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Detection of Intermediate during Electrochemical Polymerization of Azure A and X-ray Photoelectron Spectroscopy of Poly(azure A)

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The electrochemical polymerization of azure A has been investigated by the rotating ring-disk electrode (RRDE) and the X-ray photoelectron spectroscopy (XPS). The electrolysis of azure A was studied in the pH region of 1.0 and 12.0. The results from the RRDE experiments show that the electrochemical polymerization of azure A was performed by two steps, i.e., oxidation of azure A and followed by polymerization. The intermediates generated at the disk were detected at the ring electrode in the ring potential region of -0.2 – 0.20 V (vs. Ag/AgCl reference electrode). The collection efficiencies of the intermediates increase with decreasing the ring potential as well as increasing the rotation rate of the RRDE. Thus, the intermediate is to carry a positive charge species and not too stable. The results from the XPS experiments show that the anions can be doped into poly(azure A) film and be dedoped from it during oxidation and reduction processes.

Keywords: conducting polymer; electrochemistry; cyclic voltammetry, rotating ring-disk electrode; intermediate; XPS

1 Introduction

Electroactive polymers have attracted much attention for both theoretical reasons and potential applications in sensors, rechargeable batteries, electrochromic and optoelectronic devices. The different applications need conducting polymers having different properties, thus, the synthesis of new types of conducting polymers is very important in the field of material sciences. Among these polymers, polyazines present a group which produces useful electrode transfer mediators and is used as immobilization of enzymes (1, 2). Due to its conjugative ring structure, azure A, an azine derivative, may be a promising block for building high-quality conducting polymers. In fact, Karyakin et al. has reported that azure A can be polymerized electrochemically in the solution consisting of azure A, borax and NaNO_3 with pH 9.19 (3). We found that a poly(azure A) film was formed in aqueous solution at various pH values and that the poly(azure A) film has a good reversibility, high electrochemical activity

and a fast charge transfer ability at pH range of 1.0 and 4.0 (4, 5). This electrochemical behavior is better than that of polyaniline. The electrochemical activity of polyaniline decreased with increasing pH, and was almost completely lost at pH higher than 4 (6). Therefore, poly(azure A) film is expected to be a good biomaterial. However, the growth rate of poly(azure A) film is much lower than that of polyaniline film.

Recently, Agrisuelas et al. (7) reported that the dependence of the absorbance on the applied potential during cyclic voltammograms proved very interesting at two selected characteristic wavelengths: at 925 nm, attributed to an intermediate species and another at 735 nm, attributed to the oxidized form of the polymer, according to the Vis/NIR spectroelectrochemical analysis of poly(azure A) on ITO electrode. To gain a better understanding of the polymerization mechanism of azure A, we try to use rotating ring-disk electrode (RRDE) to study the electrochemical polymerization of azure A. This is due to the fact that RRDE experiment can provide a richness of information about the formation, detection and decay of an intermediate. Also, this technique can easily identify whether an intermediate generated at the disk electrode is charged or not by varying the ring electrode potential. It is also known that the X-ray photoelectron spectroscopy (XPS) has been successfully employed to

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study that the anions can be doped into polymer film and dedoped from it during oxidation and reduction processes (8). In this paper, we report the effects of the ring potential, rotation rate and pH value of the electrolytic solution on the electrolysis behavior of azure A and XPS experiments of poly(azure A).

2 Experimental

2.1 Reagents

The chemicals used were all reagent grade. Doubly distilled water was used to prepare solutions.

2.2 Electropolymerization

An electrolytic solution is usually a mixture of a solvent (here water) and an electrolyte (here H_2SO_4 or Na_2SO_4). The electroactive azure A was added into the solution to prepare a polymer. The electrolysis of azure A was carried out by using repeated potential cycling in the solution consisting of $5.0 \text{ mmol} \cdot \text{dm}^{-3}$ azure A and $0.3 \text{ mol} \cdot \text{dm}^{-3}$ Na_2SO_4 . The pH value of this solution was controlled between 1.0 and 12.0.

We used cyclic voltammetry to study the electropolymerization of azure A. The scan rate was 60 mV s^{-1} . The sweeping potential ranges were set in the region of 0 and 1.30 V. The electrochemical experiments were carried out at room temperature.

2.3 Equipment and Measurements

The pH value of the solutions was measured using a Model PXD-12 pH meter. A Model HR-103A (Japan) rotating ring-disk electrode (RRDE) was used for the investigation on the electrochemical polymerization of azure A. The electrolysis cell consisted of a platinum disk electrode, a platinum ring electrode, a platinum counter electrode and a reference electrode of Ag/AgCl with saturated KCl solution.

The diameter of the platinum disk electrode is 7.89 mm. The collection efficiency of the RRDE is 0.4187. A HPD-1A potentiostat-galvanostat was used for electrolysis of azure A. The disk current and ring current as function of potential and time, respectively, were recorded simultaneously using a Model 3086 bipen recorder. The sweeping potential range was set between 0 and 1.30 V.

XPS spectra were measured on a VG Escalab 220i-XL photoelectron spectrometer with Al-K α exciting radiation used at 15 kV and 20 mA; the base pressure was approximately 10^{-9} torr. Survey scans in the range 0–1200 eV were recorded for XPS spectra of the copolymer polymerized on platinum foil at a pass energy of 100 eV with a step size of 1 eV. Core level spectra were obtained for C 1s, N 1s, S 2p and O 1s with a pass energy of 40 eV and a step size of 50 meV.

3 Results and Discussion

3.1 Electrolysis of Azure A using RRDE

3.1.1 Effect of the Ring Potential

To know whether an intermediate generated at the disk is charged or not, the ring potential was changed at 0.1 V interval from -0.2 to 0.2 V. The electrolysis of azure A was carried out using a RRDE. The electrolytic solution consisted of 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 with pH 6.0. The rotation rate was controlled at 1000 r.p.m. The potential scan rate was set 60 mV s^{-1} . Here we present three plots with different ring potentials to explain the effect of ring potential on the ring current.

The plots A and B in Figure 1 show the i_d-E and i_r-t curves obtained at the ring potentials of -0.2 and 0.1 V, respectively. Curves 1, 2 and 3 in the above plots are the first, fifth and tenth scans, respectively. There are two peaks at 0.35 and 1.05 V on the i_d-E curve of each plot for the first scan. The first oxidation peak at 0.35 V is attributed to the oxidation of azure A. The second oxidation peak at 1.05 V is caused by the polymerization of azure A. Two corresponding reduction current peaks occur on the i_r-t curve. This means that two soluble intermediates were generated at the disk electrode during the electrolysis of azure A. The feature that i_d-E curve and i_r-t curve at each plot have in common is that their peak currents decrease with an increasing number of potential scans. This is due to the fact that poly(azure A) was polymerized on the naked platinum for

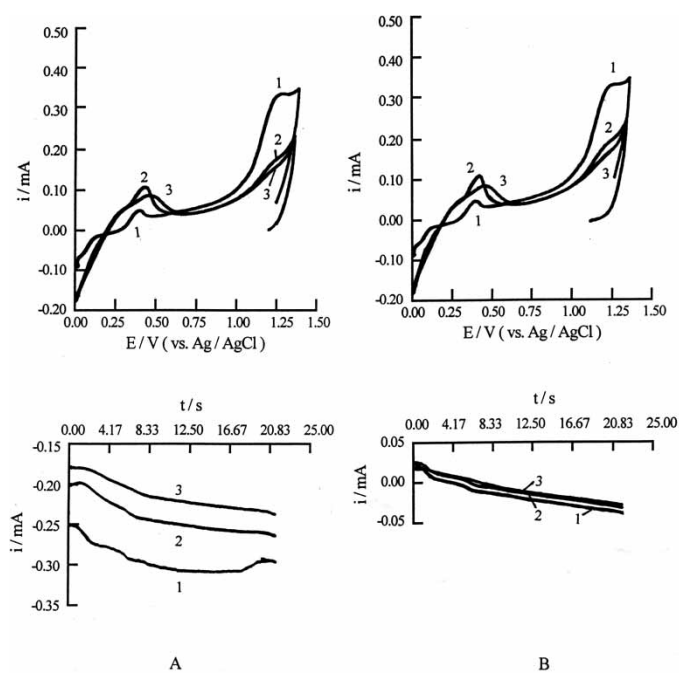


Fig. 1. Effect of the ring potential on the ring current. The electrolytic solution containing 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 with pH 6.0. Rotation rate: 1000 r.p.m. Potential scan rate: 60 mV s^{-1} . Plot (A): -0.20 V, Plot (B): 0.10 V (vs. Ag/AgCl with saturated KCl solution). Curves: (1) first scan, (2) fifth scan, (3) tenth scan.

the first scan; however, poly(azure A) was polymerized on the poly(azure A) film itself for the fifth scan. That means the oxidation and the polymerization of azure A were affected by the electrode material.

Plot A in Figure 1 shows that two soluble intermediates generated at the disk electrode were reduced at the ring electrode. Since their current values are negative, this is just contrary to the direction of the disk current. However, Plot B in Figure 1 shows that the ring current becomes positive at the beginning electrolysis, then a peak is formed as the disk potential continues to scan and finally decreases quickly on the i_r-t curve. The former is caused by the oxidation of azure A, because the ring potential is set at 0.1 V in this case, this is in good agreement with that at the disk electrode. The latter is caused by that the flux of azure A to the ring increases as the disk potential continues to scan towards the positive direction, the oxidation rate of azure A at the disk increases slowly with increasing potentials. This results in the fact that a corresponding anodic current decreases quickly on the i_r-t curve.

Figure 2 shows the relationship between the collection efficiency N , i.e., the ratio of the ring current to the disk current of the redox of azure A itself, and the ring potential. The experiments were carried out under the same conditions as described in Figure 1, but the ring potential was altered from -0.20 to 0.20 V. Curves 1, 2, 3, 4 and 5, for the first scan at 500, 1000, 2000, 2500 and 3000 r.p.m., show that their collection efficiencies increase when the ring potential was decreased from 0.2 to -0.2 V, respectively. This means that the amount of the intermediate collected at the ring electrode increases with decreasing ring potential. It follows that the intermediate is a positively charged species. The collection efficiency of the intermediate is very small compared with the collection efficiency of 0.4187 determined for the stable product generated at the disk electrode. This indicates that some of the intermediates generated at the

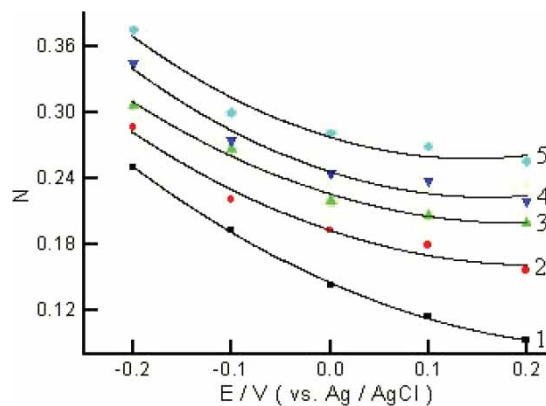


Fig. 2. The relationship between the collection efficiency N of the redox of azure A itself for the first scan and the ring potential based on the data from the effect of the rotation rate on the peak currents. The electrolytic solution is the same as that shown in Figure 1, pH 6.0. Potential scan rate: 60 mV s^{-1} . Curves: (1) 500 r.p.m., (2) 1000 r.p.m., (3) 2000 r.p.m., (4) 2500 r.p.m., (5) 3000 r.p.m.

disk were decomposed in their passage from disk to ring. So the intermediate in this case is not stable.

Based on the relationship between the collection efficiency N of the polymerization of azure A and the ring potential ($N-i_r$ plot omitted here), the result is similar to that of the redox of azure A itself. So both kinds of the intermediates in this case are positively charged and not stable.

3.1.2. Effect of pH on Electrolysis of Azure A

The electrolytic solution consisted of 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 . The pH values of this solution were set at 1.0, 6.0 and 12.0, respectively. Here we present three plots with different pH values to express the effect of pH on the electrochemical polymerization of azure A.

The potential scan rate was set 60 mV s^{-1} . The rotation rate of the RRDE was controlled at 1000 r.p.m. The ring potential was controlled at -0.1 V. Plots A and B in Figure 3 show the results of the RRDE experiments at pH 1.0 and 12.0, respectively. The i_d-E curve at each plot in Figure 3 is different in shape as well as i_r-t curve. The disk current for the electrolysis of azure A at pH 1.0 begins to rise from 0 V, then forms an anodic peak, and finally, another oxidation peak occurs at 1.25 V as the potential continues to scan towards the positive direction for the first scan (Curve 3). Also, two corresponding reduction peaks occur on the i_r-t curve. After electrolysis, a poly(azure A) film was found on the disk electrode.

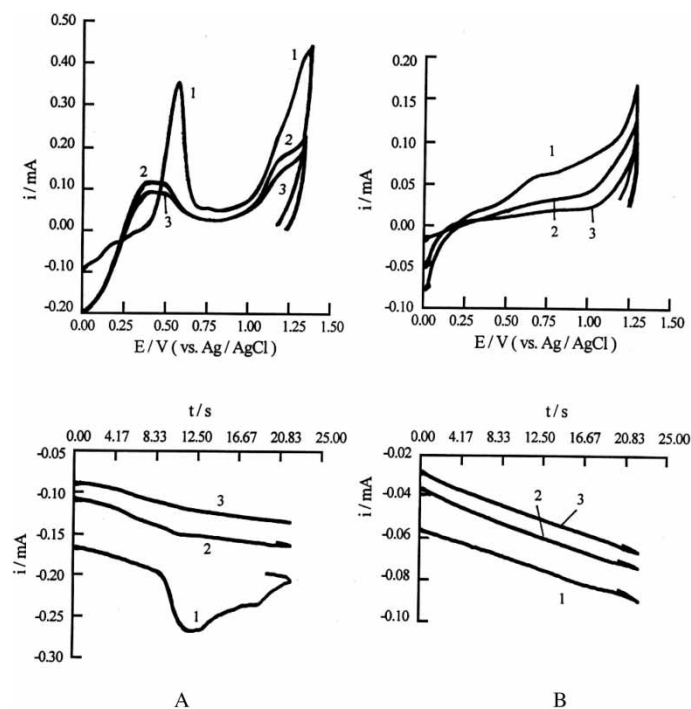


Fig. 3. Effect of pH on electrolysis of azure A. The electrolytic solution is the same as that shown in Figure 1, pH 6.0. Ring potential: -0.1 V. Rotation rate: 1000 r.p.m. Potential scan rate: 60 mV s^{-1} . Plots: (A): pH 1.0; (B): pH 12.0. Curves: (1) first scan; (2) fifth scan; (3) tenth scan.

The plot of the electrolysis of azure A at pH 6.0 (omitted here) is similar to the Plot B in Figure 1. Two oxidation peaks at 0.35 and 1.05 V occur on the i_d-E curve of the first scan (Curve 1). Also two corresponding reduction peaks occur on the i_r-t curve. This is different from Plot A in Figure 3. Plot B in Figure 3 shows the results from electrolysis of azure A at pH 12.0. An oxidation peak at 0.30 V occurs on the i_d-E curve for the first scan (Curve 1). The disk current decreases quickly as the potential is beyond this peak potential. This is much different from these shown in Plots A and B. A corresponding reduction peak is not observed at the ring electrode. This means that azure A is difficult to be polymerized at pH 12.0.

The above results show that azure A is oxidized more easily at the acidic solution than at the basic solution and the acidic solution is favorable for the formation of intermediates. The intermediate plays an important role in accelerating the oxidation and polymerization of azure A.

3.1.3 Effect of Rotation Rate

The ring potential was changed at 0.1 V interval from -0.2 to 0.2 V. The electrolysis of azure A was carried out using a RRDE. The electrolytic solution consisted of 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 with pH 6.0. The rotation rate was controlled at 500, 1000, 2000, 2500 and 3000 r.p.m., respectively. The potential scan rate was set 60 mV s^{-1} . Here, we present two plots with different ring potentials to explain the effect of rotation rate.

Figure 4 show the results from the rotation rate at 500 r.p.m. The ring potential was set -0.1 V. Comparison of Figure 4 Plot A and Plot B in Figure 3 shows that both the disk current and the ring current increase simultaneously with increasing rotation rate.

Based on the oxidation currents of two anodic peaks on i_d-E curves and the reduction currents of cathodic peaks on i_r-t curves, their collection efficiencies for the first scan were calculated. Figure 5 shows the relationship between the collection efficiency N of the redox of azure A itself and the rotation rate. Curves 1, 2, 3, 4 and 5 for the first scan for the ring potential from -0.20 to 0.20 V show that their collection efficiencies increase when the rotation rate increased. This means that the amount of the intermediate collected at the ring electrode increases with decreasing ring potential. It follows that the intermediate is a positively charged species. It is clear that the collection efficiencies of the intermediate increases with increasing the rotation rate. This indicates that a part of the intermediate generated at the disk electrode was decomposed in its passage from disk to ring. Therefore, the intermediate generated at the disk is not too stable.

Based on the relationship between the collection efficiency N of the polymerization of azure A and the ring potential ($N-i_r$ plot omitted here), the result is similar to that of the redox of azure A itself. So both kinds of the intermediates in this case are positively charged and not stable.

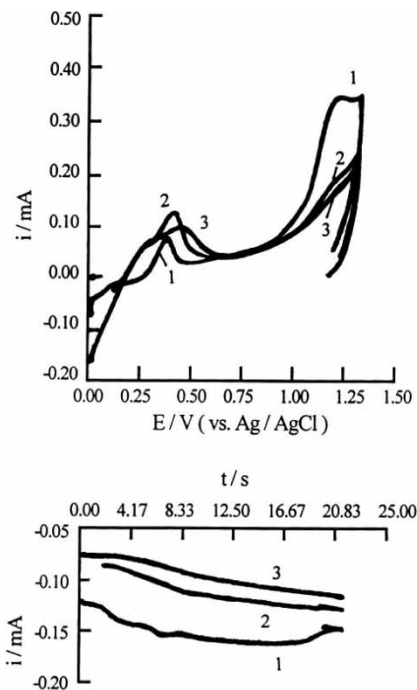


Fig. 4. Effect of rotation rate. The electrolytic solution is the same as that shown in Figure 1, pH 6.0. Ring potential: -0.1 V. Rotation rate: 500 r.p.m. Potential scan rate: 60 mV s^{-1} . Curves: (1) first scan, (2) fifth scan, (3) tenth scan.

3.1.4 Possible Intermediates

It is known that there is a redox couple of azure A monomer at a low potential region (3, 5). The redox reaction shown in Equation (1) has been proposed for azure A, in which the reduced form is unprotonated, considering that electrochemical reduction of Azure B takes place, at neutral pH, via a two-electron and one proton process (9). Since radical cations of the phenothiazine and its derivatives were obtained (10),

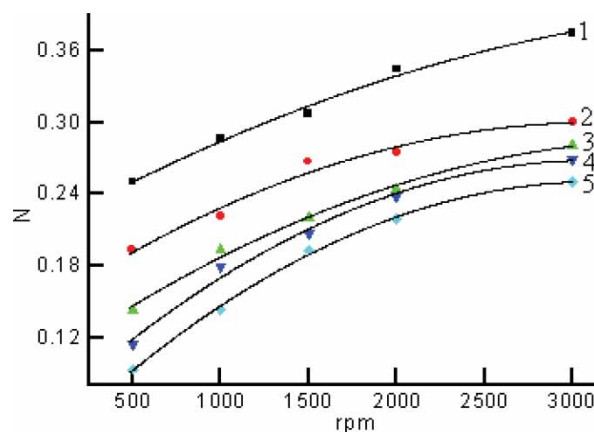
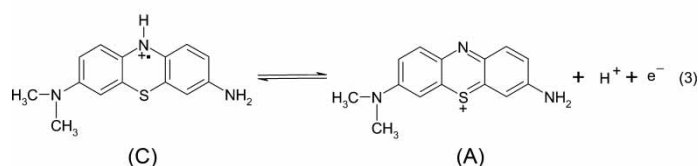
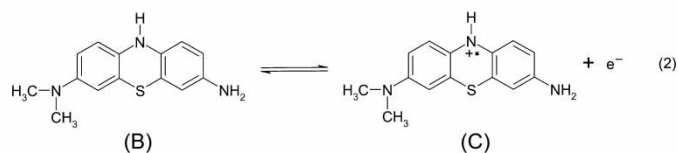
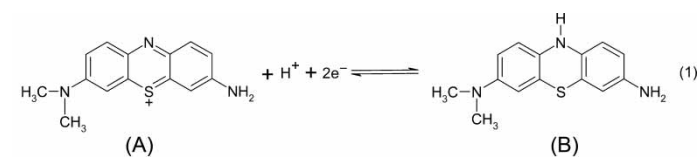
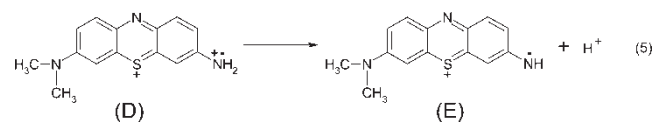
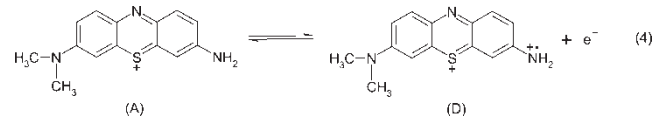


Fig. 5. The relationship between collection efficiency N of the redox of azure A itself for the first scan and rotation rate based on the data from the effect of the rotation rate on the peak currents. Curves: (1) -0.2 V, (2) -0.1 V, (3) 0 V, (4) 0.1 V, (5) 0.2 V.

the oxidations of azure A during the oxidative scan are given in Equations (2) and (3)



However, at more positive potentials the process of polymerization occurs, which is attributed to the oxidation of azure A monomer to a radical cation (structure D in Equation (4)). The radical cation formed in Equation (4) is unstable and can lose a proton to form a free radical (structure E in Equation 5)



Based on the above experimental results and discussion, two possible radical cations, C and D, were therefore proposed as the two positively charged intermediates detected with the RRDE.

We note that the possible mechanism for electropolymerization of azure A is much different from that of azure B. The RRDE studies of Azure B polymerization showed that two soluble intermediates were formed at about 0.95 and 1.20 V, respectively, at pH 4, but the oxidation peak of the monomer does not appear at lower potentials (11). Although the structures of Azure B and azure A are similar in one tertiary amino group as the parent phenothiazine ring substituents, yet there is a difference in the other substituent group that azure A contains one primary amino group in its structure, whereas azure B contains one secondary amino group.

It is known that the electropolymerization from acidic media is generally preferable for formation of an electroactive polymer (3). In fact, electrosynthesis of electroactive

polyaniline occurs only in acidic media (12). Azure A, similarly to aniline, contains a primary amino group, thus it may be electropolymerized in acidic media. In addition, acidic solutions are favorable for generation of an intermediate.

However, considering the literature reported that electropolymerization of the azines containing only tertiary amino groups in their structure is preferable for the formation of an electroactive polymer in basic aqueous media, and can not occur from strong acidic media (3), it is reasonable that the result obtained by Shan et al. (11) that less acidic media are favorable for the growth of the poly(azure B) since azure B contains one tertiary and one secondary amino groups. Thus, electrobehavior of azure B is more similar to that of methylene blue containing two tertiary amino groups, but is less similar to that of azure A.

3.2 XPS Results of Poly(azure A) Films

Poly(azure A) films for the XPS experiments were obtained from electrolysis of the solution containing 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 with pH 6.0. Figure 6 show the XPS plots of an oxidized poly(azure A) film (Curve 1) and a reduced poly(azure A) film (Curve 2). To obtain oxidized and reduced films, two poly(azure A) films were immersed in 0.5 mol dm^{-3} Na_2SO_4 solution with pH 4.0, one film was oxidized at 0.60 V for 20 min, another one was reduced at -0.20 V for 20 min, and then they were washed with doubly distilled water. Figure 6 shows that there are C, N, S and O atoms in both oxidized and reduced films. The first three atoms in both films of poly(azure A) are expected, since azure A contains C, N and S atoms.

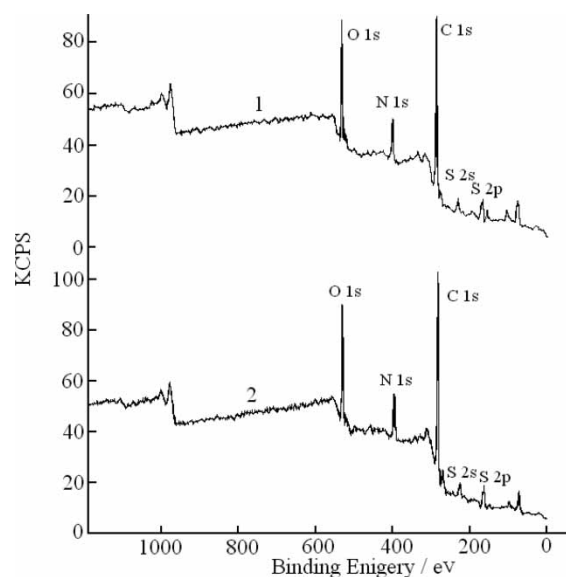


Fig. 6. XPS spectra of poly(azure A) film on a platinum foil electrode obtained from electrolysis of the solution containing 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 with pH 6.0. Curves: (1) Oxidized film; (2) Reduced film.

Table 1. The XPS experimental results of the oxidized poly(azure A) film

Peak	Binding energy (eV)	Relative intensity (%)
C 1s	284.5	70.7
N 1s	398.8	8.7
S 2p	163.8	6.3
O 1s	531.4	14.3

Oxygen atoms in both poly(azure A) films came mainly from sulfate doped in polymer films and partly from the strong adsorption of oxygen, which is like oxygen adsorbed in polyaniline (13). Evidence for oxygen adsorbed in poly(azure A) film is that there is also oxygen peak in XPS plots of poly(azure A) film synthesized in the aqueous solution containing 5.0 mmol dm^{-3} azure A and 0.5 mol dm^{-3} Na_2SO_4 .

Tables 1 and 2 list the XPS experimental results of oxidized and reduced poly(azure A) films, respectively.

It is clear that the contents of oxygen and sulfur in the oxidized poly(azure A) film are higher than those in the reduced poly(azure A) film, which is mainly caused by sulfate anions. The result from XPS experiment substantiates that anions can be doped into poly(azure A) film and dedoped from it during oxidation and reduction processes of poly(azure A), respectively.

The C 1s peak in the XPS spectra of polyaniline is generally split into three peaks in the binding energy range between 284 and 288 eV (14, 15). However, the C 1s core-level spectrum (omitted here) of poly(azure A) is split into four peaks. The positions and relative intensity of the C 1s peaks are listed in Table 3.

Table 2. The XPS experimental results of the reduced poly(azure A) film

Peak	Binding energy (eV)	Relative intensity (%)
C 1s	284.8	72.9
N 1s	398.9	8.4
S 2p	163.8	5.1
O 1s	530.5	13.6

Table 3. Peak positions of C 1s peaks

Binding energy (eV)	Relative intensity (%)
289.0	4.5
287.7	9.1
286.1	15.6
284.5	70.8

Table 4. Peak positions of S 2p peaks

Binding energy (eV)	Relative intensity (%)
167.7	41.6
163.9	58.4

Table 5. Peak positions of N 1s peaks

Binding energy (eV)	Relative intensity (%)
400.5	22.1
398.8	77.9

The peak with the binding energy 289.0 eV may be attributed to the carbon atom in azure A. Since one of the carbon atoms in azure A is attached to an electro-negative nitrogen atom, i.e., the chemical environment of C atoms in azure A is different from that of C atoms in polyaniline. The N atom plays a direct and indirect role in decreasing the shielding of the positive nuclear charges of C 1s by outer electrons. Thus the effective attractive force of the nucleus with regard to the core electrons of C 1s is increased, i.e., its binding energy should be higher than those of other carbon atoms in the polymer. In addition, the content of the C atoms having 289.0 eV is the lowest among the four kinds of C 1s, which is also an evidence for C 1s originating from azure A.

The S 2p spectrum of the polymer consists of two peaks with bending energies of 167.7 and 163.9 eV (in Table 4). The former is mainly attributed to the sulfate ions and it represents 41.6% of the sulfur. The latter is assigned to a sulfur atom of the azure A units which are electrochemically polymerized in the polymer film.

The XPS N 1s core level spectrum contains two peaks with bending energies of 398.8 and 400.5 eV (in Table 5). The latter is attributed to the imine ($-\text{N}=\text{C}$) and amine ($-\text{NH}-$) nitrogens (16), and is the more intense as it represents 77.9% of the nitrogen. The N 1s component at higher binding energy can be assigned to a positively charged nitrogen of the azure A units which are charge compensated by the sulfate ions. The fraction of positively charged nitrogen for the N 1s envelop corresponds to the doping level and a value of 0.221 is obtained from the XPS data. This compares almost well with the XPS S (Doping level)/N ratio (0.25).

4 Conclusions

The electrochemical polymerization of azure A has been studied using the rotating ring-disk electrode (RRDE) and the X-ray photoelectron spectra (XPS). The result from the RRDE identifies that both intermediates carried positive

charge produce at the disk electrode during the electrolysis process. However, their concentrations decreases as the electrolysis proceeds. This means that it is easier to generate the intermediate at the platinum disk electrode than at poly(azure A) film itself. This may be the cause why it is difficult to obtain a thick poly(azure A) film. The results from the XPS experiments show that the anions can be doped into poly(azure A) film and be dedoped from it during oxidation and reduction processes.

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