

6AZO-CONTAINING SELF-ASSEMBLY ULTRA-THIN FILMS AND THEIR PHOTOVOLTAIC PROPERTIES*

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Abstract A kind of azo-containing resin (Azo-R) was synthesized by a simple way through the coupling reaction of 2-nitro-*N*-methyldiphenylamine-4-diazo-resin (NDR) with phenol, and a new covalently attached multilayer film from Azo-R as H-donor and photosensitive diazo-resin, diphenylamine-4-diazo-resin (DR) as H-acceptor via H-bonding attraction by self-assembly technique has been fabricated. Following the decomposition of diazonium group of DR under exposure to UV light, the H-bonds between the layers of the film convert to covalent bonds and the film becomes very stable toward polar solvents or electrolyte aqueous solutions. Thus the UV-irradiated azo-containing films can be used to measure photocurrent in a conventional three-electrode photoelectrochemical cell using KCl as supporting electrolyte. It was confirmed that the azo-containing multilayer film is responsible for the photocurrent generation.

Keywords: Azo-containing resin; Self-assembly film; Photovoltaic property.

INTRODUCTION

Solar energy is the most clean, ideal energy source for mankind. Many materials such as conductive polymers, fullerenes, porphyrines, phthalocyanines and dyes take precedence over others to be selected for the modification of semiconductors or metal electrodes to develop low-cost photovoltaic devices, especially to develop the plastic thin film solar cells^[1–3].

Recently, much efforts have been devoted to the investigation of multi-layer assembly films because of their simplicity in preparation, a wide choice of materials and the versatility in film design^[4–6]. A big problem is that the self-assembly multilayer films are usually prepared via weak interaction, such as electrostatic, H-bonding attraction *etc.*^[7], are not stable in polar solvents or electrolyte aqueous solutions. This problem can be solved by the conversion of weak linkages to covalent bonds between the layers of the film^[8].

In the present study, a new azo-containing resin (Azo-R) was synthesized through the coupling reaction of NDR with phenol and a covalently attached multilayer film was fabricated from Azo-R and diazo-resin (DR) via H-bonding attraction, followed by exposure to UV light. Thus the photoelectric conversion property of the covalently attached films can be measured with a traditional three-electrode cell in KCl aqueous solution.

EXPERIMENTAL

Materials

Diphenylamine-4-diazo-resin (DR) and 2-nitro-*N*-methyldiphenylamine-4-diazo-resin (NDR) were synthesized by polycondensation of diphenylamine-4-diazonium salt or 2-nitro-*N*-methyl diphenylamine-4-diazonium salt with

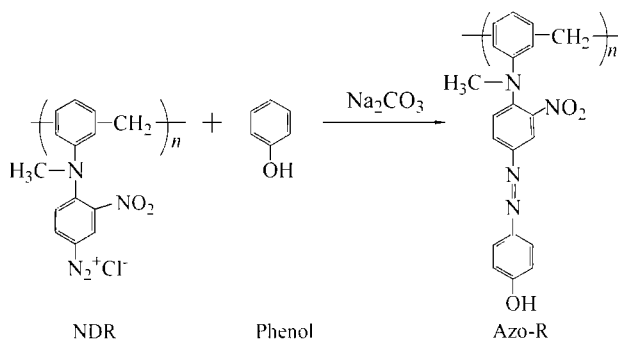
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formaldehyde in concentrated sulfuric acid respectively according to the method described elsewhere^[9]: DR: $\eta_{sp}/c = 0.12$ dL/g, $M_n \approx 2.1 \times 10^3$ g/mol; NDR: $\eta_{sp}/c = 0.15$ dL/g, $M_n \approx 2.5 \times 10^3$ g/mol.

Azo-containing resin (Azo-R) was synthesized from the coupling reaction of NDR and phenol as shown in Scheme 1. 1.5 g of NDR in 100 mL of water was dropped into a mixture of Na_2CO_3 (5 g) and phenol (4 g) in 200 mL water within 0.5 h. The mixture was kept for 4 h under stirring at 0°C in the dark, and filtered. The dark red product obtained was washed with water, ethanol and dried in vacuum (in the dark). The yield is 1.2 g. (91% calculated from $-\text{N}_2^+$ group), N/C (molar ratio): 1/5.11 (theoretical: 1/5).



Scheme 1 Synthetic route of Azo-R with the coupling reaction of NDR and phenol

Fabrication of Self-Assembly Film

Quartz wafer and indium-tin-oxide (ITO) glass slide were used as the substrate. The former was pretreated with boiling piranha solution (a mixture of 30% H_2O_2 ; 98% H_2SO_4 ; V/V = 1:3) for 10 min. ITO glass slide was cleaned in an ultrasonic cleaner with acetone and H_2O respectively. The treated substrate was immersed first in 0.5 mg/mL DR aqueous solution (or methanol solution) for 5 min, then rinsed with H_2O thoroughly and dried in flowing air. The substrate was further immersed in Azo-R acetone solution (0.2 mg/mL) for 5 min, rinsed with acetone and dried to complete a fabrication cycle. In each cycle, a bilayer of Azo-R/DR was deposited on both sides of the substrate. The completely fabricated film then was exposed to UV light (irradiation intensity: $230 \mu\text{W}/\text{cm}^2$ at 360 nm) for 2–3 min to obtain a covalently attached film. UV-vis spectra recorded on Shimadzu 2100 spectrophotometer were used to monitor the layer-by-layer deposition and the photoreaction occurring in films under UV irradiation

Photocurrent Measurement

The photocurrent was determined on a voltammetric analyzer (CH Instruments Inc. Model600, USA) and a 500 W xenon lamp (Ushio Electric, Japan) was used as light source. The light was filtrated with a GG400 filter to remove < 400 nm irradiation. The incident light used was filtrated by a filter and the intensity was measured with a power and energy meter (Scientech372, Boulder Co. USA). ITO glasses modified with Azo-R/DR multilayer films were used as working electrode. A three-electrode cell with a flat window was employed. The counter electrode was Pt wire and the reference was a saturated calomel electrode. $0.5 \text{ mol}/\text{dm}^3$ KCl aqueous solution with pH 5.6 was used as the support electrolyte solution for determination.

RESULTS AND DISCUSSION

Multilayer Films

Figure 1 shows the UV-vis absorption spectra of Azo-R/DR multilayer films (overlaid on both side of a quartz slide) with different bilayers. The absorbance of the film at 380 nm ($\pi-\pi^*$ transition of $-\text{N}_2^+$ of DR) and 400 nm ($\pi-\pi^*$ transition of $-\text{N}=\text{N}-$ of Azo-R) increases with the bilayers (inset plot), which indicates that the deposition of Azo-R and DR layer-by-layer on the substrate proceeds regularly.

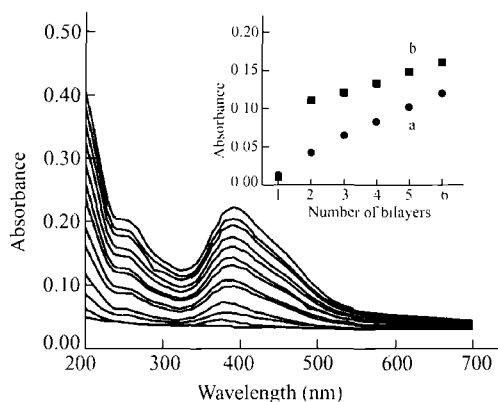
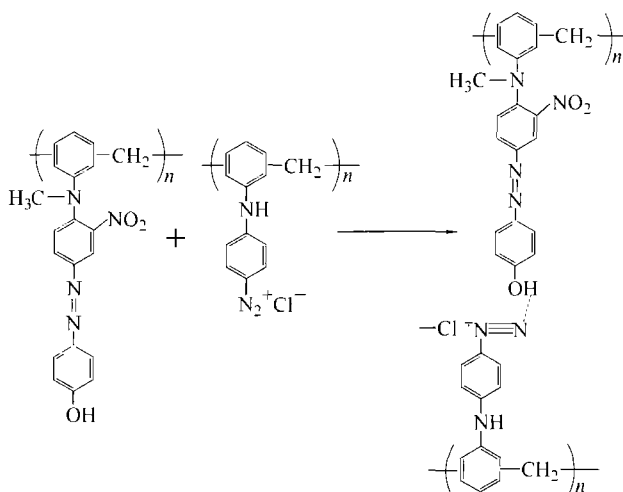


Fig. 1 UV-vis spectra of Azo-R/DR multiplayer films with different bilayers

DR layer (---); Azo-R layer(—)

Inset plot: (a) at 380 nm; (b) at 400 nm

The fabrication driving force of the multilayer film was considered to be H-bonding attraction. The diazonium group ($-\text{N}^+\equiv\text{N}:$) has two nitrogen atoms, one carries a positive charge but keeps balance with an anion Cl^- , the other has a pair of un-bonded electrons that are able to form H-bond with a strong H-donor such as phenolic hydroxy group^[10]. The formation of H-bond between $-\text{N}_2^+$ group of DR and $-\text{OH}$ group of Azo-R can be represented in Scheme 2.



Scheme 2 Schematic representation of H-bond formation between $-\text{N}_2^+$ group of DR and $-\text{OH}$ group of Azo-R

The diazonium group is photosensitive and decomposes easily under UV irradiation^[11]. Figure 2 shows the decreasing of the absorbance of the film at 380 nm originated from the decomposition of $-\text{N}_2^+$ groups of the film. From the linear relation of $\ln[(A_0 - A_e)/(A_t - A_e)]$ with time (inset plot), where A_0 , A_t , A_e represent the absorbance of the film before irradiation, irradiated for different times and the end of the irradiation (~5 min) respectively, the photodecomposition was found to follow the kinetics of first-order reaction.

It has been verified that the irradiated Azo-R/DR film becomes very stable toward polar solvents or electrolyte aqueous solutions, *e.g.* it can not be destroyed in dimethyl formamide or KCl aqueous solution. Therefore, the irradiated Azo-R/DR films can be used to determine their photocurrent in KCl aqueous solution.

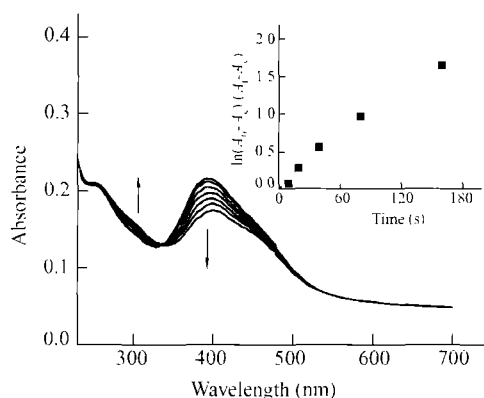


Fig. 2 UV-vis spectra of a 6 bilayers film irradiated for different time
Irradiation intensity (360 nm): $230 \mu\text{W}/\text{cm}^{-1}$
Irradiation times (top to bottom): 0, 10, 40, 80, 160 and 320 s

Photoelectric Conversion Properties

To examine the photoelectric properties of the azo-containing multiplayer films, a series of films with different bilayers were fabricated on indium-tin oxide (ITO) glass slide and were utilized as working electrode for the determination of their photoelectric conversion properties after UV irradiation. A steady cathodic photocurrent can be obtained when each ITO electrode (1 cm^2 illuminated area) modified by the mentioned film was illuminated by a white light (130 mW cm^{-2}). Figure 3 shows the photoelectric current changes with bilayers of a film. We can see that the photocurrent reaches a maximum at around 8 bilayers. It is attributed to the fact that the overall energy conversion efficiency of the film depends on its thickness strongly. The thicker film possesses more Azo-R molecules and hence generates larger photocurrent. But as the film gets thicker, the probability of recombination and the cell resistance will become larger, since the electrons have to be transported across an increasing number of layers and boundaries.

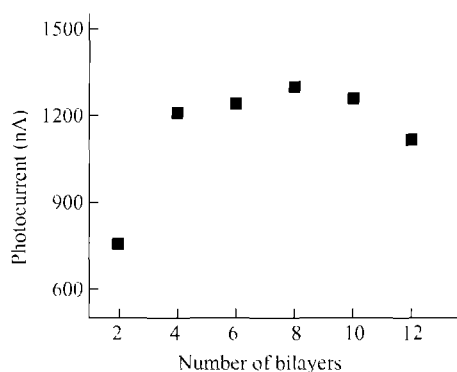


Fig. 3 The relationship between photocurrent and bilayers of the multiplayer film on ITO glass
 -0.2 V bias voltage

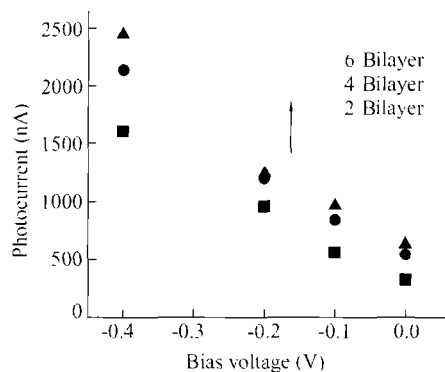


Fig. 4 Photocurrent versus bias voltage for Azo-R/DR film on ITO electrode

Effect of Bias Voltage

The generation of cathodic photocurrent indicates that electrons flow from the electrode through the self-assembly film to the electrolyte solution. As shown in Fig. 4 the photocurrent increases with the increase of negative bias potential and the negative bias potential added on the ITO electrode can promote electron transfer through this route.

Photocurrent Action Spectra

By changing the excitation wavelengths within the range of 400–700 nm, a photocurrent action spectrum for a 8 bilayer Azo-R/DR film was obtained as shown in Fig. 5, which is close to the absorption spectrum in the range of investigated wavelength. The similarity of the action and absorption spectra of the modified electrodes suggests that the Azo-R/DR multilayer film is responsible for the generation of photocurrent. Under excitation of the light with $\lambda = 420$ nm (1.07 mW cm^{-2}) in zero V and -0.2 V bias voltage, the photocurrent density was determined to be 90 and 195 nA cm^{-2} , respectively. Based on these data the quantum yields are estimated to be 0.06% and 0.12%, respectively.

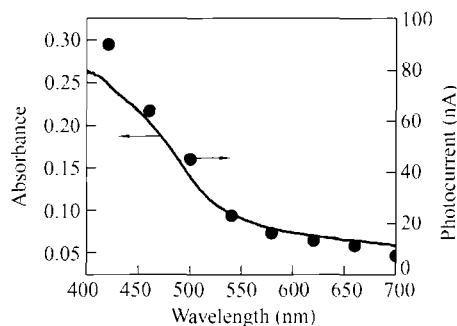


Fig. 5 Photocurrent action spectra for Azo-R/DR self-assembly film on ITO substrate
The intensities of different wavelengths were all normalized

CONCLUSION

A new azo-containing resin (Azo-R) was synthesized and self-assembled with photosensitive diazo-resin. A series of stable covalently attached ultra-thin films were formed after exposure to UV light, and their photovoltaic properties were measured on a traditional three-electrode photoelectrochemical cell. The action spectra of the modified electrodes are close to the absorption spectra of the film, which suggests that the azo-containing multilayer film is responsible for the generation of photocurrent. This kind of azo-containing resin has the potential use to fabricate plastic thin film solar cells.

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