Fabrication of a Stable Nanostructured Ternary Composite Film via Different Driving Forces

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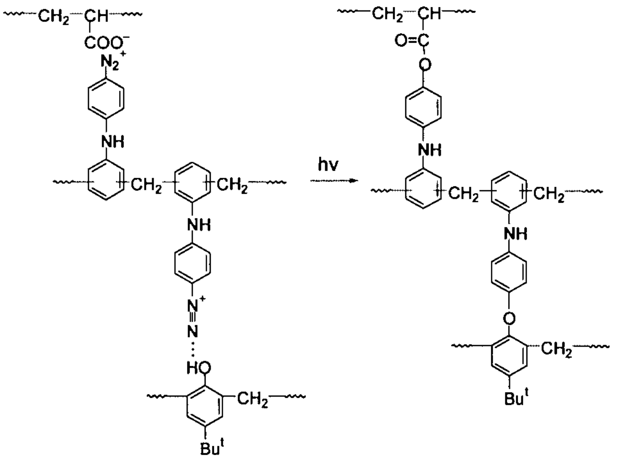
Three characteristic macromolecules have been combined to fabricate muitilayer ultra-thin film with different driving forces of electrostatic interaction and hydrogen bonding attraction, under UV irradiation, both the ionic bond and H-bond between the layers were converted into covalent bond, and the multilayer film becomes very stable towards polar solvents.

In recent years, self-assembled ultrathin films have received considerable interest because they can form supramolecular assemblies with tailored architectures and properties.[1] Through layer-by-layer self-assembly techniques, a variety of materials, including charged and uncharged species, have been successfully assembled into nanolayered structures via electrostatic interaction,[2] hydrogen bonding,[3] coordination bonding,[4] charge transfer,[5] molecular recognition,[6] stereocomplex formation,[7] covalent bond,[8] etc. Due to many advantages of the technique, such as ease in fabrication, independence of substrate size, good mechanism and so on, it has been proven that this technique is a rapid and experimentally simple way to produce a multilayer structure with precise control of the layer composition and thickness. Multicomposites make it possible to combine two or more desirable properties, as in the classic reinforced plastics, or to provide additional stability for otherwise highly labile functional bimolecules or biomolecular assemblies.[9]

Although many successes have been developed to fabricate sorts of characteristic ultrathin films, to our knowledge, most research teams fabricated films using only two components with just one driving force, such as electrostatic interaction, hydrogen bonding, coordination bonding, charge transfer, molecular recognition etc, which could be described as -AB- type. In this article, we reported a novel self-assembly process using three characteristic macromolecules as components: diazoresin (DR), poly(acrylic acid) (PAA), and phenol–formaldehyde resin (PR). The forces between the three components are different: DR as a cationic polyelectrolyte attaches PAA via electrostatic interaction,[10] and as a hydrogen acceptor[11] attaches PR through hydrogen bond to form ternary film and can be described as -ABCB- type, where A, B, C represent PAA, DR and PR, respectively. After UV irradiation, both the ionic bond and H-bond are converted into covalent bond (as shown in Scheme 1), and the film becomes very stable towards polar solvents. Multicomponent self-assembly provides a novel consideration for combining some substances, which cannot be combined in traditional two components self-assembly technique.

DR was prepared according to the method described elsewhere.[12] PR, a polycondensation product of 4-*tert*-butylphenol and formaldehyde. ($M_W \approx 2600$, Chemical Agent Factory, Zhengzhe City, Hunan Province, P. R. China) was used as received. PAA was synthesized according to reference,[13] $M_n \approx 8 \times 10^4$. The film was prepared at room temperature in the dark. A quartz wafer, which was immersed in a fresh solution of 30%H_2O_2/98%H_2SO_4 (v/v = 1:1) and heated to no bubble raising, was used as a substrate. The quartz wafer was first immersed in aqueous solution of PAA (pH was adjusted to 7, and concentration was 0.5 mg/mL) for 5 min, rinsing with deionized water for 3 min and dried. Then the wafer was immersed in 95% methanol solution of DR (pH ≈ 5, concentration was about 0.5 mg/mL) for 5 min, rinsing with 95% methanol for 3 min and dried. Subsequently the wafer was immersed in anhydrous methanol solution of PR (pH ≈ 5, concentration was about 0.5 mg/mL) for 5 min, rinsing with anhydrous methanol for 3 min and dried, finally immersed in DR solution to complete a full cycle. Subsequent cycles were proceeded as PAA–DR–PR–DR–⋯. In every immersion into PAA/DR or PR/DR solutions, a bilayer of PAA–DR or PR–DR was formed on both sides of the quartz wafer.



Scheme 1. The photoreaction of the multilayer film fabricated from PAA, DR and PR.

UV–vis spectra were recorded on a UV–vis spectrophotometer (Shimadzu 2100) which was used to monitor the self-assembly process of the fabrication as shown in Figure 1.

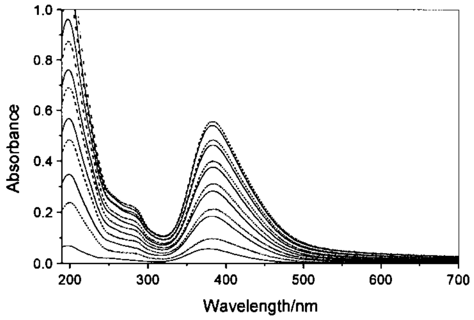


Figure 1. UV–vis spectra of multilayer film from PAA, DR and PR with 1 to 6 cycles of fabrication (from bottom to top). — absorbance of DR–PAA (electrostatic interaction), – – absorbance of DR-PR (H-bonding attraction).

Peaks at 380 nm and 280 nm are assigned to the absorptions of diazonium group of DR and the phenyl group of PR respectively. From Figure 1, we can find that the stepwise fabrication is regular but the absorbance increment of PAA–DR bilayer is much larger than that of PR–DR bilayer. It is concluded that the adsorption on DR is a competitive process, and the H-bonding attraction is much weaker than electrostatic interaction.

The diazonium group is very sensitive towards heat or UV irradiation, and decomposes rapidly. Figure 2 shows the photodecomposition of a 6 cycles fabrication film under UV-irradiation.

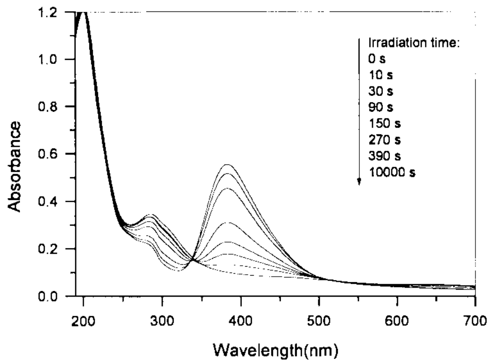
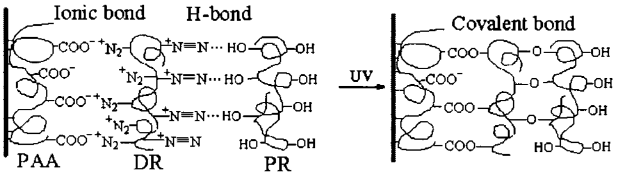


Figure 2. UV—vis spectra of a 6 cycles film irradiated for different times.

Under UV irradiation, both the ionic bond of PAA–DR layer and hydrogen bond of PR–DR layer were converted into covalent bond (Scheme 2), and the multilayer film becomes very stable towards polar solvents. The un-irradiated film will be dissolved completely as it was immersed in dimethylformamide (DMF) only for 5 min at room temperature, whereas the irradiated film shows no change as it was immersed in DMF for 24 h in the same conditions. Therefore it should be valuable in practical use for this kind of nanostructural films.



Scheme 2. Schematic representation of the bond conversion from non-covalent into covalent bond in ternary composites film.

In conclusion, a new kind of multilayer film was fabricated by combining electrostatic interaction of DR–PAA and H-bonding attraction of DR–PR. It is very interesting for nanoassemblies, and should greatly enrich the variety of the self-assemblied multilayer films, as well is important for congregating the desirable properties of macromolecules.

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