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Combination of Electrochemistry with Concurrent Reduction and Substitution Chemistry To Provide a Facile and Versatile Tool for Preparing Highly Functionalized Polyanilines

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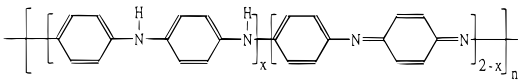
Various functional alkanethiols were found to be able to reduce polyaniline backbones from the emeraldine state **1** to the leucoemeraldine state **2**, simultaneously derivatizing the backbones to form functionalized polyanilines. X-ray photoelectron spectroscopy (XPS) studies proved that these thiols formed sulfide bond linkages with the polyanilines backbones. This concurrent reduction and substitution chemistry, which was found to happen only at the diiminoquinoid rings, provided a novel and potentially interesting way to control the degree of substitution of polyanilines. Via this novel concurrent reduction and substitution chemistry, dodecylthio substituent group can be added onto the backbone of polyaniline to enhance its solubility in THF. Moreover, acid-containing thiols, e.g. mercaptoacetic acid and mercaptoethanesulfonic acid, can also be covalently attached to the polyaniline backbone to form two new types of self-doped polyanilines. By coupling the redox capability of an electrochemical cell and the concurrent reduction and substitution chemistry, the already modified and reduced polyaniline backbone can be reoxidized to restore the emeraldine state **1**. Additional cycles of concurrent reduction and substitution chemistry can be conveniently employed to further enhance the degree of substitution and/or the functionality. Via this new approach, polyaniline emeraldine base **1** has been sequentially derivatized with three different functional groups, i.e., dodecylthio, mercaptoacetic acid, and mercaptoethanesulfonic acid, on the same backbone.

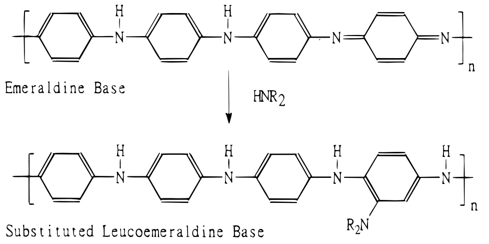
Owing to their unique electrooptical properties and market potential, polyanilines have been one of the recent focuses in the field of conducting polymer research.[1] However, polyanilines, just like other conducting polymers, are difficult to process due to their poor solubility in most common solvents. Though various approaches were made to enhance the solubility of polyaniline by the introduction of different substituents onto its backbone,[2] so far, none of the approaches enabled control of both the type of substituents and degree of substitution. Furthermore, no reports were made on the successful preparation of alkylamino- and alkylthio-substituted polyanilines. Unlike the preparation of other substituted polyanilines, so far, attempts to synthesize poly(alkylthioaniline) directly from the respective alkylthioaniline monomer via chemical or electrochemical oxidative-coupling chemistry have been unsuccessful. In our previous report,[3] it was found that various dialkylamines, e.g. pyrrolidine, piperidine, or morpholine, could reduce a polyaniline backbone from the emeraldine state **1** (Scheme 1) to the leucoemeraldine state **2** and simultaneously derivatized the backbone to form dialkylaminopolyanilines (Scheme 2). The dialkylamine nucelophiles were believed to attack the quinoid rings under the assistance of dopant residue (a protonic acid) and convert the diiminoquinoid ring into the diaminobenzenoid ring. Furthermore, though detailed discussion was not made, the same study also discovered that some alkanethiols, e.g. butane-1-thiol or dodecane-1-thiol, were more effective than dialkylamines in carrying out the above concurrent reduction and substitution (or derivatization) chemistry. Since the

Scheme 1



1 Emeraldine base (x = 1)
2 Leucoemeraldine base (x = 2)
3 Pernigraniline base (x = 0)

Scheme 2



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† Killed in a car accident on November 16, 1998.

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above nucleophiles were found to only attack the quinoid rings of the emeraldine base, the maximum amount of substituent group that can be incorporated was therefore limited to about 25 mol % of the polyaniline repeat units. In theory, the resulting modified leucoemeraldine polyaniline can be reoxidized with oxidants to regenerate the quinoid rings, which provide the active sites for a second round of concurrent reduction and substitution reaction. In practice, such bulk chemical oxidation was both time- and chemical-consuming. In addition, precise control of the degree of oxidation, homogeneity of oxidation, and isolation and purification of the product after oxidation were all difficult to achieve. All these difficulties had caused confusion on the interpretation of spectroscopic results obtained from monitoring such reactions; therefore, the fundamental chemical nature of the reaction remained unclear.

To overcome these difficulties, a facile new approach that combined the redox capability of an electrochemical cell and the above-mentioned concurrent reduction and substitution chemistry has been developed. This novel approach enabled one to control and enhance the degree of substitution on polyaniline backbones to any desirable levels beyond the 25 mol % limit, set by the number of quinoid rings in emeraldine base. In addition, more than one type of substituent could be added conveniently onto a polyaniline backbone in a sequential manner, providing the polymer with multiple capabilities, such as high solubility and/or self-doping ability.

Experimental Section

The growth of polyaniline thin films was conducted in a three-electrode electrochemical cell, using platinum plates or wires as both the working and counter electrodes and a saturated calomel electrode (SCE) as reference electrode. All the polymerization reactions were controlled by a potentiostat (EG&G 273) under a constant current density of 13.3×10^{-6} A/cm^2 for 25 min, in a 0.5 M H_2SO_4 aqueous solution that contained 0.1 M aniline. The thickness of the polyaniline film thus obtained (of about 80 nm) was measured by SIMS (secondary ion mass spectroscopy) depth-profiling and an α-step. Cyclic voltammogram of all resulted polyaniline films were performed on the same potentiostat in an aqueous solution of 0.5 M H_2SO_4. To ensure experimental reproducibility, all as-synthesized polyaniline films were converted to the same oxidation states by forcing the films at 0.5 V (vs SCE) for about 5 min, when the redox current approached zero. At this voltage, it was believed that polyaniline should have an oxidation state close to that of the emeraldine state.[4] The resulting polyaniline-coated electrodes were then cleaned by first dipping in deionized water (to remove anilinium hydrogen sulfate residue), followed by methanol (to remove the water residue), before being soaked in 0.1 M of different thiol solutions for a defined reaction time. On completion of the desired reaction period, these soaked polyaniline electrodes were cleaned and dedoped quickly by dip-washing in a series of solvents or solution in the following sequence: methanol (to remove dodecane-1-thiol residue), 5 wt % aqueous sodium carbonate (for 2 min to remove hydrogen sulfate dopant residue), deionized water (to remove Na_2CO_3 residue), and acetone (to remove the water residue).

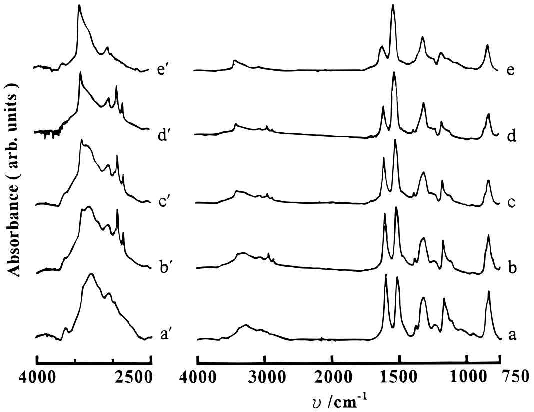

Figure 1. ATRIR spectra for the polyaniline-coated electrodes: after soaking with 0.1 M dodecane-1-thiol solutions for (a) 0, (b) 20, (c) 30, and (d) 60 min and (e) as in its leucoemeraldine state. Those corresponding enlarged spectra for the 2500−4000 cm^{-1} regions (with arbitrary magnifications) are displayed in traces a′−e′.

The treated polyaniline-coated electrodes were then dried with nitrogen gas and inspected immediately by attenuated total reflectance infrared (ATRIR) spectroscopy, using a Perkin-Elmer 2000 FTIR spectrometer equipped with a Graseby Specac single reflection diamond ATR accessory under a nitrogen atmosphere. The active area of the diamond contact probe was 0.6×0.6 mm. By assuming that the refractive index of the polyaniline films on the working electrode is 1.5, the theoretical surface penetration depths of the incident IR beam from 400 to 4000 cm^{-1} were calculated and found to be 2.3−0.23 μm. A constant clamping pressure, applied by using a torque wrench with setting at 60 cNm/m, was employed to ensure good and consistent surface contact between the diamond probe head and different polyaniline film specimens.

XPS (X-ray photoelectron spectroscopy) spectra of the polyaniline-coated electrodes were collected with a Physical Electronics ESCA PHI 1600 spectrometer, using Mg Kα as the X-ray source. The excitation area was 800×800 μm; the step-size for the survey and the chemical state spectra was 1.6 and 0.025 eV, respectively.

SIMS analysis of the polyaniline films was performed on a Cameca IMS-4f instrument, using Cs as the primary ion source. A raster area of 250×250 μm and an analysis area of 60×60 μm was employed.

Results and Discussion

Concurrent Reduction and Substitution of Polyaniline with Dodecane-1-thiol. The polyaniline thin films in this study had an average thickness of about 80 nm. After being forced to the same oxidation state (0.5 V vs SCE), the films were soaked in a 0.1 M methanolic solution of dodecane-1-thiol. The ATRIR spectra for the resultant films after being soaked for 20, 30, and 60 min are displayed in Figure 1b, c, and d, respectively. These spectra showed that as soaking time increased, a clear trend of intensity reduction at 1600

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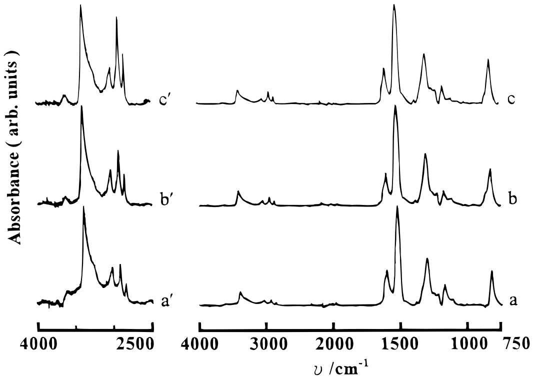

Figure 2. (a−c) ATRIR spectra for the same polyaniline-coated electrodes (b−d) in Figure 1 after being forced to −0.1 V (vs SCE). Those corresponding enlarged spectra for the 2500−4000 cm^{-1} regions (with arbitrary magnifications) are displayed in traces a′−c′.

cm^{-1} (C=C stretching vibration of diiminoquinoid rings[5]), 1169 cm^{-1} (a vibration mode associated with the diiminoquinoid ring[5]), and 820 cm^{-1} (C−H out-of-plane vibration on 1,4-ring[5]) can be observed. Similar intensity reduction of these three peaks has also been observed when polyaniline emeraldine base (Figure 1a) was reduced by hydrazine to leucoemeraldine base (Figure 1e). These results indicate that the resultant polyaniline films could be reduced to different extent when soaked in dodecane-1-thiol. The degree of reduction appeared to increase with the soaking time and reached a saturation level after about 60 min. The same ATRIR spectra also showed the appearance of new sp^3 C−H stretching peaks at 2928 and 2850 cm^{-1} whose intensities seemed to increase at the same pace with that of the C=C stretching for benzenoid rings at about 1500 cm^{-1}. The absence of the C=O vibration peak at 1715 cm^{-1} ruled out the possibility of contributions from acetone cleaning solvent being used just before the N_2-drying step. To identify the cause of these new C−H peaks, the same films were being driven to the same oxidation state with the potentiostat using −0.1 V vs SCE, in a 0.5 M H_2SO_4 aqueous solution, and ATRIR spectra were recorded immediately, as showed in Figure 2. Since all the polyaniline films were in the same oxidation state, the intensity of the peak for the C=C stretching vibration of the benzenoid rings at around 1500 cm^{-1} should remain constant and could be used as an internal standard for comparison. The intensities of the new C−H stretching peaks in the region of 2800−3000 cm^{-1} were found to be proportional to the soaking time of the film in dodecane-1-thiol solution, suggesting that these peaks are due to the dodecylthio substituent groups and the degree of substitution is proportional to the treatment time. The C−H deformation peaks for the newly introduced dodecylthio group should appear at about 1466 cm^{-1} (as for the CH_2 group in SCH_2 and other $-CH_2-$ groups) and 1378 cm^{-1} (for CCH_3), as suggested by the IR spectrum of dodecane-1-thiol. However, in Figure 2 the presence of peaks at theses positions is not obvious. This is probably due to the small intensities exhibited by these groups, for the intensities of corresponding peaks in dodecane-1-thiol were about one-half (for 1466 cm^{-1}) and one-sixth (for 1378 cm^{-1}) that of the peak at 2928 cm^{-1}.

The extent to which the dodecane-1-thiol-treated polyaniline films could be reduced was also studied by measuring the open circuit (OC) potential of each coated electrode vs SCE. Results showed that, after soaking treatments for 0, 20, 30, 60, and 90 min, the OC potential of the treated polyaniline electrode (i.e., the working electrode) was 0.5, 0.207, 0.151, 0.077, and 0.090 V, respectively. These results provided additional evidence that the films were reduced during the soaking treatment of polyaniline with dodecane-1-thiol and that the degree of reduction increased with the soaking time.

In a different experiment, a freshly prepared and cleaned polyaniline-coated electrode was forcefully reduced to the leucoemeraldine base **2** by application of −0.1 or −0.2 V vs SCE for about 5 min, when the redox current approached zero, followed by soaking in a 0.1 M methanolic solution of dodecane-1-thiol for 60 min. The ATRIR spectrum of the resulting film showed a negligible degree of substitution, as indicated by the absence of 2928 and 2850 cm^{-1} peaks, thus confirming that the thiol did not attack a fully reduced polyaniline film and that substitution activity only happened when diiminoquinoid rings were present. Contributions to the substitution and reduction reactions by methanol were not observed, as the ATRIR spectrum of an emeraldine polyaniline film (preconditioned at 0.5 V) did not showed any change after soaking in pure methanol for 4 h. The unambiguous results also confirmed that the present workup and dedoping process effectively removed all nonbonded thiol.

Multiple Cycles of Concurrent Reduction and Substitution of Polyaniline with Dodecane-1-thiol. An additional advantage of using the present electrochemical approach is that a modified polyaniline film can be reoxidized to any desirable oxidation states to repeat the concurrent reduction and substitution chemistry, thus further enhancing the degree of substitution on the polyaniline backbone.

The feasibility of the above has been demonstrated, by first preparing an electrode coated with a polyaniline film (polymerized for 25 min) and then soaking in a 0.1 M methanolic dodecane-1-thiol solution for 60 min. The modified polyaniline on the electrode was reoxidized in a 0.5 M aqueous solution of H_2SO_4 electrochemically, using a potential difference of 0.5 V (vs SCE) for 5 min, when the oxidation current approached zero. It was finally soaked in a 0.1 M methanolic solution of dodecane-1-thiol again for 60 min to undergo another run of concurrent reduction and substitution chemistry. The above reaction cycle can be repeated as many times as one desires.

The ATRIR spectra of the polyaniline film that had undergone one to three cycles of oxidation and reaction (60 min in each cycle) with a 0.1 M methanolic solution of dodecane-1-thiol are shown in Figure 3. For a clear comparison among the spectra, the resulted polyaniline films were forced to the same oxidation state at −0.1 V before ATRIR studies. The results clearly showed that the relative intensity of the sp^3 C−H peaks (at 2850 and 2928 cm^{-1}) to that for the benzenoid rings (at around 1500 cm^{-1}) increased with the number of reaction cycles, confirming the increase of the degree of substitution.

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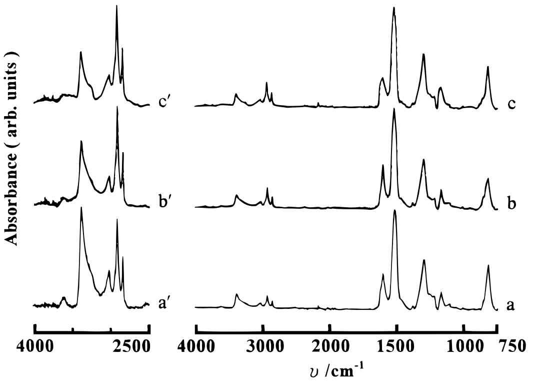

Figure 3. ATRIR spectra of dodecylthio-modified polyaniline-coated electrodes: samples after the (a) first, (b) second, and (c) third reaction cycles. The modified polyaniline electrodes were all forced to the same oxidation state, −0.1 V (vs SCE), for better comparison. Those corresponding enlarged spectra for the 2500−4000 cm^{-1} regions (with arbitrary magnifications) are displayed in traces a′−c′.

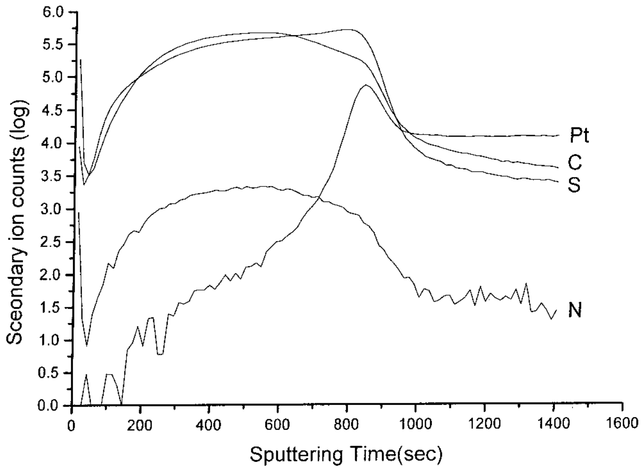

Figure 4. Secondary ion mass spectrum of dodecylthio-modified polyaniline film after the second reaction cycle.

The distribution of dodecylthio substituent within a polyaniline film was also investigated by a control experiment, in which a polyaniline film was grown and treated in an aqueous solution of $HClO_4$ instead of H_2SO_4 to prevent possible complications in the interpretation of results due to dopant residues. Figure 4 displays the SIMS spectra for a typical sample after a second reaction cycle with dodecane-1-thiol, with 60 min soaking time in each cycle. It clearly shows that the S atom (with the dodecylthio substituent group being the only sulfur source) is distributed evenly throughout the thickness of this control polyaniline specimen. Thus proving that the substitution reaction was not just limited to the surface of the film.

Results from XPS studies on polyaniline films subjected to a different number of cycle of treatments are summarized in Figure 5, with the dedoped polyaniline film represented by parts a (survey spectrum) and a′ (chemical state spectrum of S2p region) of Figure 5. The results showed no signs of S peaks in the dedoped polyaniline film, confirming that the present workup and dedoping process effectively removed the H_2SO_4 residues. The results in Figure 5b−d also clearly indicated that the intensity of the S2p lines (at ca. 160 eV) increased with the reaction cycles relative to that of the N1s lines (at ca. 400 eV). The spectra in Figure 5b′−d′ also indicated that the binding energy of the S2p$_{3/2}$ line in these modified polyanilines was 163.5 eV, confirming the formation of sulfide, but not disulfide or thiol (nor any sulfate residues from H_2SO_4 was observed), and none of the samples gave off the odor of thiols. [The S2p$_{3/2}$ line was reported to be 163.66 eV for poly(phenylene sulfide), 163.50 eV for poly(ethylene sulfide), 164.4 eV for phenyl disulfide, 164.1 eV for butyl disulfide, 163.1 eV for thiophenol, 161−163 eV for alkanethiols, and 168.23 eV for poly(sodium 4-styrenesulfonate) (ref 6).] The presence of the hypothetical alkyl disulfides is also ruled out, due to their weak interactions with polyaniline and high solubility in the methanol and acetone washing solvents being used. To further demonstrate the present proposed reaction pathway, a model compound was prepared by reacting *N*,*N*′-diphenylphenylene-1,4-diimine with an alkane-1-thiol, e.g. butane-1-thiol via the same reduction and substitution chemistry, which yielded a butylthio-substituted *N*,*N*′-diphenylphenylene-1,4-diamine. [^{13}C NMR data for the butylthio-substituted *N*,*N*′-diphenylphenylene-1,4-diamine: δ_C 13.55, 21.79, 31.39, 34.49, 116.05, 117.81, 117.97, 119.86, 120.68, 120.86, 124.96, 125.51, 129.28, 136.04, 138.52, 143.50 and 144.49. For *N*,*N*′-diphenyl-1,4-phenylenediamine: δ_C 115, 118.2, 119.6, 128.93, 136.4 and 144.8. For *N*,*N*′-diphenyl-1,4-phenylenediimine: δ_C 120.25, 120.38, 124.35, 125.04, 125.08, 125.29, 136.39, 137.7, 149.8, 149.83, 157.84 and 157.9, complicated by the presence of both *E* and *Z* forms (ref 7).]

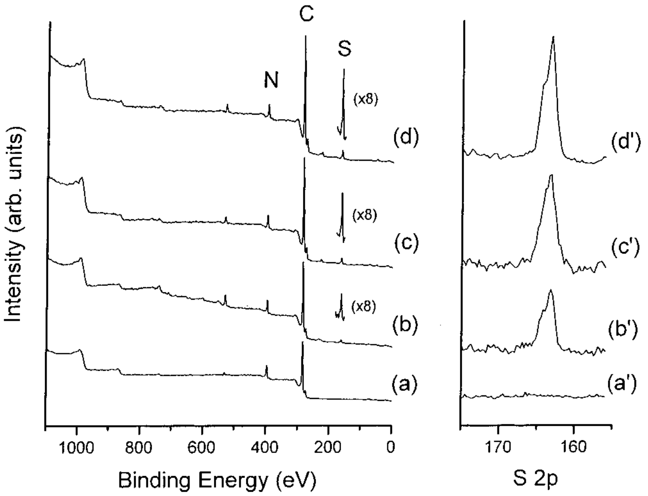

Figure 5. XPS spectra for (a) the original undoped polyaniline film and (b−d) the polyaniline films after the first, second, and third reaction cycles. The chemical state spectra of S2p for the polyaniline films are displayed in a′−d′.

Since all the S atoms in these modified polyanilines were identified by XPS to be from the alkylthio substituent and the S-containing group was found by SIMS to be homogeneously distributed throughout the film, it follows that the ratios of S to N atoms for these modified films, measured by XPS, can fairly represent the average degree of substitution. The ratio of S/N atoms for the polyaniline films resulting from the first, second, and third reaction cycle was equal to 0.247, 0.388, and 0.461, respectively. Such results showed that, apparently, the concurrent reduction and substitution proceeded at a rate that enabled near completion of the reactions in the first 60 min reaction cycle, but the reaction rate became slower in the second and third

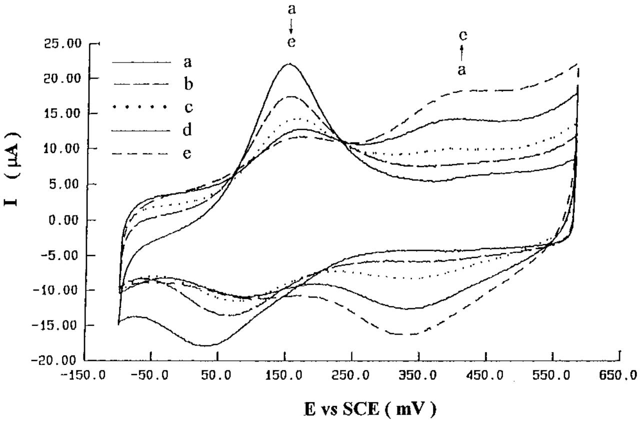

Figure 6. CV curve for the polyaniline-coated electrode: (a) before the reaction and (b)−(e) after the first, second, third, and fourth reaction cycles of 60 min soaking treatment with 0.1 M methanolic solutions of dodecane-1-thiol. All the CV curves were obtained by scanning between −0.1 and 0.6 V (vs SCE) in 0.5 M H_2SO_4 aqueous solutions, at a rate of 30 mV/s.

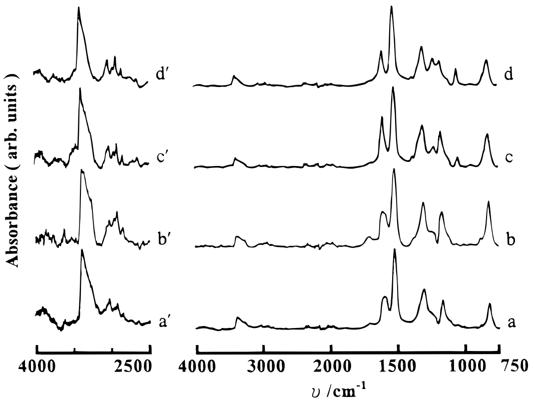

Figure 7. ATRIR spectra for the polyaniline-coated electrodes after the first reaction cycle (a, c) and the second reaction cycle (b, d) of 60 min soaking treatments with 0.1 M aqueous solutions of (a, b) mercaptoacetic acid and (c, d) 2-mercaptoethanesulfonic acid. Those corresponding enlarged spectra for the 2500−4000 cm^{-1} regions (with arbitrary magnifications) are displayed in traces a′−d′.

cycle. Although the exact reason is still unclear, it is believed that such behavior might be due to the change in surface energy of the film when substituent groups were introduced. The change in surface energy might reduce the wetting ability of the film during either the oxidation step or the reaction step after the first reaction cycle.

The results also showed a clear trend of an increase in the intensity of the C1s peak (at ca. 285 eV) relative to that of the N1s peak. The ratio of C/N atoms was found to be 8.3 (±0.8), 10.9 (±0.5), and 12.7 (±1.0) for the films obtained from the first, second, and third reaction cycle, respectively. Such a result is consistent with the expectation that the average number of carbons for each polyaniline repeat unit should increase as the number of the dodecylthio substituent increases. Assuming that the S/N ratio actually represents the degree of substitution, theoretical C/N ratios of 8.96, 10.64, and 11.53 can be calculated for the respective reaction cycle. Within permitted experimental error, such theoretical ratios are in close agreement with the experimental C/N atom ratios from XPS studies.

The cyclic voltammograms, scanned between −0.1 and 0.6 V at 30 mV/s, for the above modified-polyaniline films up to the fourth reaction cycle, are displayed in Figure 6. As the number of reaction cycles increased, the anodic and cathodic peaks of the original couple at 0.15 and 0.03 V diminished, while a new couple appeared at around 0.41 and 0.33 V. Interestingly, although the electrochemical responses for these modified polyanilines have altered significantly, the total redox peak currents (between −0.1 and 0.6 V), especially for those films resulted from the first and second reaction cycles (Figure 6, CV traces b and c), were quite similar to that of the original unsubstituted polyaniline (Figure 6, CV trace a). The results indicated that the changes in CV responses were mainly caused by the structural and electronic modifications of the polyaniline backbones, instead of by the inclusion of other hypothetical redox species, such as disulfide.

Regarding CV response within the potential range of −0.1 to 0.6 V (vs SCE), the unsubstituted polyaniline shows only one pair of CV responses. But as the number of reaction cycle increases, two pairs of CV responses begin to appear, with the intensity of the pair at higher voltage gradually overtaking that for the pair at lower voltage. Similar observation had also been reported for monoalkoxy- and dialkoxy-substituted polyanilines.[2a,8] Since both alkoxy and thio substituents are electron-donating in nature, it is reasonable to assume that both will induced similar electrochemical effect on polyaniline. Therefore, the results in Figure 6 suggest that, at the first and second reaction cycles, monosubstituted polyanilines form predominantly. While on further treatments, disubstituted polyanilines become more abundant. As one would expect, the solubility of the substituted polyaniline also increased with the degree of substitution. The present results indicated that the modified polyanilines from the third reaction cycle and thereafter were highly soluble in THF.

Concurrent Reduction and Substitution of Polyaniline with Thiols Containing Acid Functional Groups. The same reduction/substitution chemistry is also useful for bringing in other functional groups, such as mercaptoacetic acid and 2-mercaptoethanesulfonic acid, onto a polyaniline backbone. By introducing these functional acid substituents, polyanilines can easily be rendered with self-doping capability. The concentrations of such dopant substituents can also be controlled by the reaction procedures described above. The ATRIR spectra of polyaniline films from the first and second cycle of treatment with a 0.1 M aqueous solution of mercaptoacetic acid (a soaking time of 60 min in each cycle was used) are shown in parts a and b of Figure 7, respectively. The resulted polyaniline films were dedoped thoroughly with an aqueous solution of Na_2CO_3 to remove any nonbonded mercaptoacetic acid residue. After the dedoping treatment, the covalently bonded mercaptoacetic acid substituent had all been converted to the carboxylate form, whose characteristic vibration

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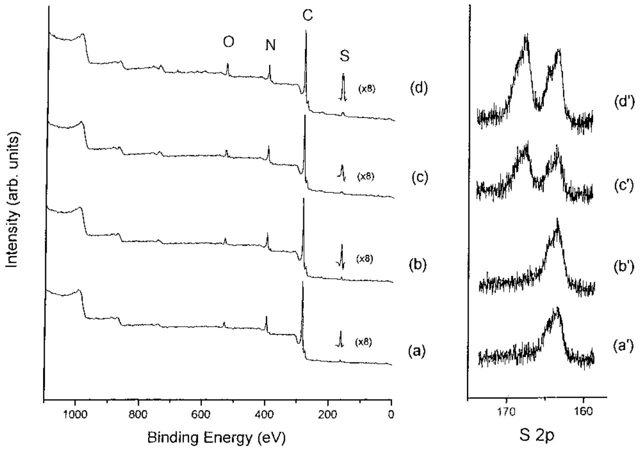

Figure 8. XPS spectra for the polyaniline-coated electrodes after the first reaction cycle (a, c) and the second reaction cycle (b, d) of 60 min soaking treatments with 0.1 M aqueous solutions of (a, b) mercaptoacetic acid and (c, d) 2-mercaptoethanesulfonic acid. The chemical state spectra of S2p for the corresponding polyaniline films are displayed in a′–d′.

peak was at ca. 1580 cm^{-1} and merged with the C=C stretching peak of polyaniline diiminoquinoid ring. To confirm the presence of the covalently bonded carboxylic groups, the above dedoped polyanilines were dipped in diluted acid solutions, such as 0.1 M HCl or 0.1 M H_2SO_4, to reprotonate the carboxylate group. The reprotonated polyaniline films were then rinsed with copious amount of H_2O (to remove the HCl or H_2SO_4 residue) and inspected immediately by ATRIR. The ATRIR spectra (Figure 7a,b) clearly showed a new C=O stretching vibration peak at 1703 cm^{-1} (for the carboxylic acid) and a broadened peak at ca. 1600 cm^{-1} (probably due to the merging of the carboxylate peak at about 1580 cm^{-1}). The position of the two peaks at 1703 and 1580 cm^{-1} is consistent with the absorption for 2-mercaptoacetic acid (1711 cm^{-1}) and its sodium salt (1581.5 cm^{-1}). The C=O stretching peak at 1703 cm^{-1} disappeared and reappeared repeatedly during every dedoping and reprotonation cycle, whereas the C=O stretching peak near 1580 cm^{-1} was present all the time.

The XPS spectra for these two carboxylic acid-modified polyanilines are displayed in parts a and b of Figure 8. The S2p$_{3/2}$ line (Figure 8a′,b′) again appeared at 163.5 eV, confirming the formation of the sulfide linkage. The ratio of S to N atoms, as measured, was about 0.109 and 0.181 for the films obtained after the first and second reaction cycle, respectively. The degrees of substitution in these two cases are much lower than for the films treated with dodecane-1-thiol. As the treatment time in dodecane-1-thiol and mercaptoacetic acid was the same, a lower degree of substitution implied a slower rate of substitution. This is believed to be due to the higher interfacial diffusion barrier encountered by mercaptoacetic acid in the aqueous reaction media. Actually, when the reaction was performed in a homogeneous single phase (e.g. in *N*-methylpyrrolidone, NMP, solution), mercaptoacetic acid was found to react with the polyaniline emeraldine base **1** at a rate about 7 times faster than dodecane-1-thiol. A control experiment was performed by reacting polyaniline emeraldine base **1** (8.8×10^{-5} M, based on the repeat unit of polyaniline) with 1 equiv of mercaptoacetic acid (8.8×10^{-5} M) in NMP solution. Under such reaction conditions, all starting materials and products dissolved completely in NMP, and the progress of the reaction was monitored with a UV–vis–NIR spectrometer. As the reaction proceeded, the quinoid ring absorption band at about 630 nm diminished, while the benzenoid ring band at about 320 nm increased in magnitude. In fact, for mercaptoacetic acid, the 630 nm band disappeared completely within 10.5 min, but for treatment with dodecane-1-thiol, it took about 70 min for the same band to disappear.

Other types of self-doped polyaniline that contained sulfonic acid group had also been successfully prepared by soaking the polyaniline (with 0.5 V oxidation state) in a 0.1 M aqueous solution of the sodium salts of 2-mercaptoethanesulfonic acid. The ATRIR spectra displayed in parts c and d of Figure 7 are for the films obtained after the first and second reaction cycle with 2-mercaptoethanesulfonic acid. The new IR peaks at about 1219 and 1043 cm^{-1} are attributable to the asymmetric and symmetric SO_3 stretching peak of the newly introduced substituent of 2-mercaptoethanesulfonic acid. The positions of these peaks were consistent with those for the sodium salt of 2-mercaptoethanesulfonic acid (1218 and 1061 cm^{-1}) and sulfonated polyaniline (1080 cm^{-1}).[9,10] Intensities of these SO_3 vibration peaks also increased with the number of reaction cycles. The XPS spectra as displayed in parts c and d of Figure 8 correspond to the films obtained from the first and second reaction cycle. The ratio of S to N atoms was 0.150 and 0.303 for films obtained after the first and second reaction cycle, respectively. Two newly appearing S2p$_{3/2}$ lines (Figure 8c′,d′) were found at 163.5 and 168.0 eV, due to the sulfide linkages and sulfonic acid terminal group, respectively. Once again, the slower reaction rate than for dodecane-1-thiol is believed to be due to the higher interfacial diffusion barrier encountered by mercaptoethanesulfonic acid. A control experiment was conducted by reacting 18.4 g of mercaptopropanesulfonic acid (as a solute) with 0.5 g of polyaniline emeraldine base **1** (as a suspension) in 45 mL of mixed solvent of NMP and H_2O (v:v = 2:1) under N_2 for 2 days. Elemental analysis showed that the resulted polyaniline had a degree of substitution of 25.1 mol % (based on the repeat unit of polyaniline).

Preparation of Polyanilines with Multiple Functional Groups. Such cyclic processing of concurrent reduction and substitution with electrochemical reoxidation steps can be further utilized to enhance the functionality of polyanilines, by introducing more than one type of substituents in a sequential manner to the same polyaniline backbone. This capability was demonstrated by first treating the as-synthesized polyaniline electrode at 0.5 V for 5 min, followed by sequential soaking treatments (60 min each) with 0.1 M solutions of mercaptoethanesulfonic acid, dodecane-1-thiol, and mercaptoacetic acid. The reduced polyaniline-coated electrode was reactivated each time at 0.5 V for 5 min to regenerate the diiminoquinoid rings between different soaking treatments. The ATRIR spectrum for a reacti-

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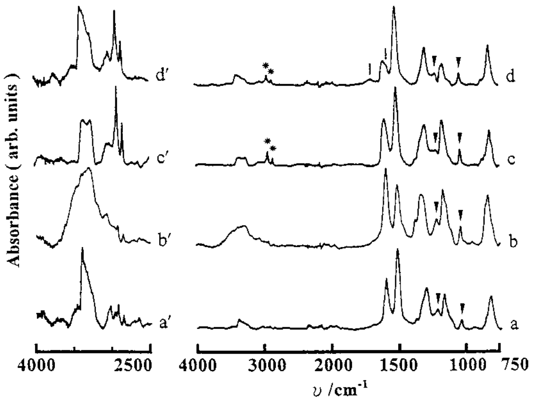

Figure 9. ATRIR spectra for the same polyaniline-coated electrode after 60 min soaking treatments sequentially with 0.1 M solutions of (a) 2-mercaptoethanesulfonic acid, (c) dodecane-1-thiol, and (d) mercaptoacetic acid. (b) ATRIR spectrum for reactivated polyaniline film after the treatment described in a. Those corresponding enlarged spectra for the 2500–4000 cm^{-1} regions (with arbitrary magnifications) are displayed in traces a′–d′. The characteristic vibration peaks for different groups are marked by: ▼ (sulfonic), * (alkylthio), and | (carboxylic).

vated polyaniline film is illustrated in Figure 9b. The ATRIR spectra in parts a, c, and d of Figure 9 clearly recorded the sequential appearance of the new SO_3 peaks (1043 and 1219 cm^{-1}; Figure 9a), sp^3 C–H peaks (2928 and 2850 cm^{-1}; Figure 9c), and C=O peaks (1703 and 1580 cm^{-1}, Figure 9d) from the treated polyaniline film. This is in complete agreement with the reaction sequence of adding mercaptoacetic acid, dodecylthio, and mercaptoacetic acid functional groups onto the polyaniline backbone, in different cycles of treatment.

Conclusion

Various functional alkanethiols were found to be capable of reducing the polyaniline backbones from an emeraldine state **1** to a leucoemeraldine state **2** and simultaneously derivatized the backbones to form functionalized polyanilines. XPS results proved that the thiols form sulfide bonds with polyaniline backbones. ATRIR results also confirmed that the reduction of the polyaniline backbones and the presence of thio substituents occurred concurrently. CV results showed that the redox behaviors of the resulting polyaniline films were altered, in accordance with the changes in backbone structures. Via this novel concurrent reduction and substitution chemistry, the dodecylthio substituent group had been added to the backbone of polyaniline to enhance the solubility of polyaniline in THF when the degree of substitution was greater than about 45–50%. Acid-containing thiols, e.g., mercaptoacetic acid and mercaptoethanesulfonic acid, could also be covalently attached onto the polyaniline backbone to form two new types of self-doped polyanilines. The attached acid functional groups remained intact after many cycles of thorough dedoping and redoping treatments.

By coupling the redox capability of an electrochemical cell and the concurrent reduction and substitution chemistry, an already modified and reduced polyaniline backbone could be reoxidized to restore the emeraldine state **1**. Additional cycles of concurrent reduction and substitution chemistry with the same or different thiols could then be conveniently utilized to further enhance the degree of substitution and/or the functionality of polyaniline. Via this new approach, polyaniline emeraldine base **1** has been sequentially derivatized with three different functional groups, i.e., dodecylthio, mercaptoacetic acid, and mercaptoethanesulfonic acid, on the same backbone. Thus, the above results indicate that the novel method reported herein is a very convenient approach for the preparation of highly functionalized polyanilines, which could not be otherwise prepared from conventional monomer polymerization or copolymerization approaches. Since the reactions only take place at the diiminoquinoid sites, the degree of substitution can be varied by controlling the oxidation state of the polyaniline backbones, when the reaction time is long enough and/or the interfacial diffusion barrier can be overcome. The utilization of a surface infrared characterization technique such as ATRIR provided a convenient and speedy method to extract reliable chemical information from specimens very close to the states right after the reaction. Although the present method did not provide instantaneous information like in situ IR studies, it did have the additional advantages of allowing the immediate quenching of a reaction at the desirable time and allowed the complete removal of undesirable residual chemicals, to clarify the chemical information being obtained.

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