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Scanning tunnelling microscopy study of activated carbon fibres

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Scanning tunnelling microscopy (STM) has been used to study isotropic pitch-based carbon fibres before and after steam activation. The results show that the present carbon fibre precursor exhibits a particulate surface which is very favourable for the formation of activated carbon fibre. After activation, the carbon fibre surface becomes much more porous and rougher, and the mesopores are evidently present on the surface. Because the scale is down to atomic resolution, the STM observations offer direct evidence for the existence of micropores on the surface of the activated carbon fibres. In addition, the surface textures of both fibres are presented and discussed.

1. Introduction

Carbon adsorbents have been applied widely in various fields of industry, especially in environmental areas [1]. In recent years, activated carbon fibres have drawn great attention because of their superior performance as compared to activated granulated and powdered carbons [2]. The advantages of activated carbon fibres include (1) a favourable combination of the filtration and sorption properties, (2) high kinetic parameters of sorption, (3) high mass-transfer coefficient, and (4) high homogeneity of fibre transverse characteristics.

The sorption properties of activated carbon fibres are essentially influenced by the surface characteristics, especially the surface micropores. It has been recognized that activated carbon fibres contain micropores in a significant proportion [3–5], and these pores are, to a large extent, dependent on the carbonization process, more particularly, the final temperature between 600 and 900 °C, prior to the activation [2, 6] and the activation conditions [7]. The direct observation of these surface pores has not been possible with conventional techniques such as electron microscopy, because of the resolution limit. However, recent development of scanning tunnelling microscopy (STM) opens up the possibility of direct observation of the surface at the atomic scale [8]. The STM has been successfully applied in a study of surfaces of high-performance carbon fibres [9–13].

This paper presents recent results from an STM study of an isotropic pitch-based carbon fibre precursor and the resulting activated carbon fibres.

2. Experimental procedure

The carbon fibre precursor (Fibre PR) used for preparing activated carbon fibres was a commercial isotropic pitch-based carbon fibre (Kureha, Japan) with a final heat-treatment temperature of about 900 °C. The specific surface area and the micropore volume of the fibres have been measured by CO_2 adsorption at 0 °C to be 400 $m^2\,g^{-1}$ and 0.158 $cm^3\,g^{-1}$, respectively [7]. This fibre was then activated by steam at 900 °C. The final activated carbon fibre (Fibre AC) had a weight loss or burn-off degree of 19.45%.

The STM equipment was a commercial Nanoscope II with a platinum/iridium tunnelling tip manufactured by Digital Instruments, Santa Barbara, CA. The typical measurement parameters are bias voltage 10–200 mV and setpoint current 0.5–2 nA. For Fibre AC, a higher bias voltage and lower setpoint current were needed. Except where indicated, the photographs were obtained in height mode, i.e. the image of the tunnel current, and are presented in three-dimensional view.

3. Results and discussion

Figs 1a–c and 2a–c show the images of Fibres PR and AC at larger scales, respectively. As expected, the surface of both fibres exhibits extreme roughness. It can be seen from Fig. 1 that the surface of Fibre PR is formed by different sized "particulates" stacked on each other, which are very favourable for the formation of pores during the activation process. In Fig. 2, the surface burn-off is clearly shown. The

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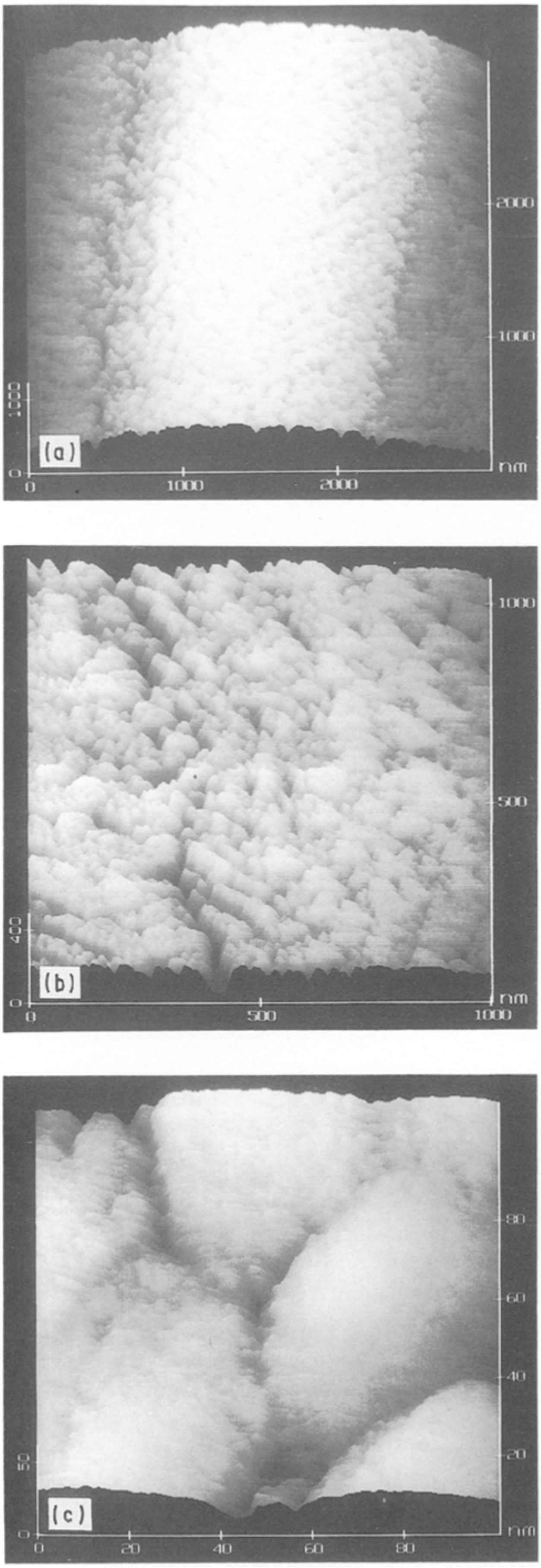

Figure 1 Large-scale STM images of Fibre PR showing a rough surface composed of "particles" and "holes". (a) 3000 nm × 3000 nm × 1200 nm, (b) 1000 nm × 1000 nm × 400 nm, (c) 100 nm × 100 nm × 60 nm.

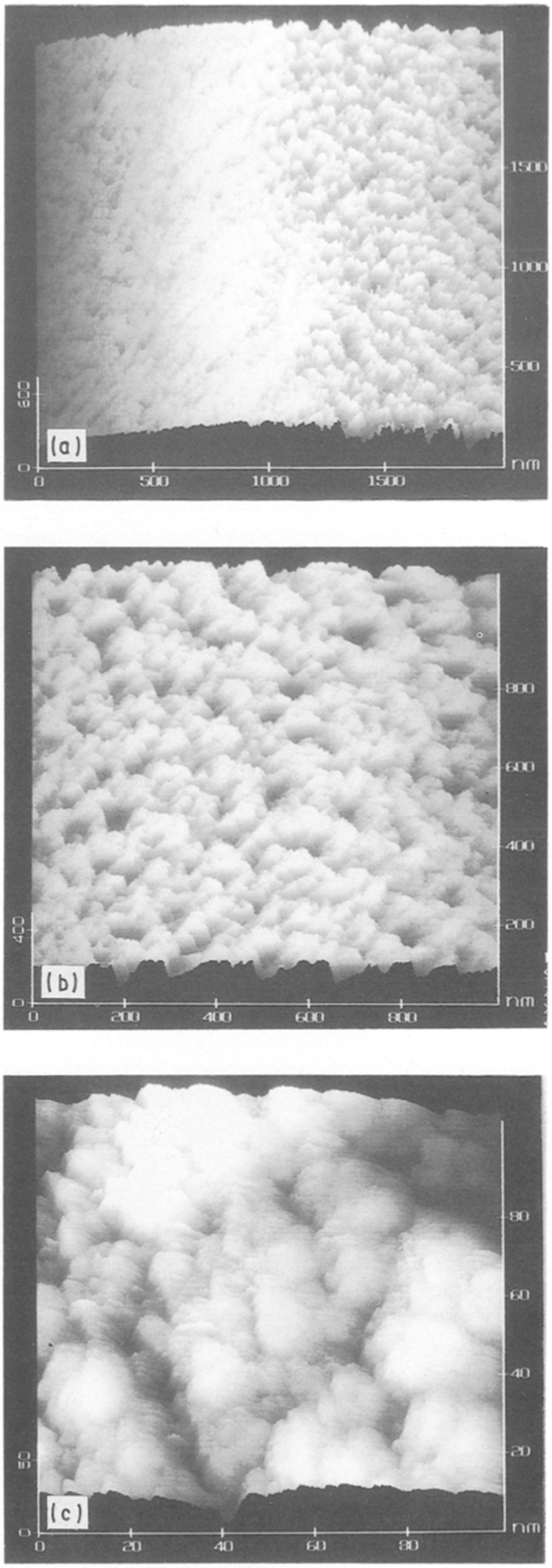

Figure 2 Large-scale STM images of Fibre AC showing burn-off and the extremely porous surface after steam activation. (a) 2000 nm × 2000 nm × 800 nm, (b) 1000 nm × 1000 nm × 450 nm, (c) 100 nm × 100 nm × 45 nm.

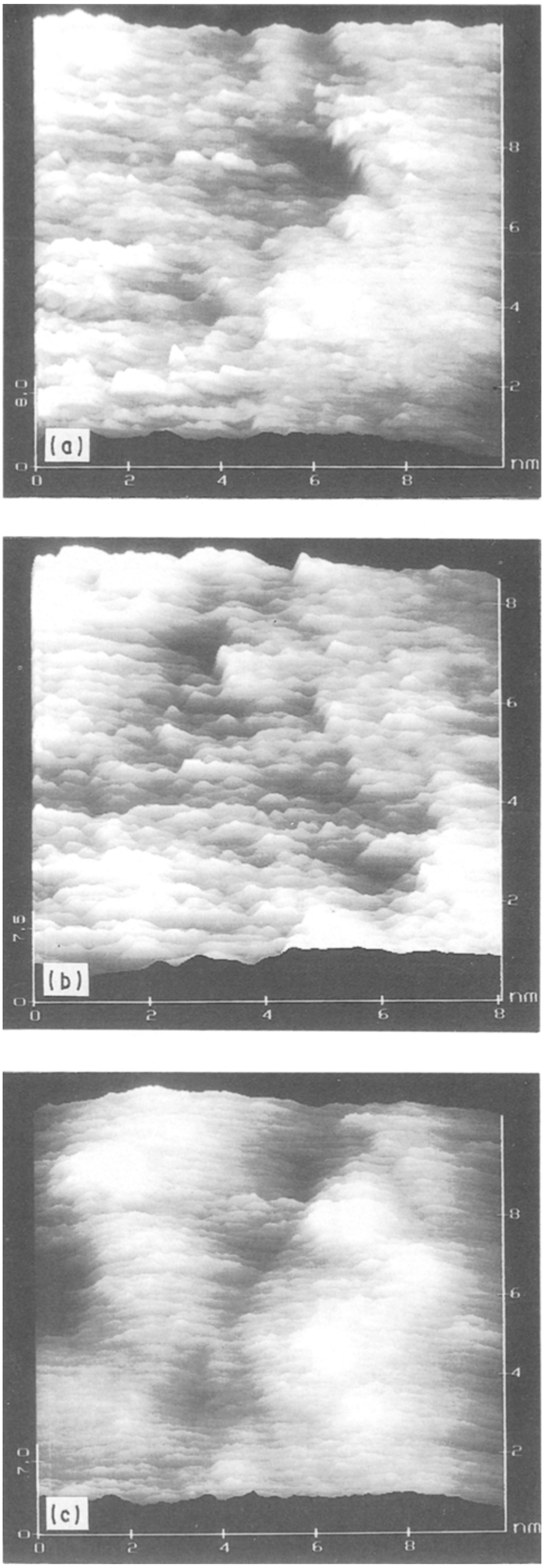

Figure 3 Atomic resolution STM images of Fibre AC showing the destroyed porous structure after steam activation; the organized crystalline pattern can hardly be seen. (a) 10 nm × 10 nm × 8 nm, (b) 8 nm × 8 nm × 7.5 nm, (c) 10 nm × 10 nm × 7 nm.

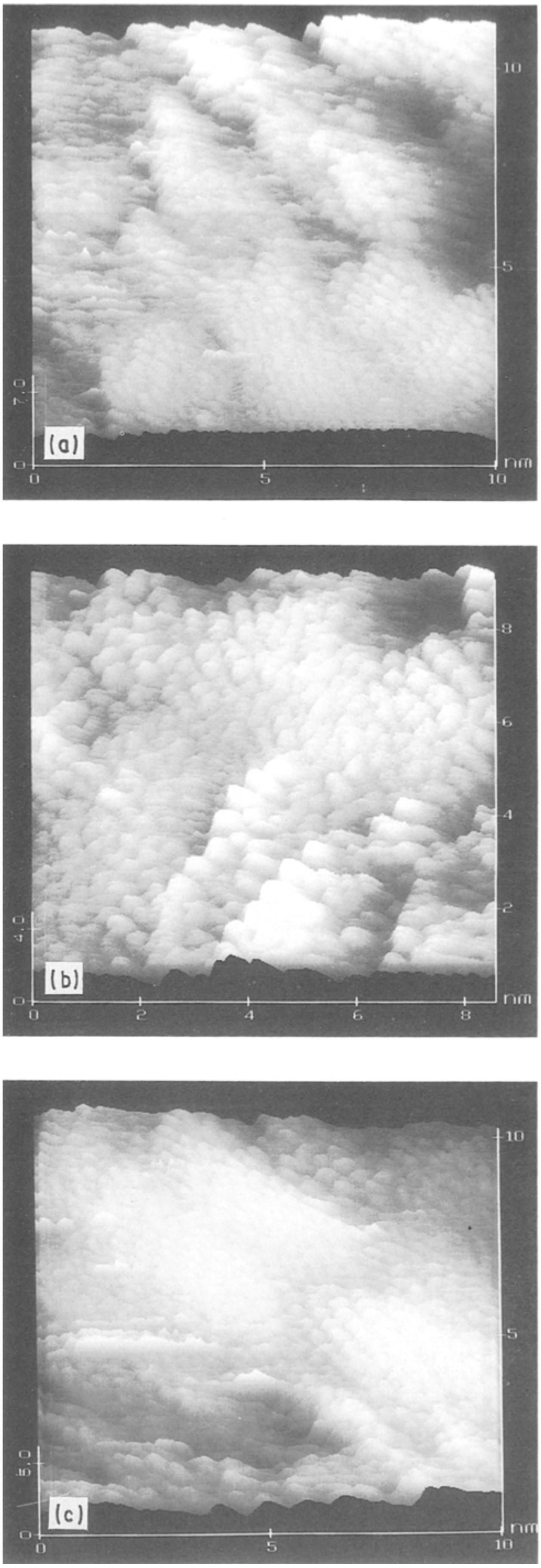

Figure 4 Atomic resolution STM images of Fibre PR showing an organized crystalline texture with amorphous zones and micropores between the crystallites (a) 10 nm × 10 nm × 7 nm, (b) 8.5 nm × 8.5 nm × 4 nm, (c) 10 nm × 10 nm × 7 nm.

"particulates" become smaller and the surface becomes extremely porous and rough. When the magnification is increased (from Fig. 2a to c), this becomes more obvious. According to IUPAC [14], the pores can be classified into three types by their width: micropores with width less than 2 nm, mesopores between 2 and 50 nm, and macropores above 50 nm. It was found that there was practically no macropore on either fibres, while the mesopores constitute considerable part on the activated carbon fibres at the present scale.

Because activated carbon fibres exhibit a Type I adsorption isotherm [7], one might expect to see micropores on the surface. This is the case, as shown in Fig. 3a–c, which show photographs of Fibre AC at atomic resolution. It is interesting to see that some micropores are already present on the carbon fibre precursor (Fig. 4a and b); this finding is in good agreement with previous adsorption experiments [15]. The round micropores imply that the present fibre was not submitted to the hot stretching process which leads to the formation of needle-shaped micropores, as revealed by small-angle X-ray diffraction studies on high-performance carbon fibres [16]. The micropores are always situated between the edges of organized crystallites which extend sometimes to 10 nm (Fig. 4c). Amorphous carbon or transition zones are also visible.

According to modern understanding, the burn-off of amorphous carbon between the crystallites results in the formation of micropore regions. The carbon atoms and/or heteroatoms at the sites around the micropores are generally very active and would be oxidized first. This has been confirmed directly by our observations as shown in Fig. 3a and b. The areas around the micropores have been completely "burnt" and more micropores have been generated in these areas. From Fig. 3, it can also be seen that under the present activation conditions, even the crystallites on the surface, as shown in Fig. 4, have been destroyed and virtually no organized patch could be observed; meanwhile, the surface of Fibre AC at the atomic scale is rougher and more porous compared with Fibre PR. The low tunnelling current (less than 0.1 nA) and high bias voltage (more than 500 mV) which is necessary to perform the observation of Fibre AC indicate that the surface of Fibre AC becomes less conductive (the STM is only applicable to conductive and semi-conductive materials). This is probably due to the oxide layer formed during the activation.

It is surprising to find that under a low carbonization temperature of about 900 °C, significant organization has already taken place on Fibre PR. The size of the crystallites can be compared favourably with L_a, the crystallite dimension, measured by X-ray diffraction. The average value of L_a was found to be about 4 nm for pitch-based carbon fibre heated at 1000 °C [16]. However, the periodicity parameter is very different from that of perfect graphite (the interatomic distance of HOPG in STM is 0.246 nm), as shown in Fig. 5a and b. This indicates the imperfection of the crystallite. It is well-known that carbon fibres are composed of two-dimensional turbostratic graphitic crystallites which are disoriented to each other. X-ray diffraction [16] showed that the average distance between two basal planes ($d_{0\,0\,2}$) for low-temperature treated (1000 °C) pitch-based carbon fibre is 0.372 nm, far higher than the single-crystal value (0.335 nm), indicating the imperfect crystalline structure. Because the STM image reflects the density of electric charge of the surface examined (more precisely, between the tip point and the surface), the imperfection of the crystallite will inevitably influence the corrugation patterns appearing during STM observation. Thus, the STM technique provides a direct means of studying the crystallite structure.

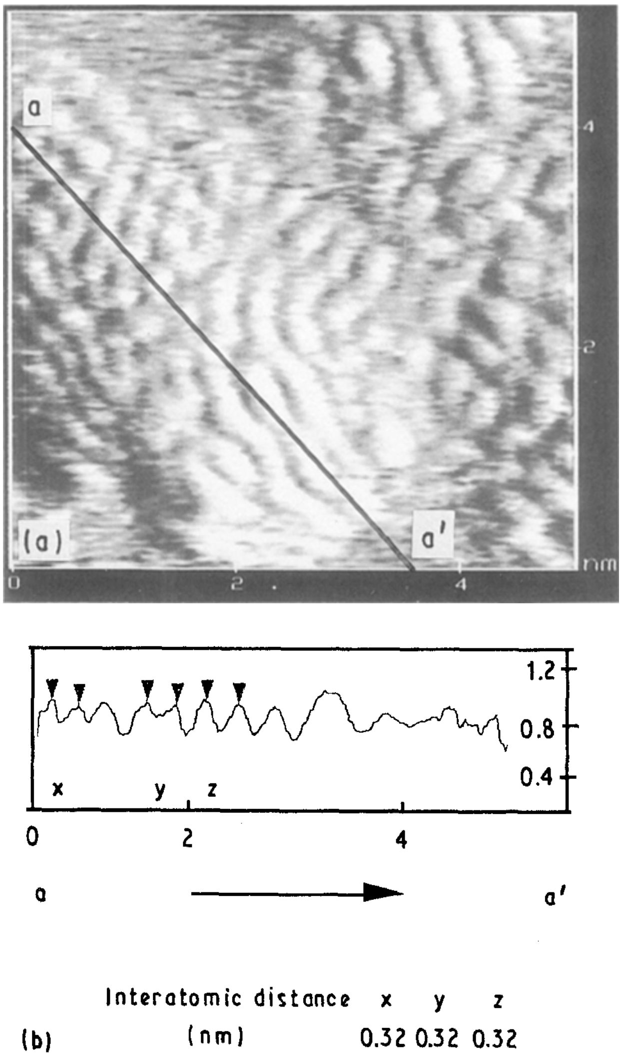

Figure 5 Cross-sectional STM image of Fibre PR, showing the imperfection of the crystallite. (a) STM image, topview, current constant mode, 5 nm × 5 nm; (b) line trace of cross-section a–a', as indicated in (a).

4. Conclusions

The study of activated carbon fibres by STM at large scales (more than 100 nm^2) shows that the activated carbon fibres examined present an extremely rough and porous surface which is composed of "particulates" and mesopores. At atomic resolution, the STM technique allows us, for the first time, to observe directly the changes in surface structure and the micropores before and after activation. It has also been found that a well-organized crystalline texture is obtained even under low carbonization temperatures of about 900 °C for carbon fibre precursor, but the crystalline structure is far from perfect.

Our results demonstrate that the STM technique is a useful tool for the study of very porous surfaces.

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