

The observation of active carbons by scanning tunneling microscopy

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Scanning tunneling electron microscopy (STM) has been used extensively for the study of well organized carbons. As a consequence, synthetic graphite of the HOPG type (Highly Oriented Pyrolytic Graphite) is used as a calibration standard in STM [1], owing to its good conductivity and its almost perfect planar structure at the atomic level. Other carbonaceous materials, such as carbon fibers [2] and, more recently, carbon blacks [3], have also been examined successfully by STM. From these studies, a number of observations have been made and conclusions have been drawn, which could not have been obtained by other means.

As far as we know this technique has not yet been applied to active carbons. This material is considered to be a bad conductor and therefore it was assumed that a study by STM would prove difficult. The aim of this communication is to show that this possibility exists, provided a number of precautions are taken. The study of active carbons by STM also requires a great deal of patience.

For our preliminary study, we used a sample provided by Société PICA (France), resulting from the activation of coconut shells by steam near 800-900°C. Its equivalent surface area, measured by argon adsorption at -77 K, is 2300 m²/g, which indicates a high degree of burn-off and consequently the presence of relatively large micropores (widths, L , in the range of 1-2 nm [4]). In order to remove oxidation by-products from the surface, which are poor conductors of electricity, the sample has been subjected for two days to toluene extraction in a 'soxhlet'. Finally it was dried in vacuum at 110°C. A small particle of the carbon to be examined by STM is fixed to a glass plate by a conducting glue which ensures electrical conductivity. Observations were carried out with a Nanoscope II microscope (Digital Instruments), equipped with a Pt/Ir (80/20) tip working at 20 mV and 1-5 nA. Filtering

was only applied to micrographs at relatively low magnifications, in order to improve their interpretation.

Active carbons are essentially microporous and their physico-chemical properties, such as the micropore volume, the internal and external surface areas and chemical centers, can be assessed by standard techniques [4-5]. Average micropore sizes, and in some cases their distribution, can also be assessed on the basis of adsorption experiments combined with the use of molecular probes [6]. Such distributions have been shown to be in good agreement with direct observations by HRTEM (High Resolution Transmission Electron Microscopy) [7]. However, this technique only applies to the edges of thin particles and the real structure of active carbons has not yet been observed directly. A possible model (Fig. 1) has been suggested by Stoeckli [5]. It describes the three-dimensional structure as a loose packing of curved aromatic surfaces, similar to wood-shavings. The resulting spaces, often slit-shaped at the molecular level, correspond to the micropores. The larger pores (meso- and macropores) result from voids between aggregates.

Fig. 2 shows a selection of STM micrographs obtained in our laboratory. At low magnifications (micrograph 1), corresponding to an area of 2000 x 2000 nm, the surface appears to be smooth, with some trenches extending over 500-1000 nm. As suggested by the corresponding profile, they are relatively deep and correspond to macropores. At a higher magnification (micrograph 2), corresponding to an area of 50 x 50 nm, the surface now appears to be rugged and one can observe typical mesopores with dimensions between 2 and 50 nm. These pores are filled by capillary condensation when vapors are adsorbed at relative pressures $p/p_0 > 0.4$. The picture also suggests the presence of smaller cavities, clearly visible at still higher magnifications (micrographs 3 and 4).

On micrograph 3, with an area of 15 x 15 nm, one observes a central region with dimensions of less than 2 nm and slits converging towards it. The overall structure is similar to that of Fig. 1. The dimension of these slits is close to 1 nm as revealed by micrograph 4, covering an area of only 5 x 5 nm. Such pores have also been observed in STM in activated carbon fibers.

Further information is provided by micrographs 5 and 6. They show the same area of 5 x 5 nm, respectively in the 'height' and 'current' observation modes. These pictures suggest that active carbons display a much higher degree of local organization at the atomic level, than assumed previously.

This first study shows that STM can be a powerful tool for the characterization of active carbons, where it confirms, by direct observation, the general picture postulated for their porous structure. Detailed results, relating the structure, the physico-chemical properties and the mode of activation of this type of carbon will be reported later.

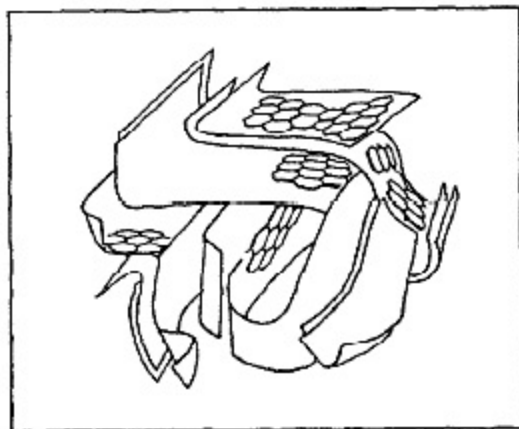


Figure 1. Schematic structure of an active carbon.

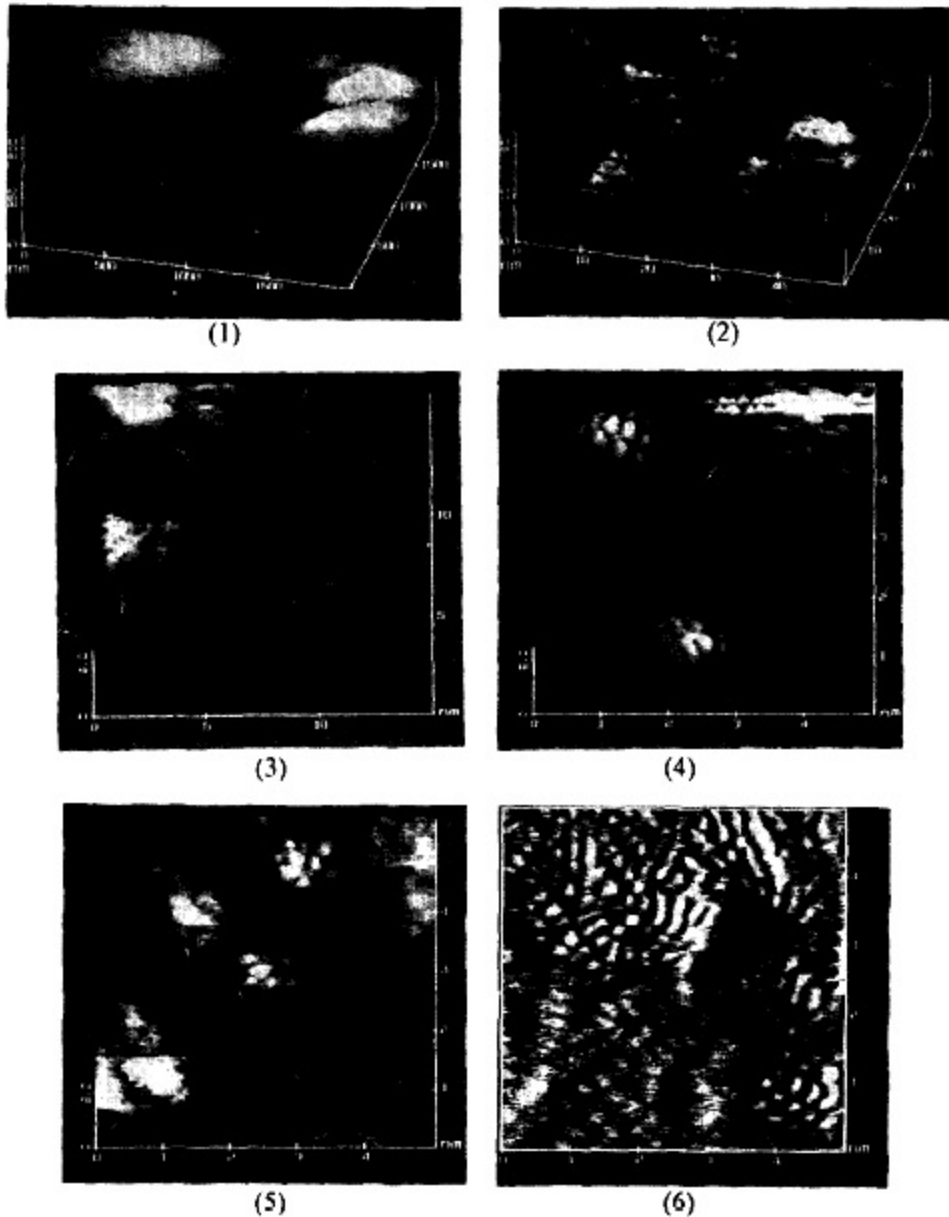


Figure 2. Scanning tunnelling microscope photos of active carbon.

REFERENCES

1. L.L. Soethout, J.W. Gerritsen, P. Groenveld, B.J. Nelissen and H. van Kempeu, *J. Microsc.* **152**, 251 (1988).
2. S.N. Magonov, H.J. Cantow and J.B. Donnet, *Polym. Bull.* **23**, 555 (1990).
3. J.B. Donnet and E. Custodéro, *CAR Acad Sci. Paris* **314**, 555 (1992).
4. R.C. Bansal, J.B. Donnet and F. Stoeckli, *Active Carbon*, Dekker, New York (1988).
5. H.F. Stoeckli, *Carbon* **28**, 1 (1990).
6. H.F. Stoeckli, P. Rebstein and L. Ballerini, *Carbon* **28**, 907 (1990).
7. R. Innes, J. Fryer and H.F. Stoeckli, *Carbon* **27**, 71 (1989).