Fabrication of a covalently attached multilayer *via* photolysis of layer-by-layer self-assembled films containing diazo-resins

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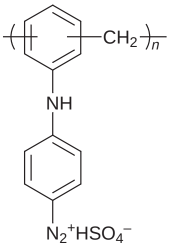
Construction of highly stable covalently attached multilayer films was achieved by UV irradiation of ionic self-assembled multilayer films of diazo-resins and poly(sodium styrene sulfonate).

A layer-by-layer self-assembly technique based on electrostatic interaction as the driving force has attracted much attention in recent years.[1–3] This technique has proved to be a rapid and experimentally very simple way to produce complex layered structures with precise control of layer composition and thickness. However, the stability of such assembled films depends on the nature of solvent and is not always adequate.[4] How to improve the stability of such films is thus still a challenge. Here, we report on photoreactive multilayer films containing diazo-resins as polycations and poly(sodium 4-styrene sulfonate) as polyanions held together by electrostatic interactions. Upon UV irradiation, the adjacent interfaces of the multilayer films react to form a crosslinking structure which greatly improved the stability of the films. These changes were confirmed by UV–VIS and FTIR spectroscopy.

UV–VIS spectra were obtained using a Shimadzu 3100 UV–VIS-NIR spectrophotometer and IR spectra were obtained using a Bruker IFS66V FTIR instrument. The synthesis of the diazo-resin, DAR has been reported elsewhere.[5] The fabrication process of multilayer films containing DAR and PSS was conducted in the dark. The freshly cleaned substrate (quartz or CaF_2 slide) was first immersed in 0.9 vol% aqueous cationic poly(diallyldimethylammonium chloride) (PDDA) solution for 20 min. After rinsing with deionized water, the substrate was alternately dipped into aqueous solutions of PSS (1 mg ml^{-1}) and then DAR (1.5 mg ml^{-1}) for 20 min, with intermediate water washing and N_2 drying. Multilayer films can be formed by repeating the last two steps repeatedly.



DAR

UV–VIS spectroscopy was used to follow the fabrication process. Fig. 1 shows the UV–VIS absorption spectra for 2, 4, 6 and 8 bilayers of DAR/PSS assembled on a quartz slide. The absorbance at 380 nm is attributed to the π–π* transition of the diazonium group.[6] The linear increase in absorbance at 380 nm with the number of layers indicates a progressive deposition. The assembled films were immersed in a ternary mixture of H_2O–DMF–$ZnCl_2$ (3 : 5 : 2, w/w/w) to investigate their stability. This ternary system was chosen because of the high solubility of the polyelectrolyte complex of DAR/PSS in this solvent. Nearly 30% of the assembled films were dissolved after 5 min immersion according to the decrease of absorbance at 250 and 380 nm, and indicates that this type of ionic self-assembled film is not adequately stable in the ternary solvent.

Owing to the well known reactivity of diazonium and sulfonate groups, the above assembled films containing 8 bilayers of DAR/PSS were irradiated with a 30 W medium power mercury lamp at a distance of 10 cm. Fig. 2 shows the changes in UV–VIS spectra of the films with different time of irradiation, from which, we can clearly see that the absorbance at 380 nm decreases dramatically due to the decomposition of the diazonium group and within 5 min, the decomposition had proceeded completely. We then immersed the irradiated films into the same ternary solvent as for the untreated film and sonicated it for 0.5 h. No detectable damage of the films was observed, according to the absorbance at 250 nm, indicating a much greater stability.

From the change of the stability of the multilayer films before and after UV irradiation, it is proposed that photoreaction takes place between the diazonium and sulfonate groups. First, DAR is converted into its phenyl cationic form after released N_2 upon UV irradiation, then an S_N1 type of nuclear displacement by sulfonate occurs[7] as shown in Scheme 1.

Photoreaction changes the crosslinking structure of the multilayer film from ionic to covalent so that a three dimensional network forms which covers the whole substrate including four side faces. This can explain, despite the interaction between the substrate and the first layer of multilayer films not being covalent, the stability of the films in

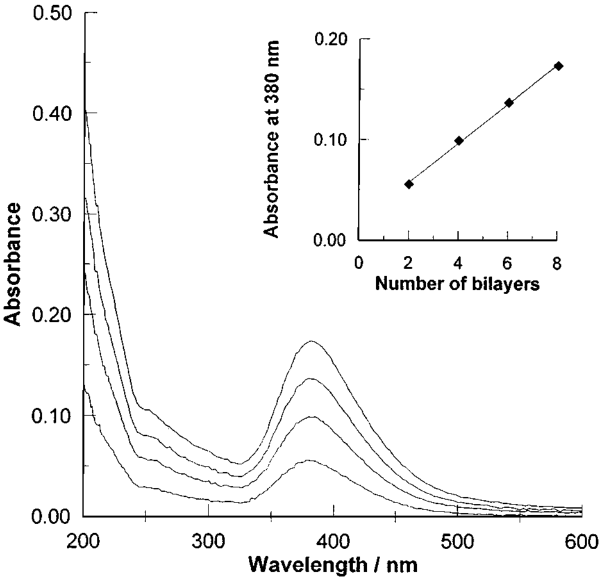


Fig. 1 UV–VIS absorption spectra of multilayer films of DAR/PSS, from the lower to upper, the number of bilayers is 2, 4, 6 and 8. Inset shows the absorption at 380 nm *vs.* the number of bilayers.

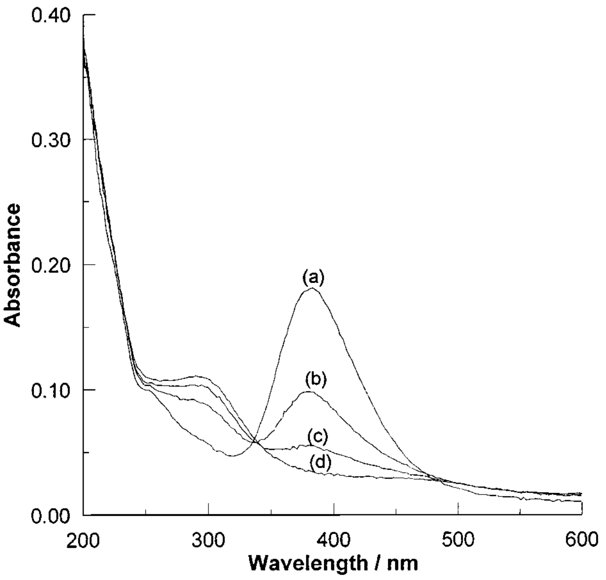
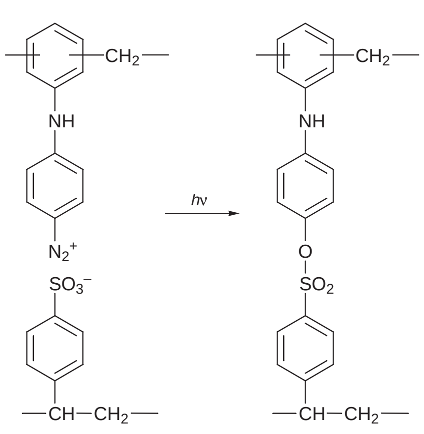


Fig. 2 UV–VIS absorption spectra of eight bilayers of DAR/PSS upon irradiation with UV light for (a) 0, (b) 0.5, (c) 1 and (d) 5 min



Scheme 1 Photoreaction of DAR and PSS

all solvents, such as MeOH, DMSO, DMF, $CHCl_3$ as well as the ternary solvent described above.

The photoreaction of diazonium and sulfonate groups in multilayer films was further confirmed by IR spectroscopy (for IR spectra see http://www.rsc.org./suppdata/cc/1998/1853). Two absorption peaks at 2166 and 1178 cm^{-1} are observed in the IR spectra of 12 bilayers of DAR/PSS assembled on a CaF_2 substrate before UV irradiation, which originate from the asymmetric stretching of CN_2 and symmetric stretching of SO_3^-, respectively. After UV light irradiation, the absorption at 2166 cm^{-1} disappeared completely, indicating the decomposition of the diazonium group. Meanwhile, a new absorption at 1162 cm^{-1} appears which corresponds to the symmetric stretching of the sulfonate coupled with the phenyl group. In layer-by-layer multilayer films, photoreaction should be facilitated to some extent by the close proximity of the diazonium and sulfonate groups.

In conclusion, a new type of covalently attached multilayer film has been fabricated by exploiting the layer-by-layer technique and then by photoreacting diazonium and sulfonate groups at the interface. Owing to the formation of three-dimensional crosslinking structure based on covalent bonding, the resulting multilayer films are much more stable than those based on ionic interactions. Further studies are in progress to assemble functional semiconductor nanoparticles and organic dye molecules into this covalently attached three-dimensional network.

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