

Environmental Stability of Electrically Conductive Viologen–Polyaniline Systems

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ABSTRACT: Viologen–polyaniline (PANI) systems were prepared by PANI being coated onto viologen-grafted low-density polyethylene films. PANI in this system could undergo photoinduced doping with ultraviolet irradiation. The electrical stability of the electrically conductive viologen–PANI systems was found to be stable in air, but the conductivity decreased rapidly when the sample was treated in aqueous media of $\text{pH} > 5$ because of the migration of the anions out of PANI into water. However, the conductivity increased by a factor of 2 after treatment in a 1M HCl solution because of the further protonation of PANI by acid. The structural changes of these systems were monitored with ultraviolet–visible absorption spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and resistance measurements. The electrical stabil-

ity of the viologen–PANI system in water could be enhanced via spin coating with poly(methyl methacrylate) (PMMA) because this layer inhibited the migration of the anions out of the system. The photoinduced doping of PANI could be carried out either before or after the spin coating of PMMA. The advantages and limitations of each method were demonstrated. A PMMA coating with a thickness of approximately $10\ \mu\text{m}$ allowed a significant doping level to be achieved within a short period of irradiation and, at the same time, effectively shielded the film from the effects of the aqueous medium. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2099–2107, 2002

Key words: conducting polymers; stabilization; irradiation

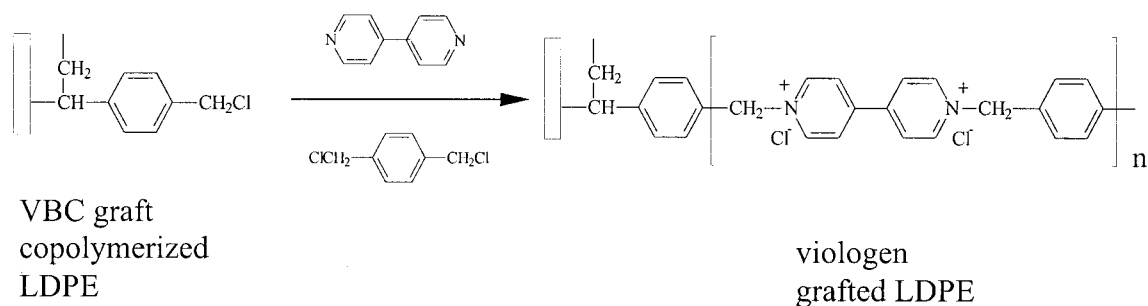
INTRODUCTION

Polyaniline (PANI) and its derivatives constitute one of the most extensively studied conjugated polymers. This family of polymers can be doped by two different processes: protonic acid doping and oxidative doping. Protonic acid doping of the 50% oxidation emeraldine base with, for example, 1M aqueous HCl results in complete protonation of the imine nitrogen atoms, yielding the fully doped emeraldine hydrochloride salt.¹ A similarly doped polymer can be obtained by oxidation of the fully reduced leucoemeraldine base.² This process actually involves the oxidation of both σ and π systems rather than just the π system of the polymer, as is usually the case in p-type doping. Attempts to dope PANI via photoinduced methods also have been reported. Onium salts have been used to prepare an onium salt/PANI blend, and with ultraviolet (UV) irradiation, the onium salts decompose and generate protonic acids, which, in turn, dope PANI.³ Nonionic photoacid generators have also been used to dope methyl-substituted PANI.⁴ Poly(vinyl chloride) (PVC)/PANI composites have been prepared in which HCl produced by the dehydrochlorination of

PVC under UV irradiation resulted in the doping of PANI.^{5,6}

Recently, we found that a PANI film can be doped in a viologen solution.⁷ Viologen, more formally known as 1,1'-disubstituted 4,4'-bipyridinium ions, is a class of compounds that readily undergo electron transfer.⁸ These compounds have electrochemically and photochemically reversible properties and interesting behaviors in different oxidation states. Further studies have shown that a PANI base can also be converted into a conductive form by photoinduced interactions with viologen in the solid state.^{9,10} This technique offers the possibility of providing conductivity to selected surface regions of substrates by photoirradiation and may have particular pertinence to pattern fabrication and electronic design. In this work, we studied the electrical stability of a viologen–PANI system prepared by the coating of PANI onto a viologen-grafted low-density polyethylene (LDPE) film exposed to hostile environmental conditions. The enhancement of the electrical stability of PANI is interesting because the potential applications of PANI include sensors and shielding and smart materials. However, because PANI undergoes rapid dedoping when exposed to an aqueous medium, the range of applications may be limited in the outdoor environment or other situations in which there is exposure to water. The resulting structural changes of the viol-

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Scheme 1

ogen-PANI system in aqueous media were monitored with ultraviolet-visible (UV-vis) absorption spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Spin coating with a transparent polymer, poly(methyl methacrylate) (PMMA), was investigated as a possible technique for enhancing the electrical stability of the viologen-PANI systems. The effects of the PMMA coating on the doping rate and doping level of the systems under exposure to UV irradiation in air and water were also studied.

EXPERIMENTAL

Preparation of viologen-grafted LDPE films

The grafting of viologen onto LDPE films was achieved through the initial graft copolymerization of vinyl benzyl chloride (VBC) on LDPE substrates, followed by the chemical reaction of the grafted groups with 4,4'-bipyridine and alkyl halides, which formed viologen moieties, as described in Scheme 1.¹¹ This method is similar to that commonly used for the preparation of viologens via the double Anderson reaction.⁸ The LDPE films (0.125 mm thick; Goodfellow, Inc., Huntingdon, United Kingdom) were first treated with argon plasma for 60 s on both sides at a pressure of about 0.6 Torr with an Anatech SP100 plasma system (Springfield, VA). The VBC monomer (97% purity; Aldrich, Milwaukee, WI) was dripped on both surfaces of the argon-plasma-pretreated LDPE films, which were sandwiched between two pieces of quartz plates and then exposed to UV irradiation in a Riko rotary photochemical reactor (RH400-10W) (Funabashi-city, Chibo, Japan) at 28°C for 40 min. The graft copolymerized films were subjected to prolonged washing with dimethylformamide (DMF) for the removal of residual homopolymers and reactants. The VBC graft copolymerized films were allowed to react in a solution mixture containing dichloro-*para*-xylene and 4,4'-bipyridine (0.06M of each reactant in DMF) at 70°C for 20 h. The viologen-grafted films were washed with DMF followed by deionized water and were finally dried under reduced pressure.

Preparation of the viologen-PANI systems

PANI was coated onto the viologen-grafted LDPE films by the immersion of the films in a polymerizing solution of 0.1M aniline and 0.025M (NH₄)₂S₂O₈ in 1M HClO₄. The polymerization was carried out at 0°C for 2 h. The PANI coating was converted into the 50% oxidized emeraldine base by treatment with excess 0.5M NaOH for 1 h followed by thorough washing with deionized water. The viologen-PANI systems were dried under reduced pressure and stored in the dark until further studies were performed.

UV irradiation and spin coating on the viologen-PANI systems

UV irradiation of the viologen-PANI systems was performed in a Riko rotary reactor with a 1000-W Hg lamp. The samples were placed in a Pyrex test tube immersed in a water bath 5 cm from the light source and subjected to the full intensity of the UV-light source. Wavelengths below 290 nm were completely cut off by the Pyrex tube (ca. 50% transmission at 305 nm). The irradiation was carried out at a temperature between 25 and 30°C.

PMMA has been widely used as a surface coating because of its stability under light and resistance to exterior weathering.¹² Spin coating of PMMA onto the surface of the viologen-PANI system was carried out with a P-6000 spin coater (Specialty Coating System, Inc., Indianapolis, IN) by dripping a 2% PMMA solution (prepared by the dissolution of a minced PMMA sheet from Goodfellow in chloroform) on the films. Before the spin coating with PMMA, two silver coils were attached to the surface of the viologen-PANI system with conductive tape to serve as electrodes. These two electrodes were used to measure the resistance of the system. During spin coating, the rotation speed was kept at 1500 rpm for 60 s. The thickness of the PMMA coating was estimated from the increase in the weight of the film. The spin-coated samples were dried under reduced pressure and stored in the dark until further studies were performed. As a comparison, the viologen-PANI system was also encapsulated

TABLE I
Surface Composition of Viologen-PANI System as Determined from XPS Analysis

| | N/C | Cl/C | Cl/N | -N=/N | -NH/N | N ⁺ /N |
|---|------|------|------|-------|-------|-------------------|
| VBC-grafted LDPE | — | 0.06 | — | — | — | — |
| Viologen-grafted LDPE | 0.05 | 0.06 | 1.2 | — | — | — |
| Viologen-PANI system | 0.17 | 0.01 | 0.08 | 0.41 | 0.53 | 0.06 |
| Viologen-PANI system after UV irradiation for 1 h | 0.16 | 0.05 | 0.34 | 0.03 | 0.61 | 0.36 |

in a piece of LDPE film 50 μm thick by a thermal sealing technique.

Testing and characterization

The UV-vis absorption spectra of the viologen-PANI systems were obtained with a UV-vis near-infrared scanning spectrophotometer (Shimadzu UV-3101 PC, Kyoto, Japan), with the pristine LDPE film as a reference. FTIR analysis was carried out on a Bio-Rad FTS 135 spectrophotometer with the pristine LDPE film as its background. The sheet resistance (R_s) was measured with the standard two-probe method. The resistances of the spin-coated viologen-PANI systems were measured with a Fluke multimeter (Everett, WA) connected to the two electrodes on the sample.

XPS measurements were carried out on a Kratos Analytical AXIS HSi 165 spectrometer with a monochromatized Al K α X-ray source (1486.6-eV photons) (Manchester, UK). The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA). The samples were mounted on the standard sample studs with double-sided adhesive tape. The core-level spectra were obtained at a photoelectron takeoff angle (with respect to the sample surface) of 90°. The pressure in the analysis chamber was maintained at 10⁻⁸ Torr or lower during each measurement. As compensation for surface charging effects, all binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum) of Gaussian peaks was kept constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios and were accurate to within $\pm 10\%$.¹³

RESULTS AND DISCUSSION

Photoinduced doping of the viologen-PANI systems

The preparation of the viologen-PANI system essentially consists of three steps: the surface graft copolymerization of VBC with the LDPE substrate, the grafting of the viologen moieties, and the deposition of the PANI layer. The surface compositions of the films after each of these steps, as determined from the XPS analysis, are shown in Table I.

When the viologen-PANI system is exposed to UV light from the 1000-W Hg lamp, the color of the film changes from blue to green. This provides an indication that the PANI coating is converted from the insulating base state to the doped state. This color change is accompanied by a sharp decrease in R_s , as shown in the Figure 1 inset. R_s decreases nearly 5 orders of magnitude, from 10¹⁰ to 10⁵ Ω/sq after UV irradiation for an hour. The conversion of PANI from the base to the conductive form under UV irradiation can also be readily seen from the UV-vis absorption spectra (Fig. 1). The absorption spectrum before UV irradiation is representative of that of PANI in the emeraldine (50% oxidized) base state, except that the absorbance in the 330-nm region is due to both PANI and the viologen moieties. After 30 min of UV irradiation, the exciton-like transition band of the PANI coating at 615 nm disappears, whereas a new band at 435 nm and a long absorption tail extending beyond 800 nm appear. The absorption tail is attributed to the intraband free-carrier excitations, and the absorption band at 435 nm is assigned to the polaron transi-

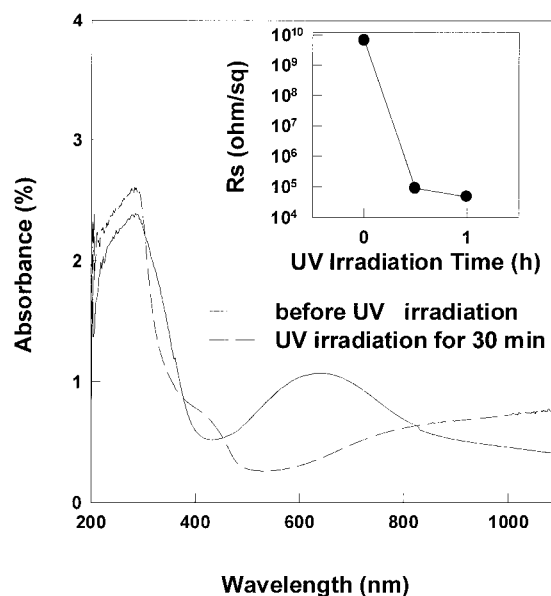


Figure 1 UV-vis absorption spectra of the viologen-PANI system before and after UV irradiation in air. The inset shows the change in R_s for the viologen-PANI system with the UV irradiation time.

tions.^{14–16} These bands are present only in doped and conductive PANI and are usually attributed to the conversion of an unprotonated quinoid imine structure to a positively charged nitrogen (polaron structure).^{14,17,18} Supporting evidence of the change in the PANI structure is provided by FTIR absorption spectroscopy, which shows an increase in the intensity and significant broadening of the 1160-cm⁻¹ absorption peak after UV irradiation of the viologen–PANI system. This implies some degree of electronic delocalization^{19,20} and, therefore, is consistent with the observed increase in electrical conductivity. The XPS results (discussed in the next section) also indicate the conversion of PANI into the doped state with UV irradiation.

Electrical stability of the irradiated viologen–PANI systems

The electrical conductivity of the UV-irradiated viologen–PANI system left at room conditions (25–28°C, 85% relative humidity, normal room light) without further UV irradiation over a period of 4 months remained high with an increase in R_s of only about 1 order of magnitude. A similarly prepared viologen–PANI system kept in the dark showed a similar trend.²¹ It can be concluded that the doped state of the viologen–PANI system after the cessation of light irradiation is quite stable in air, similar to acid-protonated PANI.

However, the electrical stability of the irradiated viologen–PANI system is poor in aqueous media. As

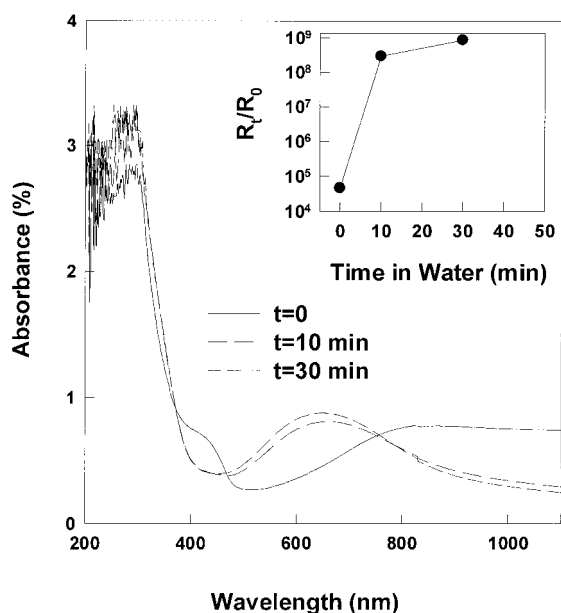


Figure 2 UV-vis absorption spectra of the UV-irradiated viologen–PANI system (1 h in air) after treatment in water. The inset shows the change in R_s for the viologen–PANI system with the treatment time in water.

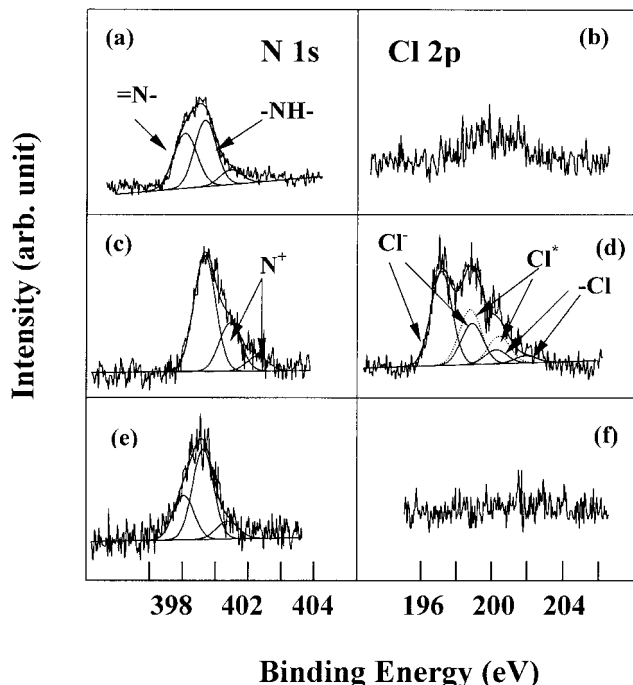


Figure 3 XPS N1s and Cl2p core-level spectra of viologen–PANI systems (a,b) before UV irradiation, (c,d) after UV irradiation in air for 1 h, and (e,f) after UV irradiation in air for 1 h followed by treatment in water for 1 h.

shown in Figure 2, the PANI coating rapidly converts from the doped state into the insulating state after treatment in deionized water. R_s increases sharply by over 4 orders of magnitude after 30 min in water (Fig. 2, inset). The undoping process is believed to be caused by the migration of Cl⁻ out of the PANI layer into water. This is confirmed by the formation of a white precipitate upon the addition of several drops of 0.1M AgNO₃ to the water in which the viologen–PANI system was treated. This process of Cl⁻ anion migration from the PANI upon treatment with water occurs similarly with PANI doped with HCl. Therefore, there is no improvement in the electrical stability of the viologen–PANI systems in aqueous media over that observed with PANI protonated in the conventional manner by HCl.

The process of photoinduced doping in air and undoping in water can be monitored by XPS. The N1s core-level spectrum of the viologen–PANI system before UV irradiation [Fig. 3(a)] can be curve-fitted with three major components. The peak at a binding energy (BE) of 398.2 eV is attributed to the imine (—N=) nitrogen of PANI, whereas that at 399.4 eV is attributed to the amine (—NH—) nitrogen of PANI²² and any neutral nitrogen of the viologen radical cation that may be formed from X-ray excitation in the analysis chamber.²³ The small peak at BE > 400 eV is assigned to the positively charged nitrogen (N⁺) on the viologen, as well as any residual oxidized nitrogen in the

PANI coating.²² The almost equal intensity of the two dominant peaks at 398.2 and 399.4 eV, shown in Figure 3(a), is consistent with the spectrum expected of PANI in the emeraldine base state. In Figure 3(b), the Cl signal of the viologen-PANI system before UV irradiation is barely discernible. This indicates that the thickness of the PANI coating is close to the probing depth of the XPS technique for organic matrices (<10 nm),²⁴ and so the contribution from the viologen layer to the N and Cl signals is minimal. Upon a UV-induced reaction with viologen for 1 h in air, the XPS results show that the proportion of imine decreases and that of the N⁺ components (1.45–1.50 and 2.9–3.0 eV from the amine peak)²² increases simultaneously [Fig. 3(c) and Table I], confirming the formation of charge carriers in the PANI coating of the irradiated system. The corresponding Cl2p core-level spectrum after UV irradiation [Fig. 3(d)] can be resolved into three spin-orbit split doublets [Cl(2p_{3/2}) and Cl(2p_{1/2})], with the BE for the Cl(2p_{3/2}) peaks at about 197.1, 198.6, and 200.2 eV.²⁵ The first BE component is attributed to ionic species (Cl⁻). The second chloride species, Cl* [the dashed component in the Cl2p spectra in Fig. 3(d)], which has been widely observed, is usually attributed to anionic chloride species resulting from the charge-transfer interactions between the halogen and the metal-like conducting state of the polymer chain.^{26–28} The small amount of covalent Cl present [Cl(2p_{3/2}) peak at 200.2 eV] in the viologen-PANI system should be from the unreacted benzyl chloride groups or the end groups of the viologen. It can be seen from Figure 3(b,d) that the Cl2p signal is enhanced by UV irradiation and that the [Cl]/[N] ratio increases from 0.08 before UV irradiation to 0.34 after UV irradiation. Because XPS is a surface-sensitive technique, a possible explanation for this observation is the “sinking-in” of the PANI layer and/or the migration of Cl⁻ from the inner viologen-dense region toward the outer PANI layer during the irradiation process because of the electrostatic attraction between the N⁺ of PANI and Cl⁻ anions. After the irradiated viologen-PANI system is treated in water for 30 min, most of the N⁺ components are converted into either the imine or amine species [Fig. 3(e)]. This conversion of N⁺ to both imine and amine species is similarly observed when PANI protonated by inorganic acids is treated with water, and it is different from the conversion of N⁺ into predominantly imine units when PANI is treated with base.²⁹ In addition, the Cl2p signal is no longer discernible [Fig. 3(f)]. This may be due to the reorientation of the PANI layer due to the conversion of N⁺ into neutral species, or the migration of the Cl⁻ species out from the viologen-PANI system into the water. The presence of the white precipitate in the water with the addition of AgNO₃ (the white precipitate is likely to be AgCl) supports the latter explanation. The pH of the water also decreases, indi-

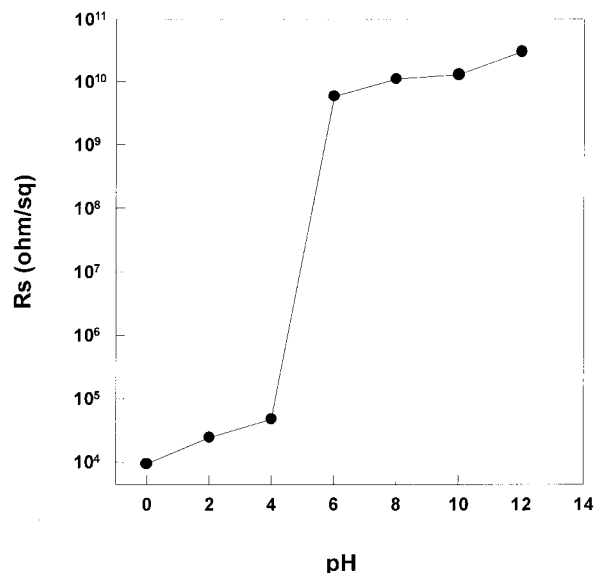


Figure 4 R_s for the UV-irradiated (1 h in air) viologen-PANI system after treatment in solutions of different pHs for 0.5 h.

cating that the migration of Cl⁻ anions out of the system is accompanied by the H⁺ ions.

The electrical stability of the conductive viologen-PANI system in aqueous media at different pH values is shown in Figure 4. With solutions of pH > 7, R_s for the viologen-PANI system increases to over 10^{10} Ω/sq after 30 min. In contrast, R_s of the sample treated in a dilute HCl solution with pH 4 does not change after 30 min of treatment. For solutions of pH 2 and 0, R_s for the viologen-PANI system actually decreases by 50 and 80%, respectively. This increase in the conductivity of the viologen-PANI systems is caused by the further protonation of PANI by the acid in the solution, suggesting that the photoinduced reaction of PANI with viologen does not result in a doping level as high as that achievable with acids of [H⁺] > 0.01M.

Enhancement of the electrical stability of the viologen-PANI systems by spin coating

To enhance the electrical stability of the viologen-PANI system in aqueous media, surface modification by spin coating with a transparent polymer was investigated. In the first method, the viologen-PANI system was irradiated with UV light for an hour, and this was followed by surface spin coating with 2% PMMA in chloroform. The sample was then immersed in deionized water for various periods of time so that the change in resistance could be measured. The UV-vis absorption spectra of the spin-coated viologen-PANI system after various periods of time in deionized water are shown in Figure 5. The spectrum after spin coating ($t = 0$ curve in Fig. 5) does not differ much in shape from that before spin coating except for

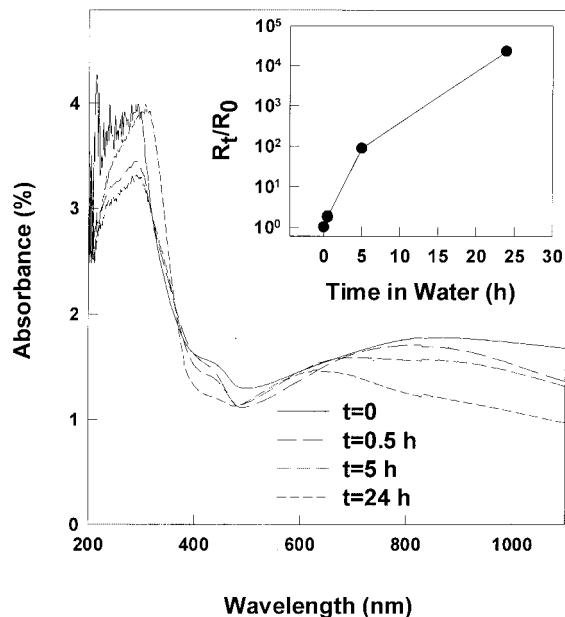


Figure 5 UV-vis absorption spectra of the viologen-PANI system (UV-irradiated for 1 h in air and spin-coated with PMMA; PMMA layer thickness $\sim 10 \mu\text{m}$) after treatment in water for various periods of time. The inset shows the change in the resistance (the resistance at time t normalized by the resistance before water treatment) of the viologen-PANI system with the treatment time in water.

an upward displacement (increase in absorbance) due to the absorption by the PMMA coating. The increase in absorbance would have been more substantial if a thicker coating layer or a less transparent material had been used. In Figure 5, it can be seen that the spectrum of the spin-coated viologen-PANI system after treatment in water for 30 min is still that of doped PANI; this suggests that the electrical stability has been substantially enhanced over that of the uncoated sample (cf. Figs. 5 and 2). Even after treatment for 5 h, the spectrum still shows the characteristics of doped PANI. However, as the exposure time is increased to 24 h, the exciton band (615 nm) becomes obvious, and the intensity of the absorbance tail decreases substantially, indicating a significant degree of undoping. The resistance correspondingly increases by over 4 orders of magnitude (Fig. 5, inset). The increase in resistance after water treatment suggests that the spin-coated PMMA layer is porous to the migration of anions from PANI into water.

In the second method, the viologen-PANI systems is first spin-coated with PMMA and then subjected to UV irradiation. Figure 6(a) shows the UV-vis absorption spectra of the spin-coated viologen-PANI system upon exposure to UV irradiation. The disappearance of the band at 615 nm together with the appearance of the bands at 435 nm and greater than 800 nm again show that photoinduced doping is achieved. However, an irradiation time of 2 h is required to achieve a

10^4 reduction in resistance, compared to an irradiation time of less than 30 min required to achieve the same decrease in the absence of the PMMA coating. The photoinduced doping process of the spin-coated sample is slower than that without the PMMA layer because of the reduction in the amount of the UV light transmitted by the PMMA coating.

The viologen-PANI system prepared by the second method (spin coating followed by UV irradiation in air) shows good electrical stability under exposure to water. The UV-vis absorption spectra in Figure 6(b) show that the system remains in the doped state even after 20 h in water, with an increase in the resistance of less than 2 orders of magnitude (Fig. 7). Comparing the spectra in Figures 5 and 6(b), we can see that the spin-coated viologen-PANI system prepared by the second method is more stable. This difference in stability may be due to the differences in the PMMA layers. In the first method, PMMA is deposited onto PANI that is already doped, whereas in the second method PANI is in the undoped state when PMMA is deposited. The presence of charged species on the PANI surface may cause it to be less compatible with PMMA in comparison with undoped PANI. When the thickness of the PMMA coating is increased, the elec-

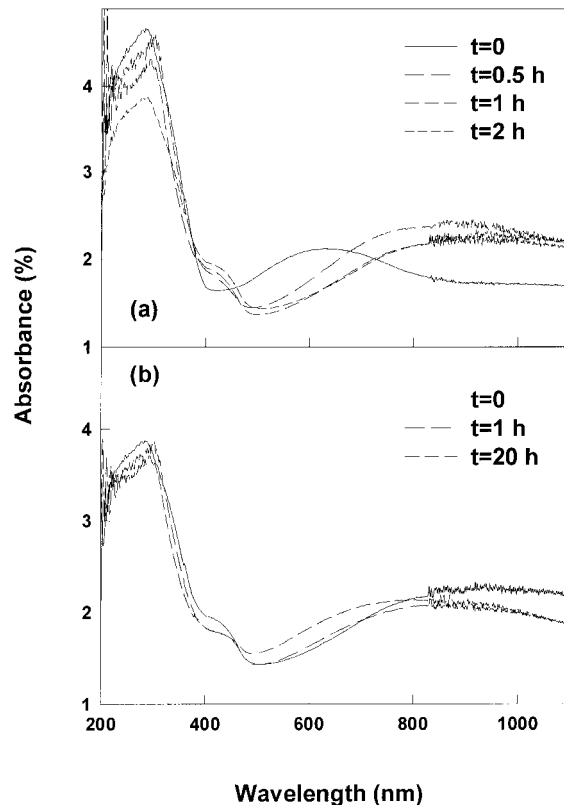


Figure 6 UV-vis absorption spectra of the viologen-PANI system spin-coated with PMMA (thickness $\sim 10 \mu\text{m}$) (a) after UV irradiation in air for various periods of time and (b) after UV irradiation in air for 2 h and subsequent treatment in water for various periods of time.

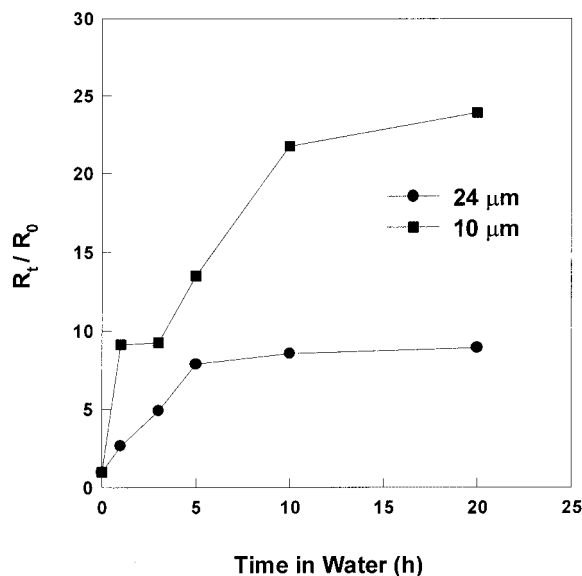


Figure 7 Changes in the resistance (the resistance at time t normalized by the resistance before water treatment) of the viologen-PANI systems with PMMA coatings of approximately 10 and 24 μm (subjected to UV irradiation in air for 2 h) after treatment in water for various periods of time.

trical stability of the viologen-PANI system is further improved, as shown in Figure 7. With a PMMA coating thickness of approximately 24 μm , the resistance of the system increases by less than 1 order of magnitude after treatment in water for 20 h. However, although the electrical stability of the viologen-PANI system can be increased, the photoinduced doping process would be slower with a thicker coating. With a UV irradiation time of 2 h, the conductivity of the viologen-PANI system with a 24- μm PMMA coating is, by a factor of 5–10, lower than that of the system with a 10- μm coating. However, after 4 h of irradiation, the same conductivity level is achieved in both cases. Therefore, a balance should be considered between the response time needed to achieve a conductive state and the extent of stability required when the viologen-PANI system is exposed to aqueous media.

To obtain an indication of the extent of loss of Cl^- anions, the PMMA spin-coated viologen-PANI systems (by the second method) before and after treatment in water were washed in chloroform to dissolve the PMMA coating and were then analyzed with XPS. Control experiments have shown that chloroform has a minimal effect on the photoirradiated viologen-PANI system. The XPS N1s and Cl2p core-level spectra of the sample after 2 h of UV irradiation and before treatment with water are shown in Figure 8(a,b), respectively. These spectra are very similar to those shown in Figure 3(c,d), respectively, and show the conversion of PANI from an insulating state to the doped state after UV irradiation. After water treatment for 20 h, the XPS data [Fig. 8(c,d)] show a de-

crease in N^+ ($[\text{N}^+]/[\text{N}] = 0.20$; cf. 0.32 in Fig. 8(a)) and Cl ($[\text{Cl}^-]/[\text{N}] = 0.17$; cf. 0.28 before water treatment). However, it is obvious from Figure 8(c,d) that PANI remains in the partially doped state, even though the doping level has decreased (and the conductivity has correspondingly decreased).

In a related experiment, the viologen-PANI system was first spin-coated with PMMA approximately 24 μm thick and then immersed in water and exposed to the 1000-W Hg lamp. A slow color change was observed after half an hour, and the film changed from blue to light green gradually. The UV-vis absorption spectrum after 5 h of irradiation shows the typical characteristics of doped PANI [Fig. 9(a)]. In contrast, a viologen-PANI system without the PMMA coating can hardly change color in water under UV irradiation for as long as 5 h because the simultaneous rapid undoping offsets the photoinduced doping.

Another technique, encapsulation, was also employed to improve the stability of the viologen-PANI system. In this experiment, a viologen-PANI system was laminated with an LDPE film ($\sim 50 \mu\text{m}$ thick), immersed in deionized water, and exposed to UV irradiation. The film gradually changed color from blue to green, as shown by the UV-vis absorption spectra in Figure 9(b). Because the viologen-PANI system was fully isolated from the aqueous medium, the same color change was achieved when the system was exposed to UV irradiation while immersed in a 1M NaOH solution. Therefore, the conductivity of the encapsulated viologen-PANI system can be maintained even when it is exposed to aqueous media of pH as high as 14.

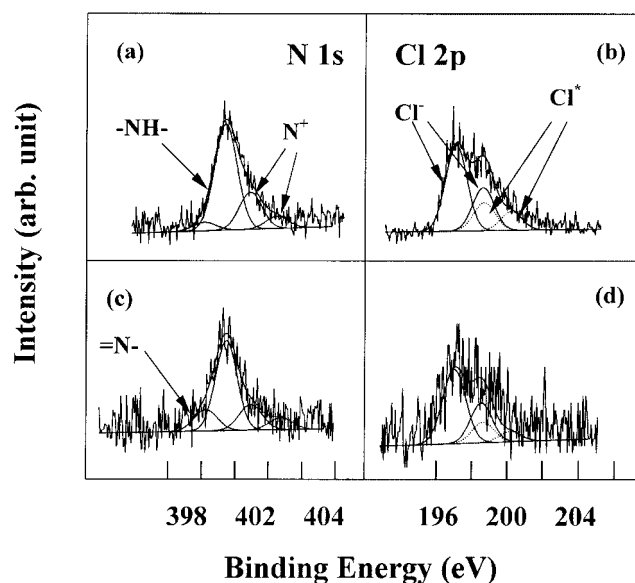


Figure 8 XPS N1s and Cl2p core-level spectra of the viologen-PANI systems spin-coated with PMMA approximately 10- μm -thick (a,b) after UV irradiation in air for 2 h and (c,d) after UV irradiation and subsequent water treatment for 20 h.

For both the spin-coated and laminated systems that were irradiated for 5 h while immersed in water, the surface analysis with XPS (after removal of the coating) confirms the conversion of PANI from the base state into the doped state, as shown in Figure 10. However, the results show that the doping levels (as indicated by $[N^+]/[N]$) of both these systems are lower than what can be achieved when the viologen-PANI system without a protective layer is irradiated in air for 1 h (cf. Fig. 10(a,c) with Fig. 3(c)). The $[Cl]/[N]$ ratios of the former two systems (0.26 for the spin-coated system and 0.22 for the laminated system) are also lower than that of the latter ($[Cl]/[N] = 0.34$).

CONCLUSIONS

UV irradiation of the viologen-PANI system prepared by the coating of PANI onto viologen-grafted LDPE film results in the conversion of PANI from the undoped emeraldine base state into a doped and conductive state. The conductivity of the doped PANI system decreases rapidly when the sample is treated in aqueous media of $pH > 5$ because of the anion migration out of PANI into water. However, the conductivity of the system increases by a factor of approximately 2 after treatment in a 1M HCl solution because of the further protonation of PANI by acid. The electrical stability of the viologen-PANI system in water

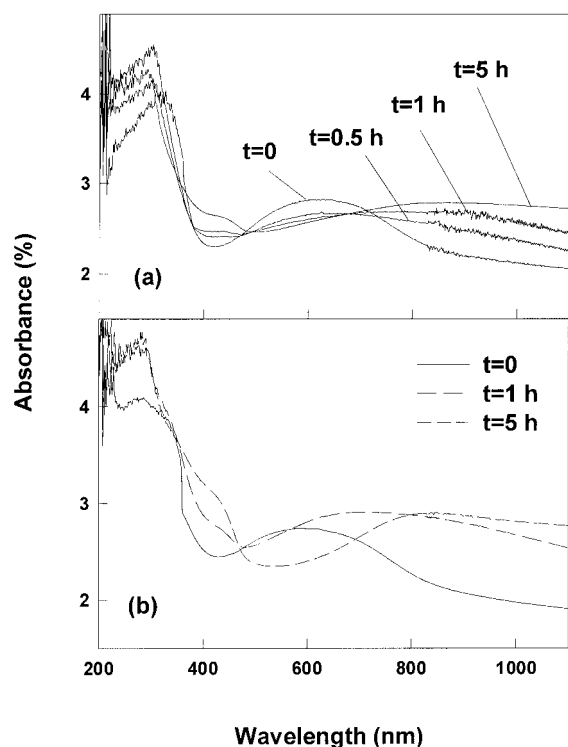


Figure 9 UV-vis absorption spectra of the viologen-PANI systems under UV irradiation in water for various periods of time (a) spin-coated with PMMA approximately $24 \mu\text{m}$ thick and (b) laminated with LDPE approximately $50 \mu\text{m}$ thick.

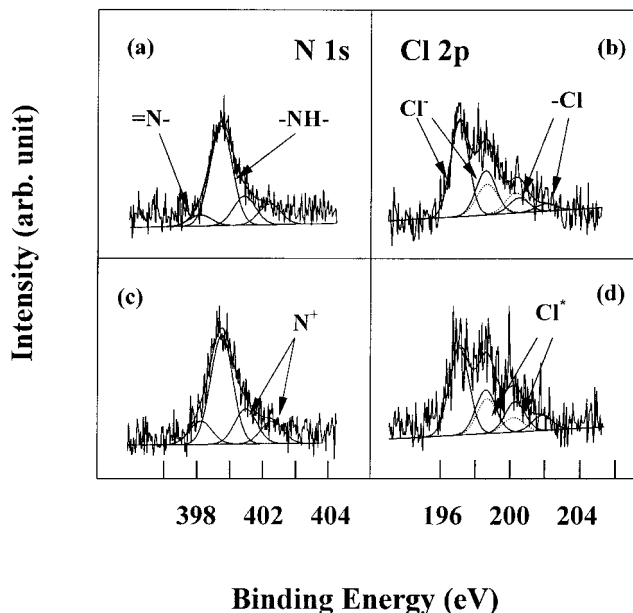


Figure 10 XPS N1s and Cl2p core-level spectra of the viologen-PANI systems after UV irradiation in water for 5 h (a,b) spin-coated with PMMA approximately $24 \mu\text{m}$ thick and (c,d) laminated with LDPE in approximately $50 \mu\text{m}$ thick (the coating was removed before XPS analysis).

can be improved by spin coating with PMMA. The photoinduced doping of PANI can be carried out either before or after the spin coating of PMMA. The PMMA coating is more effective if it is deposited on PANI before its conversion into the doped state. However, in the presence of the PMMA layer, the photoinduced doping process is slower, and the doping level is lower. A PMMA coating of about $10 \mu\text{m}$ is sufficient for a significant improvement in the electrical stability of the viologen-PANI system in aqueous media.

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