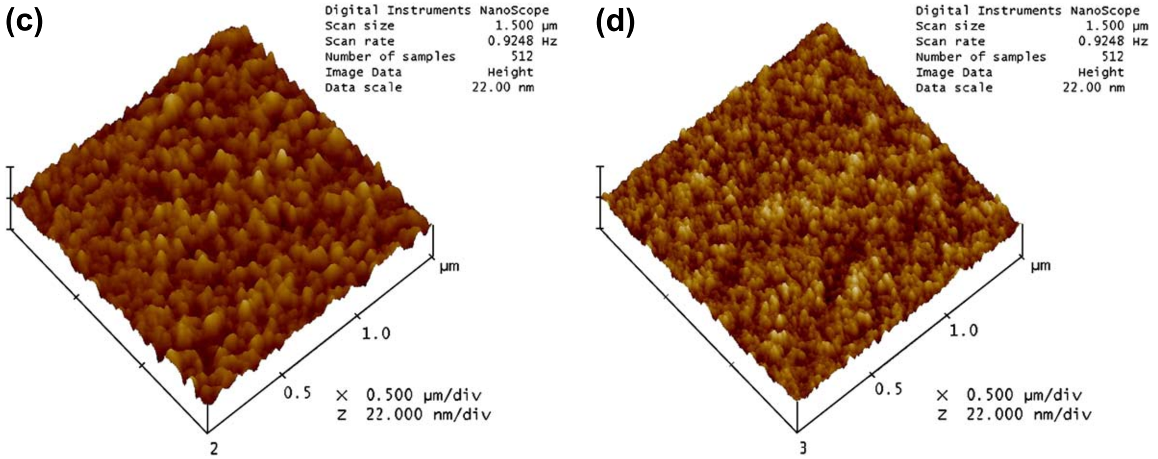


Fig. 2. UV–vis absorption spectra of SO/PSS multilayer films through a consecutive LBL deposition. The insert shows the increase in absorbance at 610 nm as a function of deposition cycles.



Glass (RMS = 3.29)

2 layers (RMS = 2.58)



5 layers (RMS = 2.14)

10 layers (RMS = 1.35)

Fig. 3. Morphology of the SO/PSS layers: (a) nude glass, (b) 2 layers, (c) 5 layers, and (d) 10 layers.

maximum at $\lambda = 610$ nm versus the number of dipping cycles applied.

More detailed information on the surface structure and the direct image of the self-assembled multilayers on glass surface can also be obtained with AFM. The morphology of 2, 5, 10 pair layer SO/PSS films was observed by AFM (Fig. 3). The mean value of the height from the cross-sectional analysis of raw glass, the surface roughness, RMS, is about 3.29 nm (Fig. 3). The roughness of the 2, 5 and 10 pair SO/PSS multilayers is determined to be 2.58, 2.14 and 1.35 nm, respectively. This decreased surface roughness arises from the stepwise chemical assembly.

The photoinduced ionic conductivity response was analyzed at 15 °C and is shown in Fig. 4. The photoinduced ionic conductivity can be estimated from the expression: $(1/R_t)/(1/R_0)$ where R_0 and R_t are the resistance before and after UV irradiation. The ionic conductivity increased upon UV irradiation which brought about the generation of zwitterion form, and subsequently decreased in dark which brought about the generation of closed spiro form. Sufficient reversibility was found in this polymer and this response was completely synchronized with that in the absorbance changes.

With bolaform amphiphile, addition of inorganic salts usually results in increased aggregation behavior, which aids in adsorption to oppositely charged surfaces [22–24]. The salt effect on the SO/PSS multilayers was investigated. The

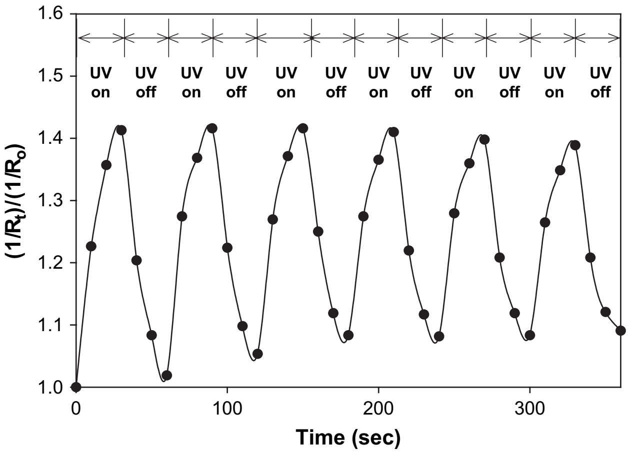


Fig. 4. Photoinduced ionic conductivity response for SO/PSS multilayer on ITO at 15 °C ($[[CH_3(CH_2)_3]_4NClO_4] = 1 \times 10^{-3}$ M).

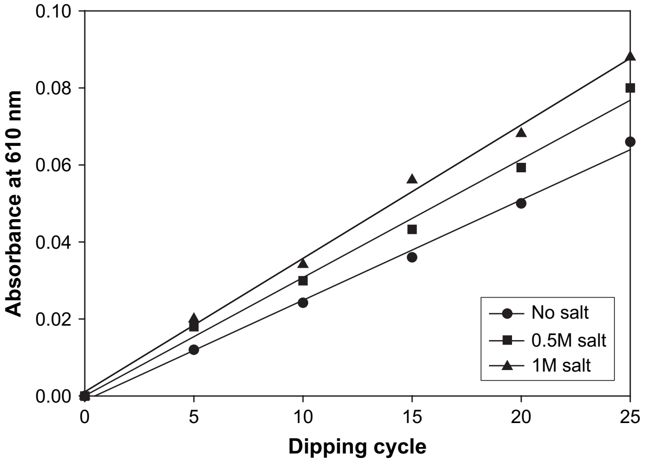


Fig. 5. Salt concentration effect on SO/PSS multilayer (measured at 610 nm after UV irradiation). The solution is adjusted to three different ionic strengths by the addition of NaCl: no salt (●); 0.5 M (■); 1 M (▲).

dipping water/DMSO solution of SO is adjusted to two different ionic strengths by addition of NaCl: 0 (no salt), 0.5 and 1 M. Fig. 5 shows the UV–vis absorbances of SO/PSS multilayers at 610 nm as a function of number of layers deposited. The results showed that high salt concentrations tend to promote adsorption to surfaces.

4. Conclusion

In this study, we investigated the synthesis and LBL deposition of positive charged spiroxazine (SO) with polystyrenesulfonate (PSS). Alternating thin films of the cationic SO and PSS were obtained by the sequential deposits of SO and PSS on to a glass substrate. UV–vis absorbance measurement reveal that the layer-by-layer (LBL) deposition process was relatively linear and highly reproducible from layer to layer. Reversible photoinduced ionic conductivity response was found in the resulting SO/PSS multilayer and was synchronized with reversible heterolytic cleavage of the C (spiro)–O bond under UV irradiation. The salt concentration plays an important role in influencing deposition for the SO/PSS pair.

Acknowledgements

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