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The reduction property of thermally treated polyacrylonitrile fibres

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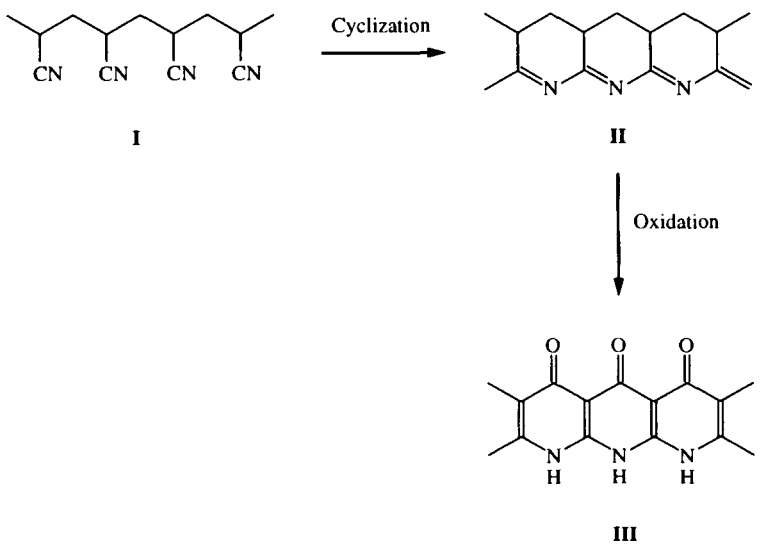
A new type of functional fibre with high reducing ability toward Au^{3+} was prepared by heat treatment of polyacrylonitrile precursor fibre in inert atmosphere. Both X-ray photoelectron spectroscopy and wide angle X-ray diffraction measurements showed that Au^{3+} was nearly completely reduced to Au^0 on the surface of the fibre after impregnation in $AuCl_3$·HCl solution at room temperature. At the same time, the fibre was oxidized. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyacrylonitrile fibre; reduction; oxidation)

Introduction

Polyacrylonitrile (PAN) fibre is the most important precursor for manufacturing carbon fibres. In the conversion of PAN fibres to carbon fibres, thermal treatment of the PAN fibre (*Scheme 1*, **I**) at about 200–300°C (stabilization treatment) is a prerequisite procedure for high temperature carbonization (≥1000°C). During the heat treatment process, PAN fibres undergo mainly two reactions: cyclization and oxidation. Cyclization turns linear PAN into a six-member ring structure of the naphthpyridine type (*Scheme 1*, **II**), while oxidation converts it into a conjugated, heteroaromatic structure (*Scheme 1*, **III**)[1–4]. As a result of oxidation, the thermal stability of the structure is greatly improved. Though the detailed mechanisms of the oxidation of structure **II** (*Scheme 1*) and the final structure of oxidized PAN fibres are still not fully understood, it is reported that the activated carbon fibres structure (ACF) has a reduction ability[5], i.e. the activated carbon fibres can be oxidized by an oxidant such as Au^{3+}, Fe^{3+}, etc. We found that the stabilized fibres (*Scheme 1*, **II**) also show a reducing ability, thus they may be developed into a new type of functional polymer with many potential uses.

In this communication, we report the preliminary results of the reduction property of stabilized PAN fibres (*Scheme 1*, **II**) under inert atmosphere, i.e. the reduction actions of the stabilized fibres on $AuCl_3$ are studied by X-ray photoelectron spectroscopy (X.p.s.) and wide angle X-ray diffraction (WAXD) measurements.



I **II** **III**

Scheme 1

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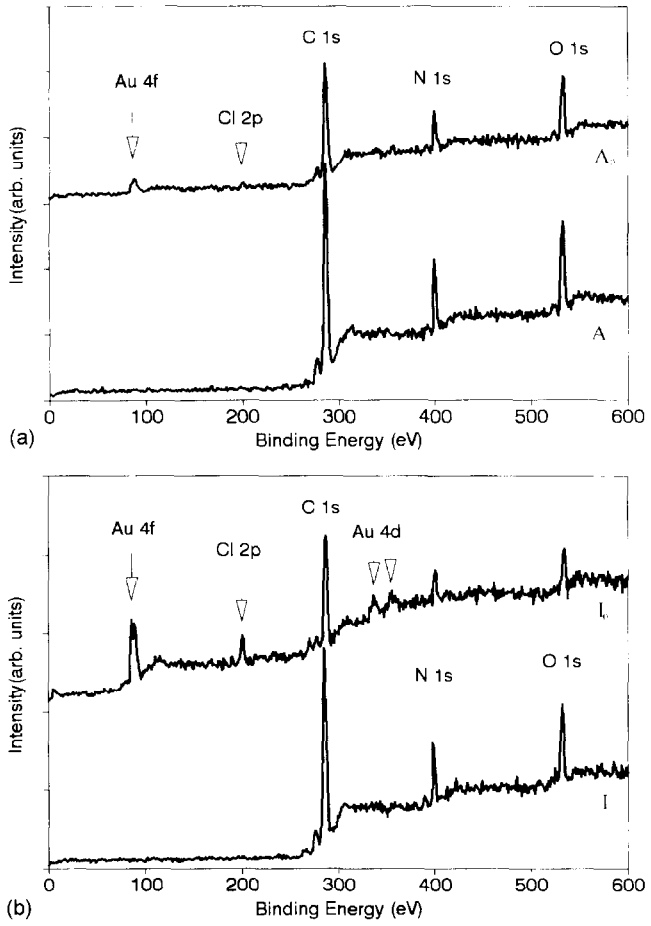

Figure 1 X.p.s. spectra of fibre A and A_0(a), and fibre I and I_0 (b)

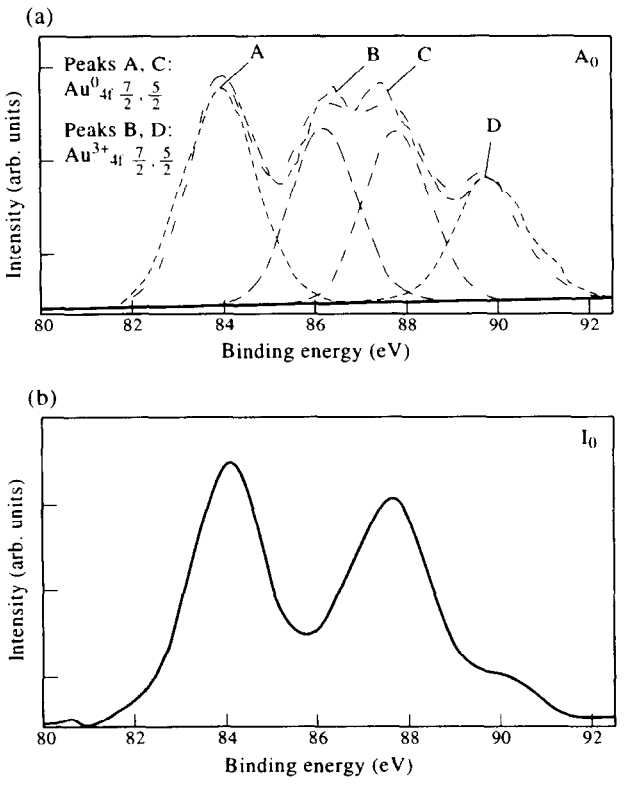

Figure 2 Curve-fit spectra of Au 4f peaks of fibres A_0 (a) and I_0 (b)

Experimental

Sample preparation. Commercially available polyacrylonitrile fibre (Courtelle fibre, Courtaulds Ltd, UK) with 3000 filaments each tow and 1.22 dtex fineness was used as the initial precursor material. Two fibre samples, A and I, were prepared according to the following. Fibre A was obtained by heat treating the PAN fibre in an air-circulated oven at 200°C for 7 h. Fibre I was obtained by heat treating the PAN fibre in argon (purity ~99.99%) at 230°C for 7 h. Then both fibres (A: 0.0947 g; I: 0.0879 g) were impregnated into 50 ml solution of $AuCl_3$·HCl (concentration of Au^{3+}: 950 ppm) for 29 h at room temperature. The impregnated fibres (A_0 and I_0), together with the unimpregnated fibres (A and I) were washed thoroughly with distilled water until the pH of the washing solution was about 7. Then the resulting fibres were dried at 90°C followed by vacuum drying at 50°C for 4 h. The fibres were cut into powder for the WAXD measurement.

X-ray photoelectron spectroscopy. X.p.s. measurements were carried out in an ESCALAB MKII system with a spherical sector analyzer. The base pressure was 1×10^{-9} mbar. A Mg$K\alpha$ radiation source ($\hbar\nu = 1253.6$ eV) was used in all measurements with an overall energy resolution of 1.0 eV. All experiments were conducted on the fibre bundles.

Wide angle X-ray diffraction. WAXD diffraction measurements were obtained on a Ragaku rotating anode X-ray powder diffractometer of D/MAX-γ A type using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 0.154$ nm). Scans were from 10° to 85° with tube voltage and current of 40 kV and 30 mA, respectively.

Results and discussion

The colour of fibre I changes from the original red to dark brown after impregnating in $AuCl_3$·HCl solution; meanwhile the colour of the solution becomes lighter. This suggests that fibre I may have undergone oxidation by Au^{3+}. If this is true, then Au^{3+} would be expected to be reduced on the surface of fibre I_0. The X.p.s. results shown in *Figure 1b* clearly indicate the existence of Au^0 on the surface of fibre I_0. The Au^0 signal on fibre A_0 is very weak (*Figure 1a*). Moreover, curve-fitting on the Au 4f peak for fibre A_0 shows the coexistence of Au^{3+} and Au^0, the peak on fibre I_0 contains only Au^0 (*Figures 2a* and *b*). *Figure 3* shows the WAXD curves of A_0 and I_0. The peaks at $2\theta = 38°$ and 79° are the characteristic peaks for Au^0 [5]. It can be seen clearly that the peaks at $2\theta = 38°$ and 79° appear for fibre I_0, indicate the existence of Au^0 after fibre I was impregnated in $AuCl_3$·HCl solution. The peak in *Figure 4* around 17° can be attributed to the (100) planes in PAN fibres[6–8]. The peak around 25° is due to (002) planes for oxidized PAN, which corresponds to the sheet-like, hetero-aromatic cyclized structure developed during heat treatment[6–8]. The broad peak around 17° for I shifts to 25° for I_0. This result suggests that the fibre I was oxidized by Au^{3+} upon impregnation in Au^{3+} solution.

Since the only difference between A and I is that they are stabilized under different atmospheres, that is fibre A is heat-treated in air, the stabilized fibre should have more oxygen-containing functional groups. There should be much fewer oxygen-containing functional

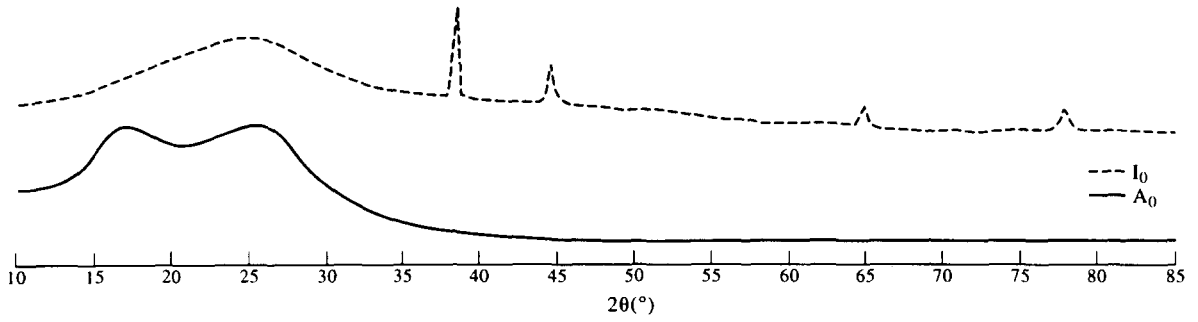

Figure 3 WAXD curves of fibre A_0 and fibre I_0 (10–85)

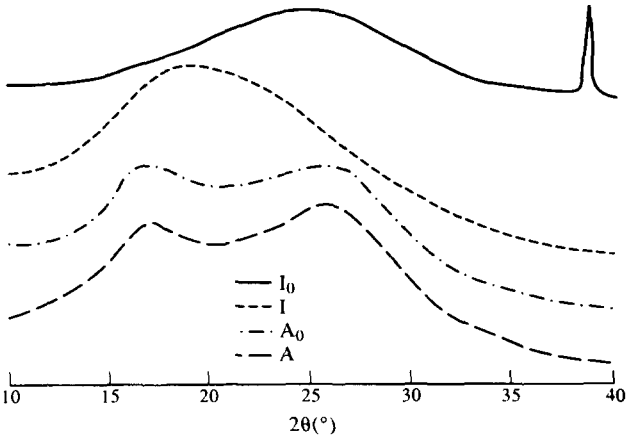

Figure 4 WAXD curves of fibres A, A_0, I and I_0 (10–40)

groups for I treated in argon atmosphere. But *Figure 1b* also shows an O1s signal for fibre I, it is perhaps due to the adsorption of water vapour and oxygen from air. So, there are great differences existing in the microstructures of fibres A and I. Based on the above experimental results it can be concluded that fibre I has undergone redox reactions when impregnating in $AuCl_3 \cdot HCl$ solution and it has strong reducing ability toward Au^{3+}. Studies of the detailed microstructures and thermal properties of those fibres are in progress.

Acknowledgement

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