

Nanoassembly Film of Carboxylic Polyaniline with Photosensitive Diazo-resin and Its Photoelectric Conversion Properties

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Poly(aniline-*co-o*-anthranilic acid) (PAAA) and photosensitive diazo-resin (DR) in aqueous solution were self-assembled into multilayer ultrathin film through electrostatic interaction. Under UV irradiation, following the decomposition of the diazonium group between bilayers, the ionic bond of the self-assembly film converts into a covalent bond, and the film becomes very stable toward polar solvent and strong electrolyte solution. Thus the photocurrent generation was studied in a conventional photoelectrochemical cell with 0.5 M KCl solution as supporting electrolyte. An action spectrum of the photocurrent generation is coincident with the absorption spectrum of the DR/PAAA self-assembly film on the ITO glass electrode, indicating that the polyaniline containing film is responsible for the generation of the observed photocurrent.

Multilayered structures of alternating nanometer thick layers for electronic and photonic applications can be fabricated by various techniques, including the Langmuir–Blodgett method, sol–gel synthesis, electrochemical deposition, and chemical vapor deposition.¹ In recent years, Decher and co-workers² extended the pioneering work of Iler et al.³ to a new preparative method of organized thin film by layer-by-layer adsorption of linear polyions. Alternate adsorption of a polycation and a polyanion is readily achieved by excessive adsorption of polyelectrolytes on oppositely charged surfaces. The technique becomes more and more attractive because of its simple preparative process and easiness in controlling the layer structure. To date, Rubner and Skotheim extended this technique to manufacture thin films of conjugated polymers, and since then the molecular-level fabrication of layer-by-layer (LBL) films of polypyrrole, polyaniline, poly(phenylenevinylene), and poly(*o*-anisidine) conducting polymers have been developed rapidly.⁴

Usually, solution processing is a preferable method for device fabrication in most cases; soluble forms of conjugated polymers are highly desirable for both practical application and fundamental studies. However, before the early 1980s no conjugated conducting polymer had been shown to be soluble in any solvent without decomposition, and conducting polymers were regarded as intrinsically insoluble. Since then, research on conducting polymers has been focused on the synthesis and study of soluble conducting polymers. Polyaniline (PAN) is an important conjugating polymer because of its good environmental stability.⁵ But the low solubility of polyaniline in most common solvents limits its industrial application. For the purpose of improving its solubility in water and to prevent dopant migration, polyaniline has been modified in the self-doped form by introducing protonic acid into the side chains⁶ or introducing with soluble groups such as carboxyl on the main chain. Diaz et al. reported the copolymerization of aniline with *o*-anthranilic

acid to give a soluble polyaniline copolymer in aqueous alkaline solutions and these solutions can be used to prepare films.⁷

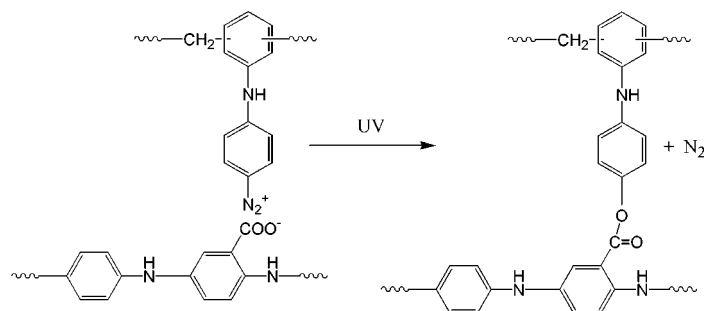
In our previous publications, we reported a novel way to fabricate covalently attached multilayer films based on diazo-resin (DR).⁸ The concept is originated from the ionic bond or H-bond self-assembly technique, and then forming a covalently attached multilayer by the photoreaction between the neighboring layers of the films. It has been proven to be a rapid and experimentally simply way to fabricate covalently attached multilayer films with precious controlled layer thickness and composition.

In this short communication, a novel self-assembly ultrathin film is fabricated with DR as the polyanion and carboxylic polyaniline—poly(aniline-*co-o*-anthranilic acid) (PAAA) as the polycation; the driving force between the alternate layers is believed to be electrostatic attraction. Then the assembled films are exposed under UV irradiation to undergo photoreaction of diazonium and carboxyl groups, and convert the ionic bonds between the layers into covalent bonds (Scheme 1). The covalent attached films are very stable toward polar solvents or the high ionic strength of the electrolyte solution. Thus we can measure the photoelectric conversion property of the covalent attached film in a traditional three-electrode cell and a 0.5 M KCl aqueous solution can be used as the electrolyte solution.

Poly(aniline-*co-o*-anthranilic acid) (PAAA) was synthesized from aniline and *o*-anthranilic acid using $\text{NH}_4\text{S}_2\text{O}_8$ as the oxidizing agent according to ref 7, and the molar fraction of *o*-anthranilic acid in the reaction mixture was 0.5. Diazo-resin (DR) was synthesized from diphenylamine—diazonium salt and formaldehyde in concentrated sulfuric acid, $M_n \approx 2000$, in our lab.⁹ Using treated quartz or indium—tin oxide (ITO) glass as substrate, the nanoassembly film was fabricated as follows: DR was dissolved in deionized water (0.5 mg/mL) and PAAA was dissolved in weak alkali aqueous solution (pH \approx 8) with the concentration of 0.5 mg/mL. The substrate was immersed first in DR solution for 5 min and then thoroughly rinsed with water and dried by flow air, followed by immersion in PAAA solution for 5 min and rinsing and drying to complete a fabrication cycle.

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SCHEME 1 : Schematic Representation of Bond Conversion from Ionic Bond to Covalent Bond in the PAAA/DR Self-Assembly Film under UV Irradiation

In each cycle, a bilayer of PAAA/DR was deposited on both sides of the substrate. Figure 1 shows the UV-vis spectra (on Shimadzu 2100) of multilayer films from the fabrication process in the quartz substrate. The characteristic band with λ_{max} at 380 nm belongs to the diazonium group of diazo-resin; the inset plot shows a good linear relationship between absorbance at 380 nm and the bilayer number, which indicates a smooth step-by-step fabrication has taken place on the quartz wafer.

The PAAA and diazo-resin were linked by electrostatic interaction from the cationic diazonium group ($-\text{N}_2^+$) of DR and the anionic carboxyl anion (COO^-) of PAAA to form a layer-by-layer ultrathin film. The diazo-resin is a photosensitive polymer and decomposes easily under UV irradiation or heat, the ionic bond between $-\text{N}_2^+$ and COO^- can be easily transformed into a covalent bond under UV light (as shown in Scheme 1), and the film is very stable toward polar solvents.

Figure 2 shows the UV-vis absorption spectra of a 12 bilayer film of DR/PAAA on a quartz substrate under UV irradiation at different times. As indicated in this figure, under UV irradiation, the diazonium groups decompose gradually with the decrease of the absorbance at 380 nm and concomitant increase of the absorbance at 292 nm. An isosbestic point at 335 nm appears. Throughout the experiments, we found that the decomposition of this 12 bilayer DR/PAAA film proceeds completely within 5 min. From the linear relation between $\ln(A_0/A_t)$ and t (inset plot in Figure 2), the photodecomposition is believed to follow the kinetics of a first-order reaction, where A_0 and A_t (corrected by baseline) represent the absorbance of the film before irradiation and after irradiation for time t , respectively.

To obtain the evidence of the bond conversion, a film with 50 bilayers of PAAA/DR was fabricated on a CaF_2 wafer. The FTIR spectra (recorded on a Bruker Vector 22 FTIR spectrom-

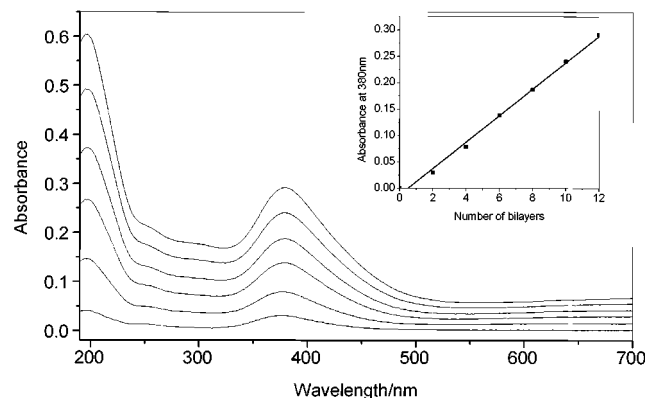


Figure 1. UV-vis absorption spectra of DR/PAAA multilayer films fabricated on a quartz wafer. The number of bilayers is 2, 4, 6, 8, 10, and 12 from the bottom to top.

eter) of the films were recorded before and after irradiation. The spectra are shown in Figure 3.

As shown in Figure 3, we can find that the peak at 2165 cm^{-1} (stretching vibration of the diazonium group) disappears after irradiation of UV light, indicating that the diazonium groups of PAAA/DR film decompose under UV irradiation. The absorbance of 1580 cm^{-1} is attributed to the phenyl groups connected with diazonium of DR because of the strong conjugation of phenyl and diazonium groups. Under UV irradiation, the peak at 1580 cm^{-1} disappears, and the peak at

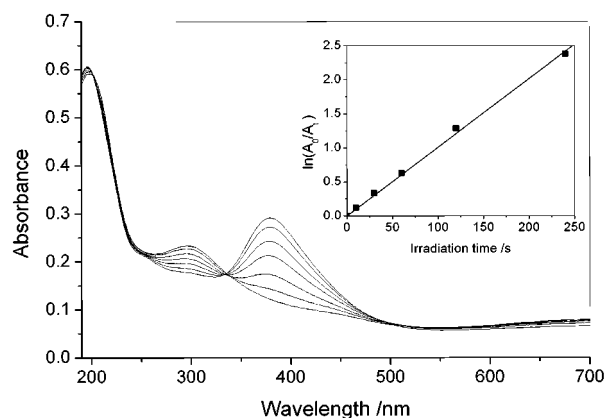


Figure 2. UV-vis absorption spectra of a 12 bilayer DR/PAAA film upon UV irradiation for different times. Irradiation time (s) (from top to bottom): 0, 10, 30, 60, 120, 240, 600. Irradiation intensity (at 360 nm): $230\text{ }\mu\text{W}/\text{cm}^2$.

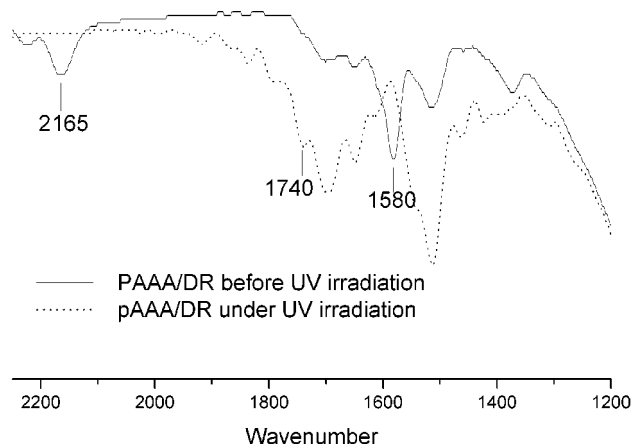


Figure 3. FTIR spectroscopy of a 50 bilayer PAAA/DR film on a CaF_2 substrate before and after UV irradiation. Irradiation intensity (at 360 nm): $230\text{ }\mu\text{W}/\text{cm}^2$ Irradiation time: 10 min.

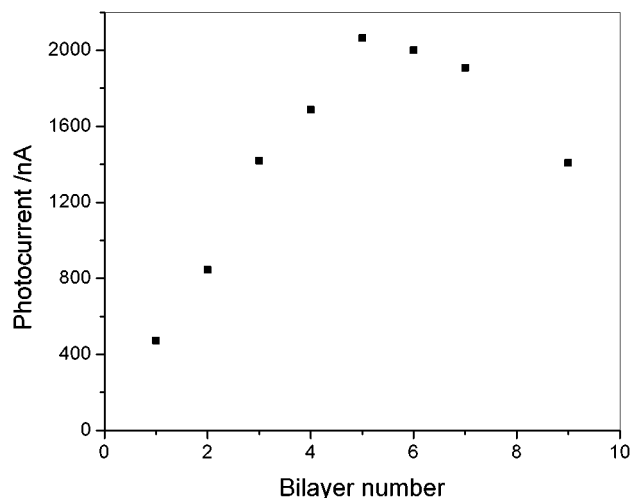


Figure 4. Relationship between photocurrent and bilayer number of polyaniline containing films.

1740 cm^{-1} increases obviously, which indicates the formation of a $-\text{COO}-$ ester bond in the film.

In our previous work, we reported the stability of covalent linked self-assembly films based on diazoresin and found this kind of film can resist the etching of polar solvents.¹⁰ Similarly, the irradiated DR/PAAA self-assembly films are very stable in DMF and 0.5 M KCl aqueous solutions; no changes in UV-vis spectra were found as the film was immersed in DMF or 0.5 M KCl electrolyte solutions for 24 h at room temperature.

As a conducting polymer, polyaniline has been widely used in photoelectrochemical cells.¹¹ But the general self-assembly films were fabricated via electrostatic interaction or hydrogen bond attraction and cannot resist the etching of polar solvents or strong electrolyte solutions; it is difficult to measure the photovoltaic properties of these film in a traditional three-electrode cell. Since the ultrathin film reported in this communication is linked by a covalent bond and is very stable toward polar solvents or KCl solution, the photoelectric conversion property of this kind of polyaniline containing film is possible to be measured in a three-electrode cell.

The indium-tin oxide (ITO) glass modified with SAM films (after UV irradiation) was used as a working electrode with an effective contact area of 1 cm^2 . A platinum wire was used as a counter electrode and the saturated calomel electrode (SCE) as a reference electrode. A solution of 0.5 M KCl was selected as the supporting electrolyte in all measurements. The photocurrent measurements were carried out on a model 600 voltammetric analyzer (CH Instruments) and a 500 W xenon lamp (Ushio Electric) was used as the light source. The intensity of incident light was measured with a power and energy meter (Sciencetech 372, Boulder, CO). The IR light was filtered throughout the experiment with a Toshiba IRA-25s.

The indium-tin oxide (ITO) glass modified with 1–9 bilayer SAM films, respectively, was utilized as the working electrode. Steady cathodal photocurrents were measured when each of the modified ITO electrodes was irradiated by a white light (100 mW cm^{-2}). The relationship between photocurrent and bilayer number of SAM films is shown in Figure 4. It shows that the photocurrent increases consecutively with the increasing bilayer number when the film is thinner (up to 5 bilayers). The increase of the photocurrent responses indicates that the polyaniline-containing multilayer film is surely an active species in the photoelectric conversion. When the film gets thicker, as shown in Figure 4, the photocurrent shows no increment and even a

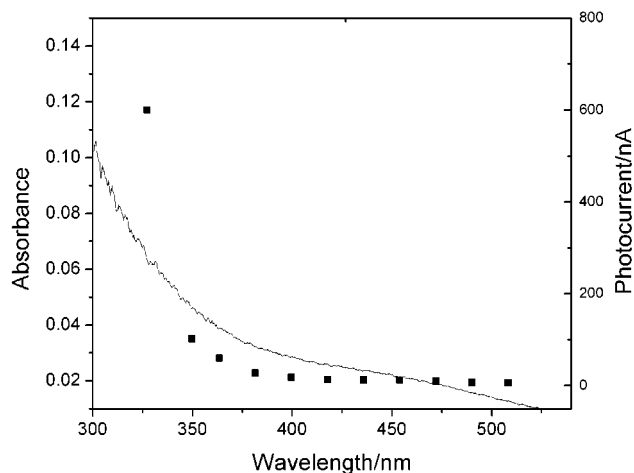


Figure 5. Action (●) and absorption (solid line) spectra of a PAAA/DR self-assembly film on an ITO substrate. The intensities of different wavelengths were all normalized.

minor decrease. It should be mainly attributed to two factors: one is the increasing probability of recombination for the thicker film and another is the cell resistance become larger with increasing film thickness.

Upon changing the excitation wavelengths within the range 340–550 nm, a photocurrent action spectrum for a 5 bilayer DR/PAAA film is obtained as shown in Figure 5, which is close to the absorption maximum in the range of investigated wavelength. The close match of the action and absorption spectra of the modified electrodes suggests that the PAAA/DR multilayer film is responsible for the generation of the observed photocurrent. When the modified ITO electrode is illuminated by monochromatic 340 nm light of 0.03 mW/cm^2 , the optimal photocurrent density of 600 nA (normalized) is obtained. The absorbance of a 5 bilayer film on ITO is 0.054. On the basis of these data, we can calculate the quantum yields of the 5 bilayer PAAA/DR film as 6.44%.

In conclusion, carboxyl-containing polyaniline (PAAA) and photosensitive diazoresin (DR) were self-assembled into an ultrathin film through electrostatic interaction. Under UV irradiation, following the decomposition of the diazonium group between layers, the ionic bond of the self-assembly film converts to a covalent bond, and the film becomes very stable toward polar solvents and strong electrolyte solutions. Thus the photoelectric conversion properties of the polyaniline containing film can be measured in a three-electrode cell with the KCl solution as supporting electrolyte. The photoelectric action and absorption spectra show that the DR/PAAA self-assembly film is responsible for the generation of the observed photocurrent.

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