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Polyelectrolytes-assisted Layer-by-layer Assemblies of Graphene Oxide and Dye on Glass Substrate

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Pyronin Y (PyY) and graphene oxide (GO) were assembled on a glass substrate by the electrostatic layer-by-layer (LbL) method with the assistance of polyelectrolytes. Firstly, the glass surface was modified with the successive adsorption of positively charged PEI (polyethylenimine) and negatively charged PSS (poly(sodium-p-styrenesulfonate)) to enhance the loading of PyY molecules and GO sheets. Secondly, PyY molecules and GO sheets were loaded on the glass substrate depending on their charges after the successive adsorption of polyelectrolyte layers via a procedure of {PEI/GO/PEI/PSS/PyY/PSS}_n. Thus, the LbL thin films containing PyY molecules and GO sheets, which were remained stable for months, were homogeneously coated on the glass substrate. The photophysical and morphological features of the LbL films were examined. The spectroscopic data of the LbL films based on PyY revealed that H-aggregate and monomers structures of the dye molecules in the LbL films were formed by a function of the number of layers. Furthermore, the effect of immersion time on the molecular interaction of PyY molecules with the other components were studied in detail. SEM (Scanning electron microscope) was used to examine the morphologies of as-prepared LbL thin films. SEM images revealed that the morphologies of LbL thin films were changed by the immersion time and the number of layers.

1. Introduction

Nowadays, graphitic materials, which are graphene and graphene oxide, have attracted a great deal of attention due to their fascinating features for various applications.¹ A flexible material graphene oxide (GO) is used in possible applications containing adsorption processes,² sensors,³⁻⁵ energy storages,⁶ Li-ion batteries,⁷ supercapacitors,⁸ solar cells⁹ and electronic-optoelectronic devices.¹⁰⁻¹¹ The chemical structure of GO are commonly known that the hydroxyl and epoxy groups are mostly found in the basal plane while carboxylic acid and carbonyl groups are available at the sides.¹² These functional groups on GO sheets result in the covalent and non-covalent modification of GO sheets. The electrostatic impulsion among GO sheets is due to the fact that their negative surface charges form a stable GO aqueous dispersion¹² while graphene tends to form big domains via π - π stacking and van der Waals interactions.

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†Electronic Supplementary Information (ESI) available: Normalized UV-Vis absorption spectra of {PEI/GO/PEI/PSS/PyY/PSS}_n multilayer film at various layers and SEM image of {PEI/GO}₁ multilayer film

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Avoiding the accumulation of GO and graphene layers on a surface is of great significance in the carbon-based applications since the unmatched properties of graphitic materials are solely related to individual sheets.¹³ To overcome this problem, GO layers can be respectively modified by immersing the oppositely charged polyelectrolyte solutions and its self-aggregate is prevented.^{2,13}

Dye molecules have attracted a considerable attention in electronics and optoelectronics due to their low-cost and controllable design at the molecular level. In this regard, many dye molecules having various absorption maxima are synthesized. PyY, which is a positively charged organic dye compound, is a xanthene derivative such as acridines and rhodamines, and it is comprehensively researched in the literature. One intriguing property of dye molecules is the presence of molecular aggregation playing an essential role in many technological applications as photographic industry, photosensitization, molecular optoelectronic devices, light-harvesting biological systems and nonlinear optical materials owing to their unexcelled optical behaviors. Molecular aggregates are formed due to a highly ordered association of dye molecules. The driving forces in the associations are electrostatic interactions (Coulomb, Van der Waals etc.), hydrogen bonding and hydrophobic interactions. The molecular interactions among dye monomers causes to energy splitting and spectral shifting in the

absorption spectra of the dyes compared to that of monomers. Considering molecular stacking and optical properties, the aggregates are mainly two types as H-type (head-to-head stacking) and J-type (side-by-side stacking). The absorption profiles of aggregates are definitely different: J-aggregates have narrow and a red-shifted absorption band, while H-aggregates have generally a broad and blue-shifted absorption band compared to those of monomer and J-aggregate. Moreover, the fluorescence properties of aggregates reveal that H-aggregates are non-fluorescent while J-aggregates are strong fluorescent species. The presence of H-aggregates decrease the quantum yield and fluorescence lifetime of dyes.⁴⁻¹⁶ The molecular aggregation process of pyronin dyes in various aqueous solutions are reported depending on the host-guest interaction.^{12,14-16} The host-guest interaction causes the formation of the dye aggregation at diluted concentration due to the localized high dye concentration in the host material. Recently, we have reported that the unique colloidal features of GO sheets in aqueous dispersions can be used as a platform causing dye aggregates.¹² Dye molecules and GO sheets on a solid surface are assembled by using various methods. The layer-by-layer (LbL) technique, which is a versatile method having many advantages such as simplicity, low-cost and controlling film thickness and structure, is used for this purpose. To achieve a high level of surface content, sequential layer of oppositely charged materials, which are polyelectrolytes, inorganic particles, dyes, nanoparticles, are used.¹⁷⁻²² The morphology and thicknesses of LbL film can be easily controlled by adjusting the number of layers, immersion time, temperature,²³ ionic strength¹⁹ and pH.^{17,20}

In the present study, the fabrication of polyelectrolyte-assisted LbL film composed of PyY and GO was reported. The interaction among PyY, GO sheets and the polyelectrolytes caused the formation of H-aggregates of PyY molecules on a multilayer film. The effects of immersion time on the film properties were evaluated. The photophysical properties of LbL films were investigated by UV-Vis. and steady-state fluorescence spectroscopies. The morphological variations of LbL film was monitored by SEM.

2. Experimental section

2.1. Materials

PEI (Mw=25.000), PyY, acetone, methanol, NaOH and HCl was purchased from Sigma-Aldrich. PSS (Mw=70.000) was purchased from Acros Organics. PEI is cationic polyelectrolyte while PSS is negatively charged. Solution pH was adjusted using an appropriate amount of NaOH or HCl. Natural graphite flakes (average particle size 325 mesh) were purchased from Alfa Aesar. All chemicals were used as received. Deionized (DI) water obtained from GFL 2002.

2.2. Characterization methods

SEM (Scanning Electron Microscopy) images were obtained with a Zeiss EVO40. UV-Vis absorption spectra were collected using

a Perkin-Elmer (Model Lambda 35) spectrophotometer at room temperature. Steady-state fluorescence spectra of the sample were performed by a Shimadzu RF-5301 PC spectrofluorophotometer.

2.3. Preparation of stable GO dispersions

GO was synthesized from graphite powder according to the modified Hummers method. The synthesis and characterization data of GO sheets have been given in our previous work.¹² GO of 0.5g/L were dispersed in DI water by an ultrasonication bath for 3.5 hours at room temperature. In order to remove the water-insoluble GO particles due to gravitational force, the dispersion was stayed for a week at room temperature and decanted. Thus, the GO aqueous solution became homogeneous and remained stable for months. The GO aqueous dispersion of 15mg/L was prepared for LbL thin film applications.

2.4. Preparation of glass slides

The glass slides were cleaned by immersing in pure methanol and acetone for thirty minutes in sonicator, respectively. Thereafter, the substrates rinsed with deionized water three times for ten minutes in sonicator and then dried at 100°C. As a result, the hydrophilic glass slides were obtained for LbL thin film fabrication.

2.5. Preparation of Multilayer Assemblies

The dye solution was prepared from a fresh stock solution of PyY (1.0×10^{-3} M). A multilayer film containing GO sheets, PyY molecules and the polyelectrolytes was assembled according to the following procedure: Firstly, the glass slide was immersed in the PEI aqueous solution (wt 1%, pH 7.9) in order to obtain a positively charged surface. After that, the PEI-deposited glass slide was immersed in the GO aqueous dispersion (15 mg/L, pH 4.6) for a specified period. In this way, the negatively charged GO sheets were loaded on the PEI-modified glass surface. Secondly, the PEI-GO-deposited glass slide was immersed again in the PEI solution, and then it was immersed in the PSS aqueous solution (wt 1%, pH 6.5) to form a strong negatively charged surface. The upper layer PSS-coated glass slide was immersed in the PyY aqueous solution (1.0×10^{-5} M, pH 6.5 in phosphate buffer). Finally, the latest glass slide was immersed in the PSS aqueous solution (wt 1%, pH 6.5). The explained procedure was called one-cycle for multilayer film (Fig. 1), and the time for the slide hold in the solutions are equal. After each immersion, the film was washed by water for 30 sec and dried by argon. The procedure was successfully repeated to attain the desired number of layers, which was scheduled as $\{\text{PEI/GO/PEI/PSS/PyY/PSS}\}_n$ (Fig. 1). All LbL films were homogeneously prepared and stayed stable for months.

3. Results and discussion

A facile route to prepare GO-based composites is significant because the composites are used in many technological applications. In this study, PyY molecules and GO sheets were loaded on the glass substrate with the assistance of PSS and PEI polyelectrolytes taking into account the order of

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{PEI/GO/PEI/PSS/PyY/PSS}_n. Herein, the strong interaction between PSS and PEI ensured the formation of perfect LbL films, in which many charged groups on PSS and PEI adsorbed highly PyY molecules and GO sheets, respectively. Briefly, PyY molecules were located between PSS layer in the LbL films when GO sheets were existed between PEI layers. This work causes many studies that various charged components such as organic, inorganic and biomolecules are loaded together in thin film at a desired ratio for various applications. The details of the characterization data for GO sheets were given elsewhere.¹² The optical and morphological properties of the fabricated LbL thin films were characterized with absorption, fluorescence spectroscopies and SEM. The optical properties of the LbL thin films were examined depending on PyY.

3.1. Absorption spectroscopy

3.1.1. LbL assembly of {PEI/GO/PEI/PSS/PyY/PSS}_n

GO sheets, which have many functional groups, are highly probable to constitute a well-dispersed aqueous dispersion except for its irreversible accumulations. The adsorption of water-soluble polyelectrolytes on GO sheets prevents its undesired accumulations in aqueous dispersions. This phenomenon allows forming a perfect coating related to the GO-based thin films on a substrate. A suitable method to prepare a thin film containing GO sheets is the LbL method. However, the loading of dyes and GO sheets on substrates are limited depending on their charged groups. The undesired condition is solved by using water-soluble polyelectrolytes that have many charged groups. Herein, hydrophilic PEI and PSS polyelectrolytes were used as an intercalant for GO sheets and PyY molecules, which enhanced loading the dye and GO on the substrate. According to LbL film process, {PEI/GO/PEI/PSS/PyY/PSS} multilayer film was grown on the glass substrate. One cycle designed as {PEI/GO/PEI/PSS/PyY/PSS} was represented in Fig 1.

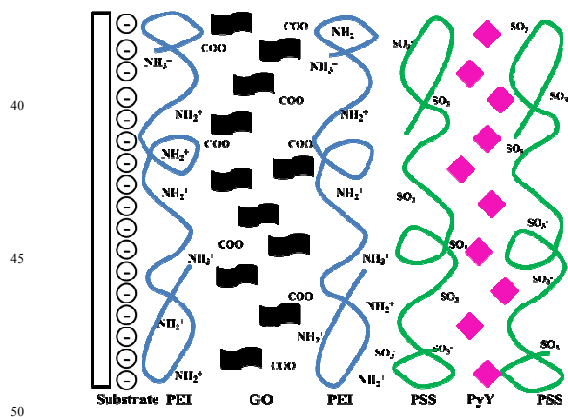


Fig. 1. Representation of one-cycle LbL coating for a multilayer film.

UV-Vis spectroscopy is an excellent technique to follow the film assembly in an LbL method due to the strong visible light harvesting property of dye molecules. Therefore, the growth process of {PEI/GO/PEI/PSS/PyY/PSS} multilayer film on the glass substrate can be monitored by UV-Vis spectroscopy after each cycle. In the alternate LbL films, the interaction of PyY molecules with the other materials on the substrate affects the photophysical properties of the dye. Moreover, the photophysical properties of the dye molecules depend on the loaded dye on the substrate. UV-Vis absorption spectra of {PEI/GO/PEI/PSS/PyY/PSS}_n multilayer film fabricated at various layers were shown in Fig. 2.

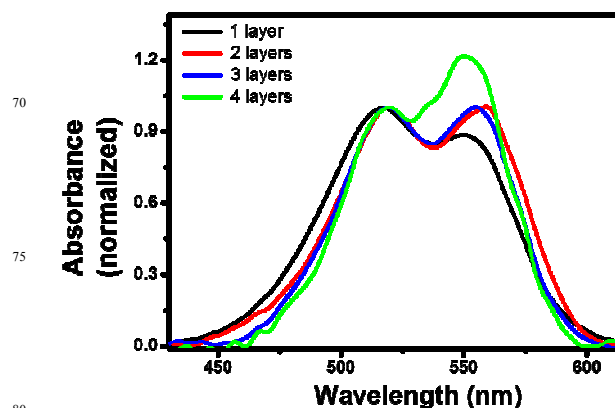
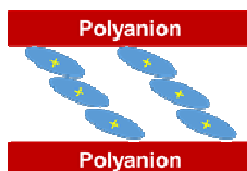


Fig. 2. Normalized UV-Vis absorption spectra of {PEI/GO/PEI/PSS/PyY/PSS}_n multilayer film at various layers.

The spectra in Fig. 2 were normalized at ~519 nm to monitor the changes in the absorption characteristic of PyY depending on the number of layers. The immersion time of the glass substrate in each solution were kept constant as ten minutes during the film growth period. In the single layer LbL film, two absorption bands, which their maxima located at 517 nm and 550 nm, were observed. The absorption band at 550 nm was attributed to monomeric PyY molecules while the other band at 517 nm originated from H-aggregates of the dye in the LbL thin film. The absorption band at 517 nm was more intense than that of the other band. This revealed that H-aggregates were predominant due to the dye molecules interacted with PSS, which was localized high dye concentration on the polyanion. As can be seen from Fig. 2, the absorption properties of LbL films are changed depending on the number of layers. In the two layers LbL film, the positions and relative intensities of the absorption bands were changed. The monomer band maximum was shifted from 550 nm to 559 nm while the aggregate band was monitored at 519 nm. At the same time, the intensity of the monomer band increased compared to that of the aggregate band. Additionally, it was shown that an absorption shoulder at approximately 550 nm was formed when the absorption spectrum was carefully examined (Fig. 2 and Fig.

S1). These results revealed that PyY molecules interacted with different substances such as GO sheets and PSS polyelectrolytes taking into account their charges. By comparing the absorption spectra in Fig. 2 and the LbL film growth procedure, the absorption band at 550 nm belonging to the dye monomer interacted with PSS while the band at 559 nm corresponds to the monomer attached with GO sheets or the organized monomers between PSS layers. Since the interaction of PyY with GO sheets in the LbL films had a very weak possibility taking into account the procedure given in Fig. 1, the other alternative was predominate. In this regard, molecular organization resulting in this type absorption spectrum of PyY was considered as follows:



Scheme 1. Molecular arrangement of PyY molecules between two PSS layers.

For the three layers LbL film, the monomer absorption band of PyY was located at 555 nm while its H-aggregate band was formed at 519 nm. When the number of layers for LbL film was reached four, the absorption spectrum of the film was very different compared to those of one and three layers LbL film. The monomer absorption band at 550 nm increased while H-aggregates at 520 nm decreased. Additionally, the absorption shoulders at ~ 535 nm were ascribed to H-dimer formation of PyY. When the absorption spectrum given in Fig. 2 was carefully evaluated, it was observed that an absorption shoulder at ~ 570 nm was appeared depending on the number of layers. The explanations mentioned above for PyY-based LbL film can be clearly observed from Fig .S1. By increasing the number of layers, both the interaction between LbL layers and the loading the dye caused the alteration of the photophysical properties of PyY in the LbL film. Consequently, the absorption study revealed that both monomeric and H-aggregate LbL films of PyY were fabricated depending on the number of layers.

3.1.2. The effects of immersion time on LbL film of {PEI/GO/PEI/PSS/PyY}₁

The effects of immersion time on the LbL film properties were evaluated with UV-Vis spectroscopy. Increasing the immersion time from 10 min to 50 min into each solution for the substrate in {PEI/GO/PEI/PSS/PyY}₁ multilayer film was observed to change the monomer-aggregate balance of PyY (Fig. 3). As clearly seen from Fig. 3, the immersion time supported the formation of H-aggregates of PyY molecules because of increasing the loading and rearrangement of PyY molecules during film growth period. The aggregation tendency of PyY depending on the immersion time caused the broadening of their absorption spectrum as a function of the aggregation degree.

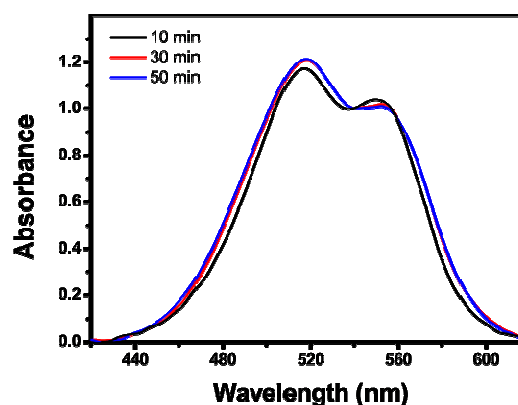


Fig. 3. UV-Vis absorption spectra of {PEI/GO/PEI/PSS/PyY}₁ multilayer film prepared at various immersion time (the spectra were normalized at 540 nm).

3.2. Fluorescence spectroscopy

3.2.1. LbL assembly of {PEI/GO/PEI/PSS/PyY/PSS}_n

The molecular organization of PyY in the LbL thin film causes the alteration of its fluorescence property since the monomeric dye is highly fluorescent. Especially, the presence of nonfluorescent H-aggregate structures formed in the LbL thin film was evaluated for the fluorescence intensity of dye. As seen from Fig. 2, the absorption spectrum of LbL film was depended on the number of layers. It is known that the fluorescent property of dye considerably changed compared to that of the monomer when the dye aggregation took place. The fluorescence spectra of {PEI/GO/PEI/PSS/PyY/PSS} multilayer film depending on the number of layers were taken at an excitation wavelength of 510 nm (Fig. 4).

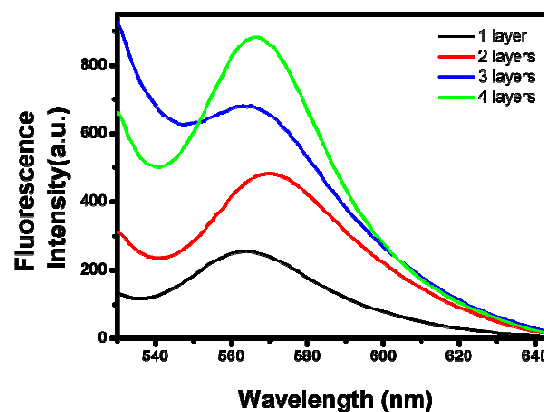


Fig. 4. Fluorescence spectra of {PEI/GO/PEI/PSS/PyY/PSS}_n multilayer film at various layers (λ_{ex} = 510 nm).

The dilute concentration of PyY in water is strongly fluorescent and its band maximum is located at 570 nm.¹² For the single layer LbL film, the fluorescence band maximum of dye was observed at 565 nm. When the number of layers for the LbL film was increased, the band maximum was shifted and its fluorescence intensity was remarkably changed. At the four layers LbL film,

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the fluorescence intensity of PyY in the LbL film was very high than those of the others since the monomeric formation of the dye was dominant (Fig. 2).

3.2.2. The effect of immersion time on the LbL film of {PEI/GO/PEI/PSS/PyY}₁

The immersion time on the LbL thin film was followed by fluorescence spectroscopy. As seen from Fig. 3, increasing the immersion time induced to form nonfluorescent H-aggregates. Since the presence of H-aggregates quenched the fluorescence of dye,¹² the immersion time was changed from 10 min to 50 min in the fabrication of {PEI/GO/PEI/PSS/PyY}₁ multilayer film. The fluorescence spectra of the LbL films were given in Fig. 5. As seen from Fig. 5, the fluorescence band of PyY was formed at 565 nm and its fluorescence intensity was quenched increasing the immersion time. This observation depending on the immersion time confirmed that H-aggregates increased in the LbL film quenched the fluorescence intensity of the LbL film.

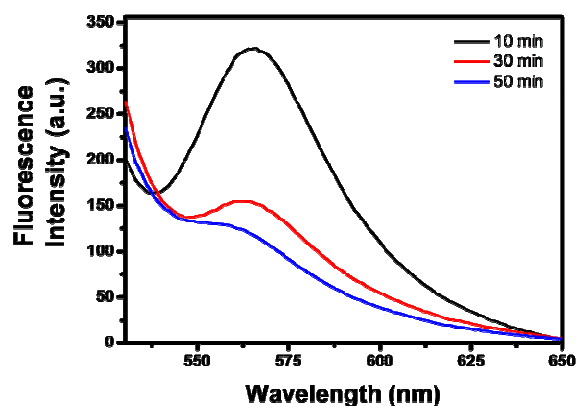


Fig. 5. Fluorescence spectra of {PEI/GO/PEI/PSS/PyY}₁ multilayer films via different immersion time ($\lambda_{\text{exc}}=510$ nm).

3.3. Morphological analysis of LbL films

The LbL film morphology can be studied depending on the film preparation conditions such as the number of layers and the immersion time. The spectroscopic data revealed that the photophysical properties of LbL films were changed with the mentioned film parameters. In this regard, SEM is a widespread and unique technique to examine the surfaces of LbL thin films. Firstly, the effect of the number of layers on the LbL film morphology was examined for one cycle and four cycles multilayer film (Fig. 6). Herein, the immersion time kept constant as 10 min.

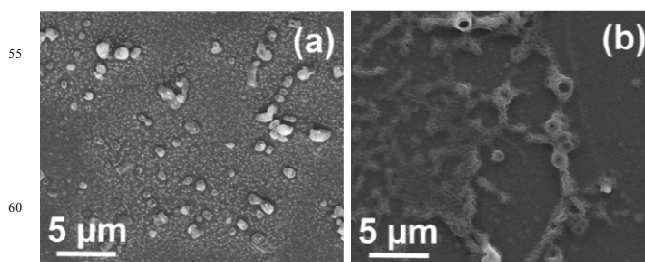


Fig. 6. SEM images of the LbL film: (a) one cycle and (b) four cycles.

As shown in Fig. 6a, the film surface was covered with small particles with some individual domains. Fig. 6b revealed that the surface became rough and porous by increasing the number of layers when SEM image of single layer LbL film compared to that of four layers LbL film.

The morphologies of the LbL film were also monitored depending on the immersion time from 10 min to 50 min. SEM images of the LbL film grown at the immersion times of 10, 30 and 50 min were shown in Fig. 6a and 7.

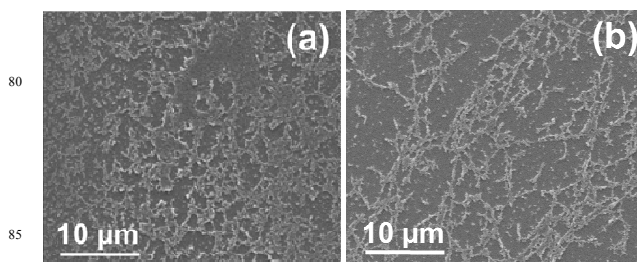


Fig. 7. The immersion time effect on LbL film morphology: SEM images of PyY-based LbL film (a) 30 min and (b) 50 min.

The morphological variations of the LbL films were clearly observed by the immersion time varied from 10 min to 50 min. While the morphology of the LbL film fabricated at 10 min had been covered with small particles (Fig. 6a), the surface formed at 30 min was composed of irregular domains in micrometer scale (Fig. 7a). When the immersion time was 50 min (Fig. 7b), it was seen that the branch-like structures were formed on the substrate. The observations obtained from Fig. 6a and 7 revealed that the morphology of the LbL film from the small particles to the branch-like structures resulted from increasing the formation of H-aggregates. The presence of GO sheets in the LbL film was checked by SEM study. In the one-cycle, SEM image was taken after GO sheets adsorbed on the surface (Fig. S2). As seen from the figure, GO sheets were homogeneously loaded on the film surface.

4. Conclusions

The LbL thin film process was used to fabricate thin film containing PyY molecules and GO sheets by the assistance of polyelectrolytes. The most appropriate and stable alternate LbL films were fabricated according to {PEI/GO/PEI/PSS/PyY/PSS} cycle. It was determined that the photophysical and morphological properties of the LbL films depended on both the number of layers and the immersion time. Increasing the number of layers caused the LbL film of monomeric PyY while increasing the immersion time supported the formation of H-aggregates of the dye. SEM studies revealed that the branch-like structures at the immersion time of 50 minutes were uniformly formed on the surface while the surface was composed of small particles at the immersion time of 10 minutes. The variations in SEM images were compatible with the spectroscopic results. Consequently, the presented LbL film procedure in this study can be used for various charged components such as organic, inorganic and biomolecules which are loaded together in thin film at a desired ratio.

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