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The XPS studies of the dedoping processes of polyalkylthiophenes

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Abstract

The room temperature doping and auto-dedoping processes of $FeCl_3$ and $AuCl_3$ doped polyalkylthiophenes were studied with X-ray photoelectron spectroscopy. The redox chemistry of both the carbon and sulfur atoms on polymer backbone was revealed with the ESCA data. The reactions of counter anions, $FeCl_4^{-1}$ and $AuCl_4^{-1}$ during dedoping were carefully studied. The ESCA data also indicated that no chlorination on polymer backbone occurred in either doping or dedoping reactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyalkylthiophene; XPS; Dedoping

1. Introduction

Organic conjugated polymers, since their discovery in the late 1970s, have shown potential as next generation materials for application in electronic devices [1]. Polyalkylthiophene is one of the most interesting conducting polymers, because of its characteristic properties, such as solubility for various organic solvents, fusibility at relatively low temperature [2], gel characteristics [3], solvatochromism [4] and thermochromism [5–8]. The solubility of the polyalkylthiophene comes from a decrease in the attraction between polymer chains and the introduction of favorable interactions between the substituents and the solvents. Unfortunately, side chain substitution also causes thermal instability of the doped polymer. Thermal dedoping appears to be a critical technological problem for the application of the P3ATs. A considerable number of studies have been carried out in order to understand the instability of the doped P3ATs, and several groups have provided valuable insights into this rather complex phenomenon [9–11]. It was reported that the dedoping (or conductivity decay) rate depends on the dopants [12,13], degree of doping and temperature [14], as well as the humidity level of the surrounding atmosphere [15,16]. On the other hand, some studies had shown that the dedoping process also depended on the arrangement of alkyl side chains in the polymer backbone [17]. A reduction of the number of alkyl side chains in a regular way increased the stability against thermal dedoping.

The dedoping mechanism in P3AT has been explained by the increasing reactivity of the conducting oxidized state toward the reducing species, such as water [18,19]. However, Horowitz [20] found that the oxidized polymer (in solution) is reduced to a neutral state when acetone is added, but the exact nature of this reaction is still unknown. Pei et al. believed that the thermally activated side chain mobility was the reason for the dopant to be kicked out of the polymer backbone. Therefore, the bigger dopants will be kicked out more easily than small ones [21]. However, Ciprelli et al. discovered that the size of the dopant ions does not appear to be a determining factor in the dedoping process [22]. Instead, the electronic properties of the counter anion play a key role in this process. Wu et al. [23] found that the dedoping process was exactly the reverse of the doping: the bipolarons were reduced to polarons, the polarons were then reduced to neutral polymer. The structure regularity, alkyl side chain length, dopant, solvent, and light all affected the dedoping rate of conducting polyalkylthiophenes. Moreover, it was reported by Abdou et al. that for thin films (<1 μm), photochemical dedoping dominated over thermal dedoping under ambient lighting [24]. Nevertheless, direct evidence for the reduction of the polymer backbone and the distribution of the counter anions after dedoping had not been reported in detail. Understanding the dedoping mechanism is the first step toward improving the performance, and therefore the applications, of conducting polyalkylthiophenes. In this article, an X-ray photoelectron spectroscopy (XPS) was used to probe the dedoping process of $FeCl_3$ and $AuCl_3$ doped polyalkylthiophenes.

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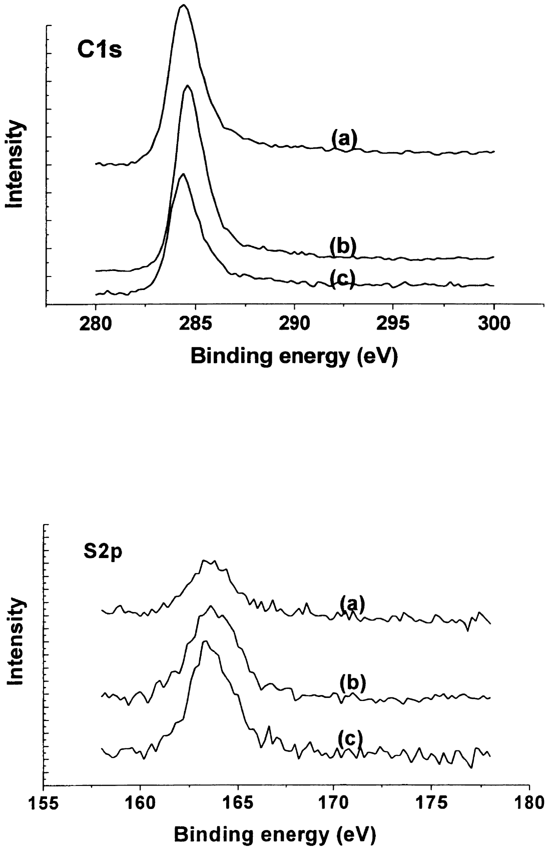

Fig. 1. The C1s, S2p binding energies of polydodecylthiophenes: (a) neutral; (b) $FeCl_3$ doped; (c) dedoped.

2. Experimental section

2.1. Reagents

3-Bromothiophene (stored in a molecular sieve), $Ni(dppp)Cl_2$, Mg, $FeCl_3$, $AuCl_3$, bromoalkane were purchased from commercial sources and used as received unless otherwise specified. All solvents are HPLC grade and distilled over Na or CaH_2 prior to use (bromoalkane was distilled over $MgSO_4$).

2.2. Preparation of poly-3-alkylthiophenes

3-Alkylthiophenes were prepared by a published procedure [25] (Ni catalyzed coupling of the alkyl Grignard with 3-bromothiophene). The purity of monomers was checked by ^1H NMR and found to be >95%. Regio-random P3ATs were prepared by chemical oxidative coupling of corresponding monomers with $FeCl_3/CHCl_3$, according to the procedure described by Sugimoto et al. [26]. Removal of the oligomers and impurity of the obtained polymers was achieved by Soxhlet extraction with MeOH. The dark red neutral P3AT was dried under vacuum. Dried P3AT (25 mg) was dissolved in 2.5 ml of solvent. The solutions were then cast onto a silicon wafer or a glass slide. The thickness of all the films was kept between 4750 and 5250 Å.

2.3. Doping of the polyalkylthiophene films with $FeCl_3$ and $AuCl_3$

Chemical doping was carried out by dipping the film (casted on substrate) in 0.1 M nitromethane (or acetonitrile) solutions of $FeCl_3$ or $AuCl_3$ for 30 min. After oxidation, all films were rinsed with the solvent several times and blow-dried with N_2 gas. The UV/Vis/NIR absorption measurement was used to monitor the doping process. The doping completeness was judged by the total disappearance of the $\pi-\pi^*$ transition absorption of the neutral polymer.

2.4. Dedoping of the conducting polyalkylthiophenes

The doped polymer films were stored in a vial in an ambient atmosphere at room temperature. The dedoping processes, which can be monitored with a UV/Vis/NIR spectrometer, occurred automatically. The ex situ XPS studies were performed on the neutral, doped, partially dedoped, and totally dedoped polyalkylthiophenes.

2.5. Physicochemical studies

X-ray photoelectron spectroscopy measurements were performed with a Perkin–Elmer PHI-590AM ESCA/XPS spectrometer with a Cylindrical Mirror Electron (CMA) energy analyzer. The X-ray sources were Al Kα at 400 W and Mg Kα at 400 W. Argon ion sputtering was performed by using an Ar-ion gun at 4 kV beam energy and 25 mÅ emission current for 180 s (or 300 s) intervals. Samples for the XPS studies were made as polymer films on the gold substrates. Gold spectra were taken as a calibration standard before, during and after measuring the samples. UV/Vis/NIR spectra were obtained with a Varian Cary 5E spectrometer in an ambient atmosphere at room temperature. The thickness of the polymer films was measured with a Dektak 3 surface profile measuring system and was further calibrated by UV/Vis absorptions [27]. Scanning Electron Microscopy (SEM, Hitachi S-800 at 15 kV) and Energy Disperse Spectroscopy (EDS, Delta Class Analyzer) were also used to characterize the surface morphology and surface component.

3. Results and discussion

3.1. The XPS spectra of neutral and $FeCl_3$ doped polyalkylthiophenes

The ESCA spectrum of the neutral polymer showed only carbon and sulfur peaks, indicating that there is no reaction residue left in the polymer films. However, the binding energy of both C and S shifted irregularly when the polymer films were deposited on the glass substrate, due to the

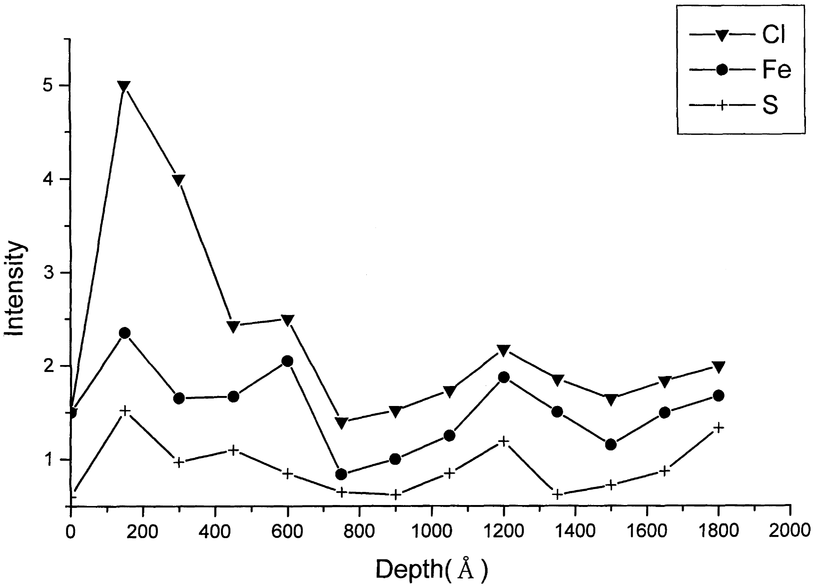

Fig. 2. The depth profile Auger concentration analysis of S, Cl and Fe in the $FeCl_3$ doped polydodecylthiophene.

charging that occurred in the insulating samples. To avoid the charging problem, neutral polymers were deposited on gold substrates for ESCA measurements. The ESCA spectra of $FeCl_3$ doped polyalkylthiophenes showed C1s, S2p, Fe2p, Cl 2p signals and a very weak O1s peak (the oxygen came from the iron oxidant impurity produced during doping). It was found that, after doping, the binding energy of C1s and S2p had shifted to higher energy (284.6, 163.6 eV) compared to those of neutral polymers (284.4, 163.2 eV) (Fig. 1), suggesting that both carbon and sulfur were oxidized. In other words, the positive charges of polarons and bipolarons on the polymer backbone were distributed on both carbon and sulfur atoms. In the literature, considerable discrepancies were found in the photoelectron spectroscopic data of doped polyalkylthiophenes. Mohammad [28] suggested that the positive charges of p-doped polythiophenes were largely located on the carbon atoms. On the other hand, Riga et al. [29] argued that in the oxidized state, both carbon and sulfur atoms in oxidized polythiophenes were positively polarized. We also found that both the carbon and sulfur atoms were oxidized when the polymer backbone was doped. The ESCA spectra of the fully doped polymer films showed no observable Fe^{+2} peak, suggesting that $FeCl_4^{-1}$ is the only counter anion in $FeCl_3$ doped polyalkylthiophenes. However, due to the small difference in the binding energies of Fe^{+3} and Fe^{+2} ions, whether the Fe^{+2} ions existed in the fully doped polymer films or not remained uncertain. Depth profile Auger analysis, Fig. 2, of the doped polymer showed that both the Fe and Cl atoms (with the Fe/Cl mole ratio of 0.30 ± 0.05) were rather evenly distributed on the whole polymer film, indicating homogeneous doping. There is an uncertainty as to whether Cl^{1-} or $FeCl_4^{1-}$ is the counter anion of $FeCl_3$ doped polythiophenes [30–35]. Our ESCA results supported the conclusion that $FeCl_4^{1-}$ ion was most probably the counter anion for the $FeCl_3$ doped polymer. It is interesting to note that the surface of the $FeCl_3$-doped polymer film has a higher concentration of Cl atoms and, inside the polymer film, the Fe/Cl ratio is larger than 0.25 (the right Fe to Cl ratio of $FeCl_4^{1-}$). This suggested that the dedoping process (producing HCl and/or Cl_2 gas [23]) occurred immediately after the polymer film was removed from the oxidant solution and exposed to air.

3.2. The XPS studies on the dedoping process of $FeCl_3$ doped polyalkylthiophenes

The ESCA spectra were taken on both partially and totally dedoped polymer films. The partially dedoped polymer film is the doped film that has stayed in the ambient atmosphere at room temperature for one day. As the dedoping proceeded, the binding energies of C1s and S2p shifted to lower energy gradually, see Fig. 1, indicating the reduction of both carbon and sulfur atoms. Unfortunately, due to the weak and broad signals of iron, it is difficult to reveal the redox reactions of Fe^{+3} in $FeCl_4^{1-}$. Depth profile ESCA analyses, Fig. 3, of the just doped, partially and totally dedoped P3ATs showed that the Fe atoms were homogeneously distributed on the polymer films, and no migration and aggregation of Fe atoms occurred during dedoping. The ESCA data also showed that the concentration of Cl atoms decreased as the dedoping reaction proceeded, consistent with what had been reported [23] previously, that $FeCl_4^{1-}$ reacted with H_2O to form HCl gas and iron complexes during dedoping. It is worth noting here that the totally dedoped polyalkylthiophene films contain almost no Cl atoms. This indicated that no chlorination reaction on the polymer backbone occurred in the doping and dedoping reactions.

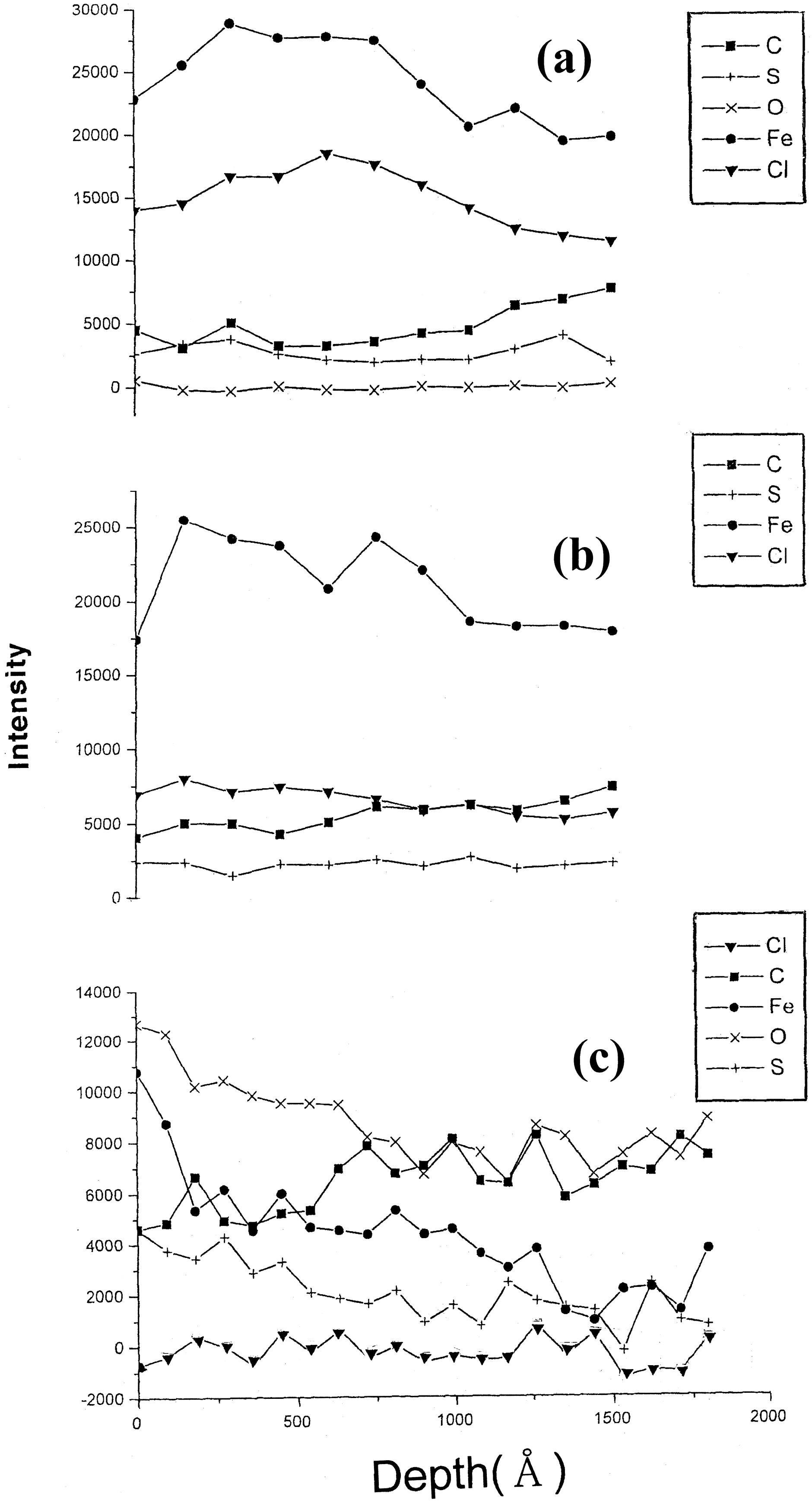

Fig. 3. The depth profile ESCA analyses of the $FeCl_3$ doped polydodecylthiophenes: (a) just doped; (b) dedoped for one day; (c) totally dedoped.

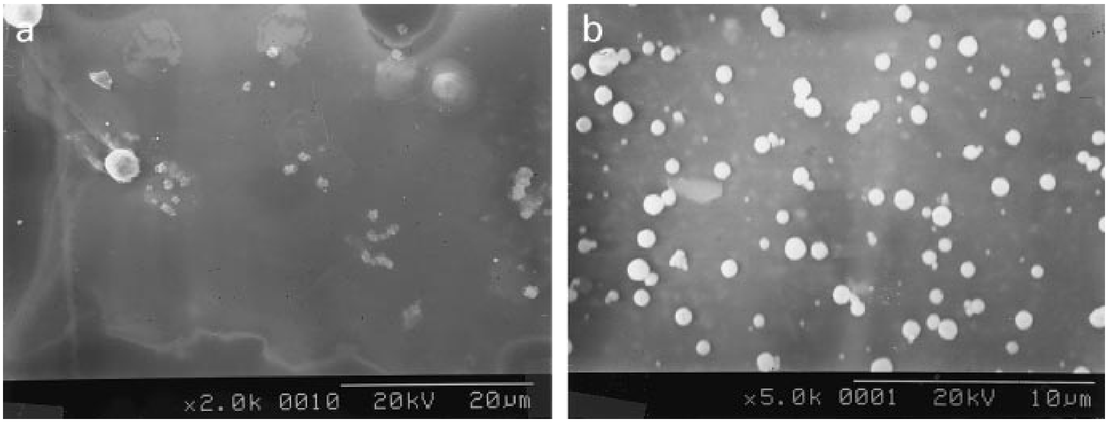

Fig. 4. The SEM micrographs of polydodecylthiophenes: (a) doped with $AuCl_3/CH_3CN$; (b) doped with $AuCl_3/CH_3NO_2$.

3.3. XPS spectra of $AuCl_3$ doped polyalkylthiophenes

Both nitromethane and acetonitrile can be used as solvents for $AuCl_3$. The binding energy of C1s and S2p, as well as the degree of doping in the $AuCl_3/CH_3CN$ doped polymer films, was very similar to that of the $FeCl_3/CH_3NO_2$ doped polymer. However, when CH_3NO_2 was used as a solvent, after doping for 10 min using a 0.1 M $AuCl_3$ solution, an overlay of gold metal was formed, as observed on the SEM micrographs (Fig. 4b). The Au^0 particles deposited on the $AuCl_3/CH_3NO_2$ doped polymers was formed by the disproportionation [36] of Au^{+1} ions as well as the reduction of Au^{+3} ions (by ambient water) in solution. On the other hand, since CH_3CN is a better ligand for gold ions than CH_3NO_2, only a small amount of Au grains (probably from the reducing of Au^{+3} ions by ambient water in solution) was found on the surface of the $AuCl_3/CH_3CN$ doped polymer (Fig. 4a). Unfortunately, Au^{3+} ions were easily reduced to Au metal during the ESCA analysis, and it is difficult to distinguish between metal gold and gold ions by ESCA studies. Therefore, the exact stoichiometry of the counter anion of the $AuCl_3$ doped polymers cannot be calculated from the ESCA data. Nevertheless, the counter anions of the doped polymers were proved to be $AuCl_4^{1-}$ by the UV/Vis/NIR spectrum [37,38] which has the absorption peaks at 232 and 324 nm (Fig. 5b). In spite of the differences in the morphology of the gold particles, the $AuCl_3/CH_3NO_2$ doped polymers and the $AuCl_3/CH_3CN$ doped polymers showed a similar dedoping mechanism (vide infra). Therefore, the $AuCl_3/CH_3NO_2$ doped polymer films were used for studying the dedoping process.

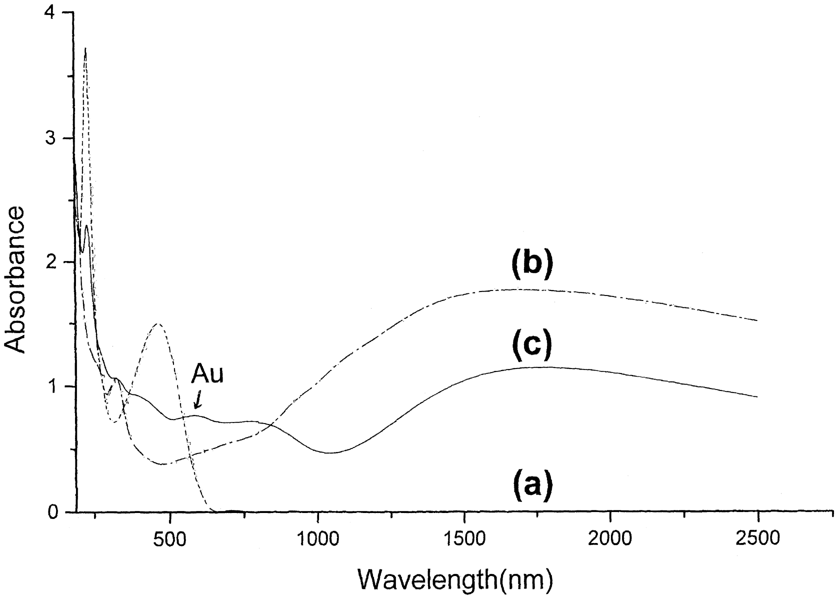

Fig. 5. UV/Vis/NIR spectra of: (a) neutral polydodecylthiophene; (b) $AuCl_3$ doped polydodecylthiophene; (c) partially dedoped polydodecylthiophene.

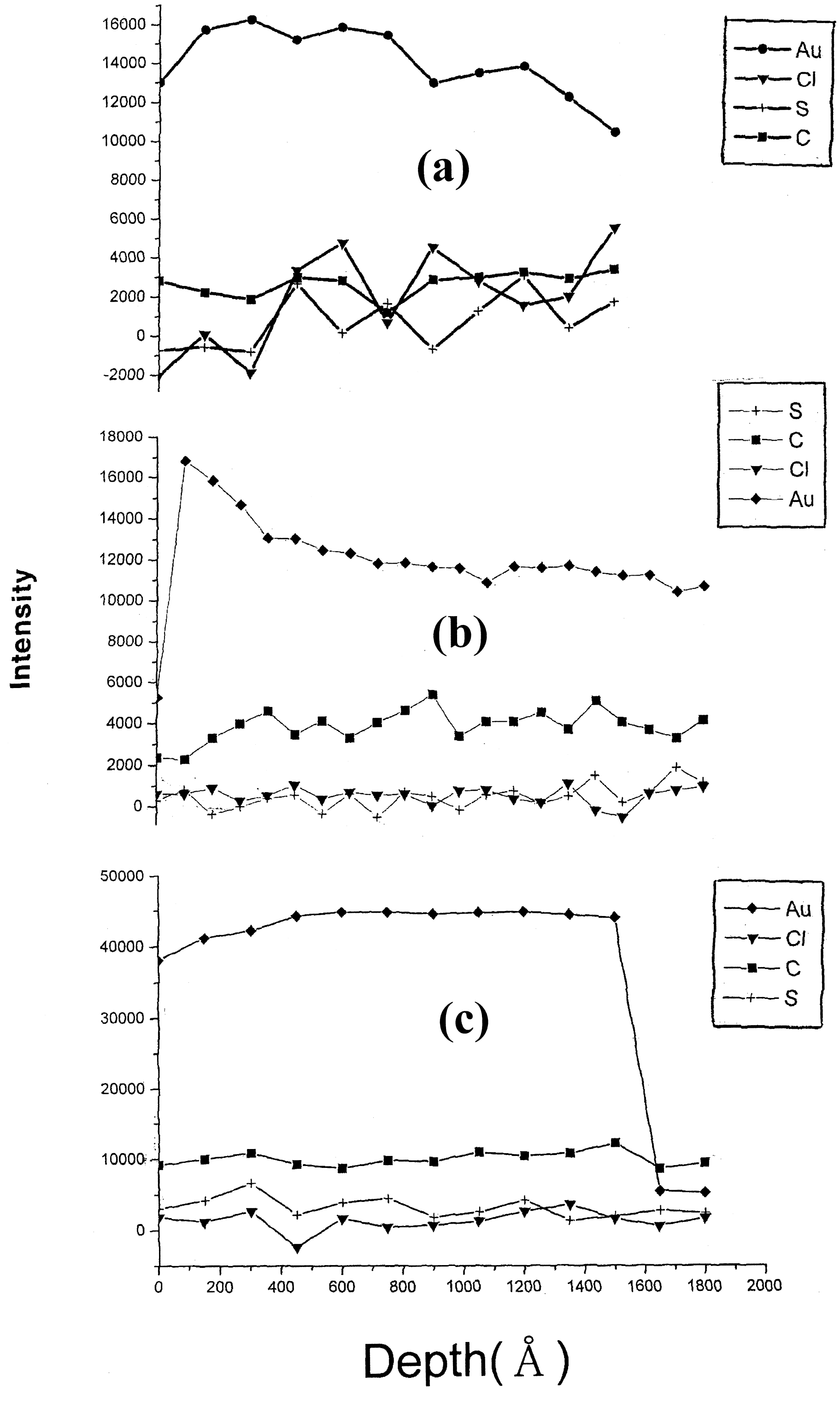

Fig. 6. The depth profile ESCA analyses of the $AuCl_3$ doped polydodecylthiophenes: (a) just doped; (b) dedoped for three days; (c) totally dedoped.

3.4. The XPS studies on the dedoping process of $AuCl_3$ doped polyalkylthiophenes

The binding energies of C1s and S2p on the $AuCl_3$ doped polymer decreased as the dedoping proceeded, which was similar to what was observed in the $FeCl_3$ doped polymer.

The reaction of the counter anions $AuCl_4^{-1}$ was quite interesting. It was found that the Au^{+3} ions in $AuCl_4^{-1}$ were reduced to Au^0 during dedoping. As mentioned above, we are not able to distinguish Au metal from Au^{+3} ions with the ESCA spectra, due to the self-redox reaction between Au^{+3} and Cl^{-1} ions that occurred under the excitation with an

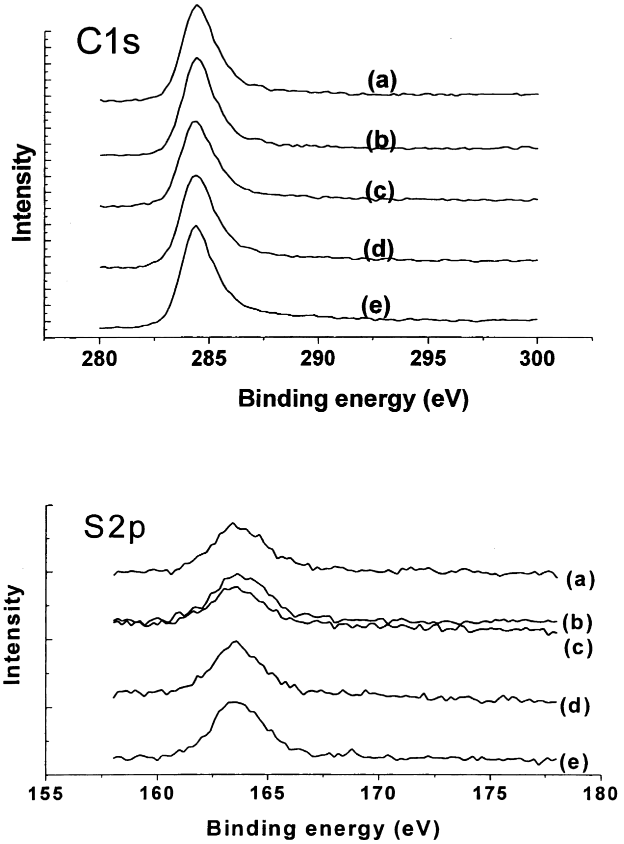

Fig. 7. The depth profile binding energy analyses of C1s and S2p of the $AuCl_3/CH_3NO_2$ doped polydodecylthiophene after standing in ambient atmosphere for three days: (a) on the surface; (b) 500 Å beneath surface; (c) 1000 Å beneath surface; (d) 2000 Å beneath surface; (e) 3000 Å beneath surface.

X-ray beam. Nevertheless, the reduction of Au^{+3} ions can be evidenced by the disappearance of the UV/Vis absorption at 232 and 324 nm and a new peak at ca 530 nm (the absorption of small metallic gold particles [39]) sprouted (Fig. 5). Furthermore, the Au^{+3} ions reduced to Au metal and then moved toward the surface of the polymer film, as revealed by the depth profile ESCA analyses, Fig. 6. The results showed that an overlay gold metal was formed on the surface of the polymer and this gold layer became thick during dedoping. In Fig. 6, we also observed that the concentration of Cl atoms decreased as the dedoping proceeded. The decrease of the Cl concentration indicated that HCl (and/or Cl_2) gas was also produced and released out of the polymer film during dedoping in the $AuCl_3$ doped polymer.

It is valuable to know whether the dedoping process occurred on the surface then went through the inside of the polymer film or it occurred on the whole film simultaneously. Depth profile chemical shift analysis of C1s and S2p on the partially dedoped polymer film was undertaken to reveal this question. It was found that the binding energies of C1s and S2p did not change through the whole film, (Fig. 7). This result suggested that the dedoping process occurred simultaneously and homogeneously on the entire polymer film.

3.5. The morphologies of polyalkylthiophenes after dedoping

The change in morphology of the $FeCl_3$ doped polymer films is shown in Fig. 8. The SEM micrographs revealed that the surface of the $FeCl_3$ doped polymer film became relatively rough after dedoping. It was known that when polyalkylthiophene films dedoped, HCl gas was produced and released out of polymer films. The rapid dedoping of the $FeCl_3$ doped polymer produced a large amount of HCl gas in a short period of time. The HCl gas released from the polymer film caused the damage to the film surface, resulting in a rough morphology. On the other hand, the $AuCl_3$ doped polyalkylthiophenes also released HCl (and/or Cl_2) gas during dedoping, however, at the same time, Au^{3+} ions were reduced to Au^0 and moved toward the surface. The

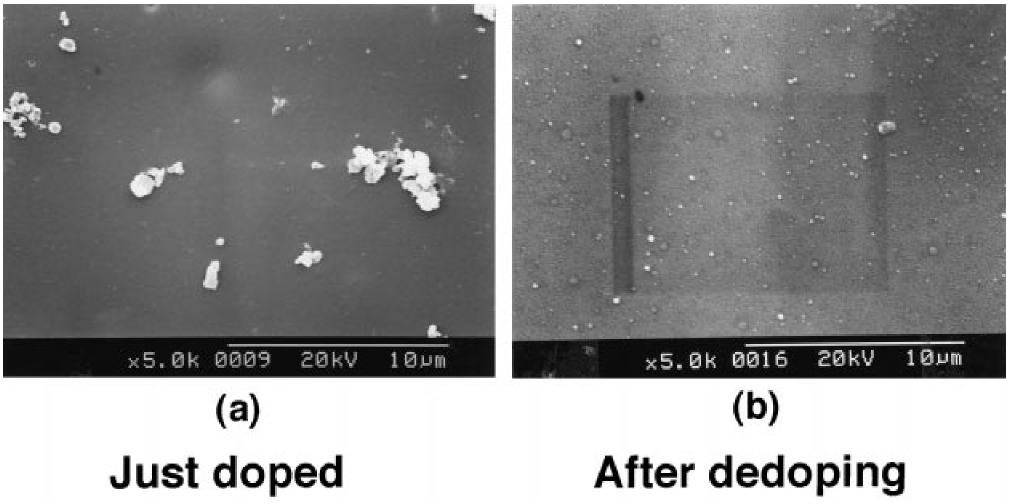

Fig. 8. The SEM micrographs of the $FeCl_3$ doped polydodecylthiophene: (a) just doped; (b) totally dedoped.

surface of the dedoped polymer films was covered with gold metal and no pinhole was observed.

4. Conclusions

The dedoping of conducting polyalkylthiophenes was the reversible process of doping. The XPS data revealed the redox chemistry of both carbon and sulfur atoms on the polymer backbone and the reaction of the counter anions during dedoping. It was found that both carbon and sulfur atoms on the polymer backbone were oxidized in the doping process and reduced when the doped polymer films dedoped. Depth profile ESCA analyses showed that the dedoping reactions occurred simultaneously and homogeneously through the whole polymer films regardless of the dopants. The counter anion $FeCl_4^{-1}$ reacted with water to form HCl and iron complexes. HCl gas released from the polymer films and iron complexes were distributed homogeneously throughout the polymer films. Nevertheless, Au^{+3} ions in $AuCl_4^{-1}$ were reduced to Au^0 and moved toward the surface, forming a gold overlay on the surface of the polymer film. No Cl atoms were found on the totally dedoped polymer film indicating that no chlorination reaction occurred on the polymer backbone during doping and dedoping. Understanding the doping and dedoping mechanism of polyalkylthiophenes may provide clues to search for other high performance dopants.

Acknowledgements

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