Layer-by-layer self-assembled multilayer films of sulfonated-\(\beta\)-cyclodextrin and its reversible adsorption of methyl orange

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Abstract. Multilayer film based on photosensitive \(p\)-diphenyl diazonium salt (biPh-N\(^{2+}\)) and sulfonated-\(\beta\)-cyclodextrin (S-\(\beta\)-CD) were fabricated by layer-by-layer self-assembly. The ionic bonds formed between diazonium salt and sulfonic acid ion in the multilayer film converted to covalent bonds and formed stable ultra-thin film when the diazonium groups decomposed under UV light irradiation. Meanwhile, the concentration of S-\(\beta\)-CD aqueous solution can influence the self-assembled multilayer films, while the pH value (pH=3~9) had little effect on the self-assembled process except the strong alkaline solution (pH=11). Moreover, based on the electrostatic interactions of S-\(\beta\)-CD and MO to form a host-guest complexation, the multilayer film of (biPh-N\(^{2+}\)/S-\(\beta\)-CD)\(_{12}\) can absorb methyl orange (MO), and which can release reversibly in ethanol.

1. Introduction

Layer-by-layer (LBL) assembly, a common convenient method to fabricate functional multilayers, coatings, nanocapsules, and so on, has aroused broad attention from the first introduction by Decher in 1992 \cite{1,2}. Cyclodextrin and its derivates (CDs) are a large family as macrocyclic receptor with hydrophilic exterior and hydrophobic interior cavity. It has attracted more attention in environmental treatment due to its efficient absorption\cite{3-5}. Similarly, as host-guest molecules, CDs have been utilized to construct surface multilayers, monolayer films and layer-by-layer assemblies containing selective binding sites\cite{2-8}.

At present, organic dyes are widely used in many industries \cite{9}, such as leather, ink, textiles, printing, coatings, and beauty. During the dyeing process, organic dyes will enter the industrial wastewater. Such as, methyl orange (MO) as a typical synthetic dye, is ubiquitous in various industrial effluents and causes bad influence to environment even human health\cite{10,11}. Therefore, it is important to detect and eliminate MO in industrial effluents. There are various methods proposed to adsorb MO, including physical, biological and chemical, etc \cite{12,13}. Among them, using multilayer film to adsorb MO is a promising technology because of its low cost, high efficiency and environmental friendly \cite{14}.

Herein, a self-assembled ultra-thin film ((biPh-N\(^{2+}\)/S-\(\beta\)-CD)\(_{12}\)) was prepared with sulfonated-\(\beta\)-CD (S-\(\beta\)-CD) and photosensitive diazonium salt (biPh-N\(^{2+}\)), which was monitored using UV-vis absorption. And the absorbing and desorbing behaviours of the multilayer film (biPh-N\(^{2+}\)/S-\(\beta\)-CD)\(_{12}\) toward MO were investigated.
2. Experimental Section

2.1. Preparation of layer-by-layer self-assembly of multilayer film (biPh-N2+/s-β-CD)12

![Figure 1 schematic diagram of the preparation of multilayer film (biPh-N2+/s-β-CD)12](image)

The pre-treated quartz plate was etched in HF solution for 30 minutes. Taked it out and then washed the quartz plate with deionized water. After the quartz plate was dried, placed it in biPh-N2+ aqueous solution for 5 minutes. After it was dried, placed the quartz plate in the S-β-CD aqueous solution for another 5 minutes. Repeated the above operation 12 times and obtained the assembled multilayer film of (biPh-N2+/S-β-CD)12. The multilayer film was irradiated under strong ultraviolet light (230 μW/cm², 360 nm) for 45 minutes, so that the diazo groups in biPh-N2+ were completely decomposed and generated benzene radicals [11]. As shown in Figure 1, the benzene radicals reacted with S-β-CD by stable covalent bonds and formed stable ultra-thin film by monitoring the UV-vis spectra.

3. Results and discussion

3.1. Self-assembly of multilayer film (biPh-N2+/S-β-CD)12

Figure 2 shows the entire assembly process by monitoring UV-vis spectra. The absorption band of the multilayer film at 403 nm attributed to the π-π* transition of the diazonium groups of biPh-N2+ gradually increases with the rise of the number of bilayers, and the absorbance increases linearly with the number of bilayers, accompanied by a high correlation coefficient (R²=0.997) (Figure 3). It indicates that biPh-N2+ and S-β-CD can be used to prepare multilayer ultra-thin films by electrostatic interaction of positive and negative charges, and the deposition amount of biPh-N2+ and S-β-CD is relatively uniform in every bilayers. Simultaneously, the diazo group in biPh-N2+ is sensitive to light and heat, thus, the absorption peak at 403 nm due to diazo group disappears after irradiating the multilayer film using strong UV light (Figure 1), indicating the decomposition of diazo group. Subsequently, the benzene radical generates after the photolysis of biPh-N2+ reacts with S-β-CD by sulfonate bond to form a stable self-assembled nano-ultra-thin film[6]. Moreover, the rod-like structure of biPh-N2+ would make the self-assembled film with more ordered microstructure and uniform thickness, resulting in the controllability of layer-by-layer self-assembly process[2,6].
3.2. Effect of pH value and solution concentration on assembled film

The layer-by-layer self-assembled process of multilayer may be influenced by pH value and concentration of s-β-CD solution. As shown in Figure 4, the pH value has a little effect on the absorbance of the assembled film when the S-β-CD solution with pH=3~9, however, higher pH value solution (pH=11) can cause the decrease of the absorbance at 403 nm, indicating the decrease of the multilayer film thickness. It mainly because the combination of N\textsuperscript{2+} and S-β-CD is disturbed by the competitive interaction of N\textsuperscript{2+} and OH\textsuperscript{-} in the strong alkaline solution of pH=11. Moreover, the concentration of S-β-CD aqueous solution has effect on the assembled film (Figure 5), and the largest amount of deposition layer is obtained at the concentration of 0.005 mol/L, and too low or too high concentration is not conducive to the self-assembled process. Because the biPh-N\textsuperscript{2+} density on the surface of the assembled film is constant, only a certain amount of S-β-CD can be adsorbed through the electrostatic interaction of -N\textsuperscript{2+} and -SO\textsubscript{4}. When increasing the concentration, the competitive assembly will affect the ordered arrangement of S-β-CD molecules and reduce the film thickness. Similarly, decreasing the concentration can reduce the S-β-CD molecular density on the surface of the
assembled film, which affects its adsorption quantity on the film, resulting in the thickness of the assembled film decreasing.

3.3. **Adsorption and desorption of (biPh-N\(^2+\)/S-β-CD)\(_{12}\) film to MO**

![Figure 6 The UV-vis spectra of (biPh-N\(^2+\)/S-β-CD)\(_{12}\) film before and after being dipped in MO solution (0.01 mmol/L)](image)

![Figure 7 UV-vis absorbance changes of (biPh-N\(^2+\)/S-β-CD)\(_{12}\) film adsorbed MO with releasing time in water and ethanol](image)

Figure 6 shows the UV-vis absorption spectra of (biPh-N\(^2+\)/S-β-CD)\(_{12}\) film before and after being dipped in the methyl orange (MO) solution, a clear absorption peak at 426 nm appears, which attributing to the absorption of MO infiltrated into the (biPh-N\(^2+\)/S-β-CD)\(_{12}\) film. Further research indicates that the absorbance at 426 nm increases with the dipping time. Simultaneously, MO molecules adsorbed in (biPh-N\(^2+\)/S-β-CD)\(_{12}\) film can release when immersing the film in water and ethanol, as shown in Figure 7, the absorbance at 426 nm decreases with the immersing time. When immersing in ethanol, the absorbance reduces quickly in 10 minutes, indicating a fast release of the MO molecules, then the releasing rate slowed down, no more MO releases after 30 minutes. But in deionized water, only few MO molecules desorbs from the multilayer film. It is mainly because the solubility of MO in ethanol is much higher than that in water\(^6\). According to the above result, the electrostatic interactions of S-β-CD and MO to form a host–guest complexation make MO molecules in the inside of the self-assembled multilayer film instead of the film surface. The hydrophobic cavity of cyclodextrin interacts strongly with the non-polar segment of MO molecule, so it is difficult for MO to release in water. In addition, because the outermost layer of the prepared multilayer ultra-thin film is biphenyl with Poor hydrophilicity. The organic solvent ethanol can slightly swell the multilayer film, resulting in three times MO desorption in ethanol than in water.

4. **Conclusion**

In summary, multilayer film (biPh-N\(^2+\)/S-β-CD) were prepared by layer-by-layer self-assembly, and a stable multilayer ultrathin film obtained after UV light irradiation to form covalent bonds between S-β-CD and biphenyl. This film can selectively absorb MO molecules and release in ethanol.

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