

Fabrication of a covalently attached self-assembly multilayer film *via* H-bonding attraction and subsequent UV-irradiation

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A photosensitive ultrathin film has been fabricated from a diazo resin (DR) and phenol-formaldehyde resin (PR) *via* hydrogen bonding, covalent bonds are formed UV irradiation giving a covalently linked ultra-thin film; as a consequence the stability of the film towards polar solvents increases dramatically.

Recently a self-assembly technique to form ultra-thin films *via* H-bonding attraction was developed by Zhang *et al.*¹ and Stockman and Rubner.² However, such H-bonding attraction is very weak, which leads to the films being readily destroyed in polar solvents. In this contribution, we report a new multilayer film fabricated from a diazo-resin (DR) and phenol-formaldehyde resin (PR) formed *via* H-bonding attraction between N⁺N: of DR and -OH of PR in methanol. It has been confirmed that under UV irradiation, following the decomposition of the diazonium group, that covalent bonds form in the film structure and the stability of the film towards polar solvents is substantially increased. To our knowledge, this is the first report of the formation of stable ultra-thin films from a precursor film formed *via* hydrogen bonding attraction.

DR was prepared according to the method described elsewhere.³ PR, a polycondensation product of 4-*tert*-butylphenol and formaldehyde, ($M_w \approx 2600$, Chemical Agent Factory, Zheng-zhe City, Huinan Province, P.R. China) was used as received. The films were prepared at room temperature in the dark. A fresh quartz wafer (fused silica), which was modified with a monolayer of *N*-[3-(trimethoxysilyl)propylethyl]enediamine according to ref. 4, was used as substrate. The quartz wafer was first immersed in a methanol solution of polyvinylpyrrolidone (PVP) (1 mg ml⁻¹) for 5 min. After rinsing with methanol and drying, the wafer was immersed in a methanol solution of PR (1 mg ml⁻¹) for 5 min followed, after rinsing with methanol by immersion in a methanol solution of DR (0.2 mg ml⁻¹) for 5 min. The wafer was then rinsed again with methanol and air dried. In each cycle of immersion into PR and DR solutions, a bilayer of PR-DR is formed on both sides of the quartz wafer.

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 Fig. 1. Peaks at 384 and 284 nm are assigned to the absorptions of diazonium group of DR and the phenyl group of PR. Results show that the

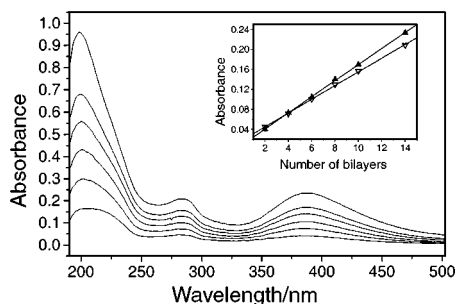


Fig. 1 UV-VIS spectra of multilayer films from PR and DR with various numbers of bilayers; bilayer number (bottom to top): 2, 4, 6, 8, 10, 14; Inset: absorbance at 384 nm (\blacktriangle) and at 284 nm (∇).

absorbance increases uniformly in the assembly process and indicates that the step-by-step fabrication is smooth. The inset plot shows the linear relationship of the absorbance at 384 nm (or 284 nm) with the number of bilayers. Unfortunately, this multilayer film is unstable in the presence of polar solvents. For example, upon immersion of a multilayer film (14 bilayers) deposited on a quartz wafer in DMF for 10 min, most of the layer (>90%, as calculated from the decreased absorbance at 384 nm) was destroyed. This result shows that the stability towards polar solvents of multilayer films formed *via* H-bonding attraction is poorer than for films formed by electrostatic attraction.^{5,6}

It is known that DR decomposes readily under UV-irradiation or upon heating. Fig. 2 shows the photodecomposition of a 14 bilayer film under UV-irradiation (230 μ W cm⁻²). The inset of Fig. 2 drawn from the absorbance at 384 nm shows that this reaction follows first order reaction kinetics under the experimental conditions. The absorption at 284 nm (Ph-O-Ph absorption) increased with a decrease of the absorbance at 384 nm (-N₂⁺ group absorption), which indicates the formation of the Ph-O-Ph ether bond. The conversion of the H-bond to a covalent bond (Ph-O-Ph) is shown in Scheme 1.

The stability of the film towards polar solvents increases dramatically upon exposure of the films towards UV radiation.

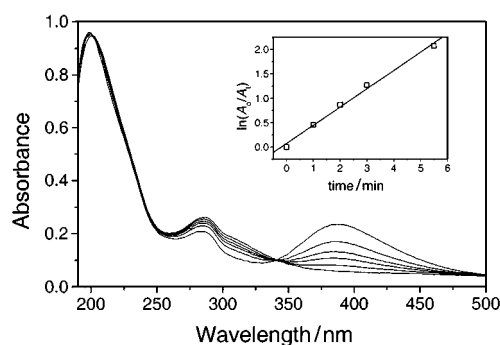
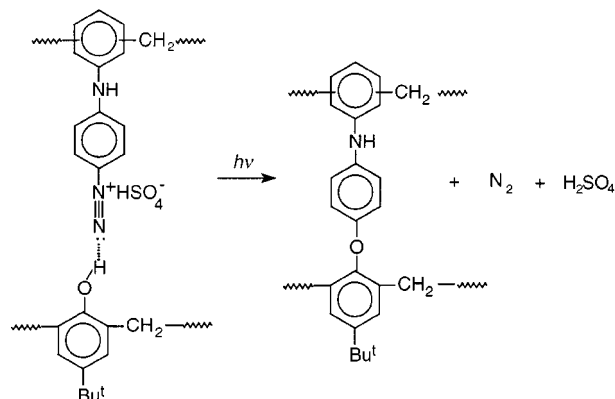


Fig. 2 UV-VIS spectra of a 14 bilayer film irradiated for different times (irradiation intensity = 230 W cm⁻²). Irradiation time (min) 0, 1, 2, 3, 5.5, 20 min. Inset: absorbance at 384 nm.



Scheme 1 The photoreaction of DR and PR in a self-assembled film.

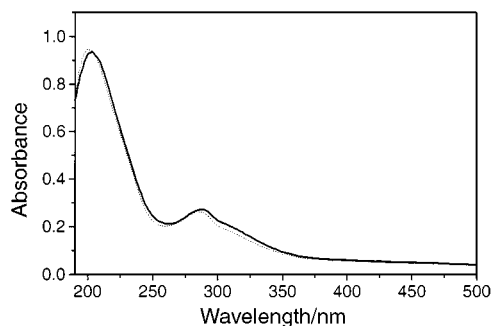


Fig. 3 UV-VIS spectra of a 14 bilayer film before (---) and after (—) etching in DMF for 10 h at 25 °C.

For example after irradiation for 20 min, the film was then immersed in DMF at 25 °C for 10 h with no decrease in absorbance (Fig. 3) being observed. This shows that the film is very stable towards polar solvents after UV irradiation.

To verify the assembly driving force is from the formation of a hydrogen bond between N⁺N of DR and -OH or PR rather than NH of DR and -OH of PR, we studied PVP as an H-acceptor and DR as an H-donor in an attempt to prepare a layer-by-layer film, but this was unsuccessful. It can thus be assumed that the NH group of DR does not form a H-bond with PVP although the latter is a strong H-acceptor.

To further verify the formation of a hydrogen bond and subsequent reaction in the film upon UV irradiation, a film with 20 bilayers was fabricated on a CaF₂ wafer from DR and PR and its IR spectrum (not shown) recorded. A broad peak at 3251.0 cm⁻¹ and a peak at 1371.4 cm⁻¹ indicate the OH group of the PR is in an associated state. A peak at 2155.9 cm⁻¹ is assigned

to the stretching vibration of the diazonium group which is shifted by 11 cm⁻¹ as compared with the free-molecule (2167 cm⁻¹).⁵ Both observations indicate formation of an H-bond between N⁺N: and OH. The film was then exposed to UV irradiation for 20 min at 230 μW cm⁻² and the IR spectra (not shown) were recorded again. The broad peak at 3251.0 cm⁻¹ was found to be weakened with both the peak at 1371.4 cm⁻¹ and the absorption of the diazonium group (at 2155.9 cm⁻¹) disappearing. This result indicates that after exposure to UV light the original H-bond has been destroyed.

In conclusion, *via* hydrogen bond attraction between the diazonium group of DR and the hydroxy group of PR and subsequent UV-irradiation, an ultra-thin film which is stable towards polar solvents was fabricated from DR and PR by a self-assembly technique.

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Notes and references

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