A new adsorption substrate: Single crystal exfoliated graphite

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We describe the controlled exfoliation of single crystal graphite flakes intercalated to stage eleven with $SbCl_5$. The resulting exposed surface remains well oriented in the basal plane. Our best sample to date has an internal surface area of 6 Torr cc and an in-plane mosaic of 2.3° HWHM (half-width at half-maximum). High resolution x-ray scattering from adsorbed krypton reveals an average step-free surface size of at least 2000 Å. Experiments which probe orientational information in the layer planes should now be possible.

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Synthetic graphite (e.g., Union Carbide HOPG)[1] has provided the basis for studies on a broad range of physical systems.[2] For example, it is commonly used as a matrix for intercalation and as a substrate material for catalysis and adsorption experiments. Although samples of synthetic graphite can be prepared with much larger volumes than natural graphite flakes, they are oriented only along the c axis, precluding detailed structural analysis of adsorbed or intercalated layers.

In this communication, we describe a procedure to exfoliate *single crystals* of graphite, resulting in a well-oriented substrate with high specific surface area. This substrate makes possible new classes of experiments in fields as diverse as superconductivity, two-dimensional melting,[3] magnetism, and commensurate-incommensurate transitions.

The exfoliation procedure is as follows. Single crystals of natural graphite[4] (typically $6 \times 6 \times 0.2$ mm^3) were carefully intercalated to Stage 11[5] with $SbCl_5$. The two-bulb vapor intercalation technique[6] was used, with the graphite held at 200 °C and the liquid $SbCl_5$ at 40 °C. This particular intercalant is chosen for several reasons. Firstly, its graphite intercalation compound (GIC) is unusually stable[6] in ambient atmosphere and is therefore easy to handle. Secondly, the intercalant gallery spacing, at ~9.4 Å,[7] is among the largest encountered in well-staged GIC's. This is undoubtedly related to the ease with which $SbCl_5$-graphite can be exfoliated.[8]

Intercalation to precisely stage 11 is not crucial for this purpose except that high stage gives an ideal balance between the requirement for a large internal surface area (exposed on deintercalation) and the desire to introduce as few defects[9] as possible into the graphite layers. For the latter reason we avoided low intercalation stages.

After intercalation, the sample was mounted in a vertical furnace containing an evacuable (~10^{-5} Torr) piston and cylinder device, and was slowly heated to 1100 °C. A magnet was attached to the top of the quartz piston, and by means of a solenoid we could vary the compressional force on the surface of the graphite sample from 0 –1 N. With the upper limit of compressional force, we could control the exfoliation of samples of initial thickness up to 0.3 mm. The

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exfoliation was marked by a sharp[10] onset at approximately 300 °C and continued until the sample was 30–50 times its original thickness, as monitored *in situ* by a traveling microscope. Until the intercalant starts to escape from the graphite (at ~800 °C), the expansion is reversible and both slow heating (1–2 °C/min) and full compression are required to prevent the sample from exploding or shearing. At temperatures above 800 °C the quartz piston was lifted from the graphite surface; the sample was baked for 1 h at 1100 °C in order to clean it, and, finally, the sample was allowed to cool to ambient in a helium atmosphere.

Electron microprobe experiments on samples baked at 1100 °C show a small (1–2 mole %) residue of metallic Sb and this contaminant results in a spurious x-ray diffraction peak at 1.62 Å^{-1}. Higher baking temperatures (e.g., 1500 °C) would probably eliminate this residue. It is worth pointing out here that other GIC's, such as HNO_3-graphite,[2] have potential advantages in terms of lower process temperatures and less contamination. However, we find that exfoliation proceeds much more rapidly in this case and is harder to control. We have so far been able to exfoliate only very thin (<0.1 mm) samples of HNO_3-graphite, and these are too flimsy for experimental work.

Figure 1 shows a side view of a $SbCl_5$-exfoliated single crystal $6 \times 6 \times 7$ mm thick. A puckering of the graphite layers can be clearly seen in this photograph. This is caused by the way in which the sample expands during exfoliation: a closer inspection of the puckered surface reveals a network of interconnected "pockets." These probably contain gaseous intercalant in the temperature region between the onset of exfoliation (~300 °C) and deintercalation (~800 °C), suggesting a mechanism for the reversible expansion of the sample. It is interesting to note that the observed expansion behavior and the resulting connectedness of the exfoliated sample are both entirely consistent with the Daumas and Hérold picture[11] of stage formation in GIC's. In this model, the intercalant is not homogeneously distributed in layers within the matrix but instead forms macroscopic islands between every pair of contiguous carbon layers. This requirement is necessary to explain many features of GIC's, especially the redistribution of intercalant within the matrix. One example where the latter is important is in pressure-
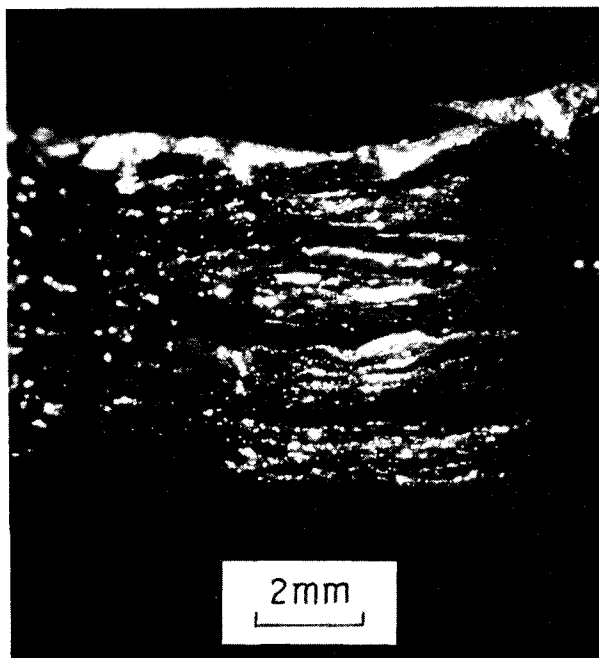
FIG. 1. Optical micrograph of exfoliated graphite crystal; side view.

FIG. 3. In-plane ω scans through (a) graphite (10) peak, (b) primary krypton peak. Solid lines are Lorentzian fits (see text).

induced staging transitions.[12]

Our best sample to date has an internal surface area of 6 Torr cc $(2 \times 10^{17}$ atoms/adsorbed monolayer) and an in-plane mosaic of 2.3° HWHM. The adsorption isotherm is shown in Fig. 2 and was obtained using the gas handling system and cryostat discussed previously.[13] Structural characterization was performed with $CuK\alpha$ radiation from a Rigaku 12 kW rotating anode source. The x rays were collimated in-plane with a single-crystal germanium (111) monochromator before the sample, and a Ge (111) crystal analyzer after the sample.

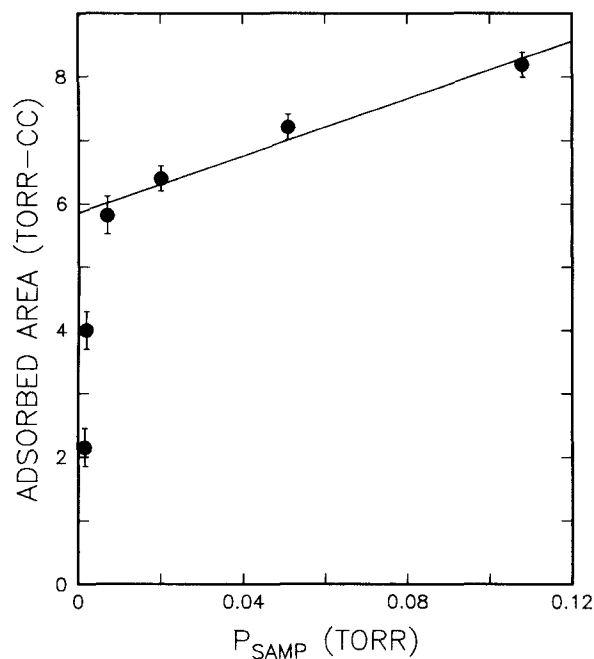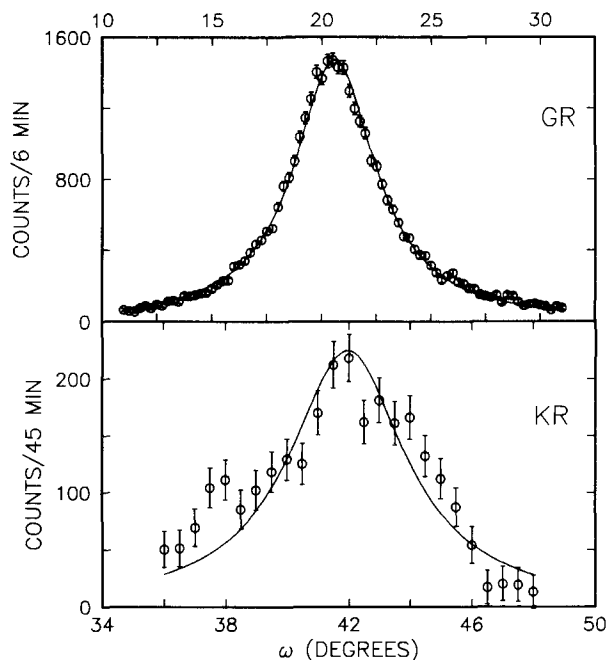Figure 3 shows in-plane ω scans through one of the six

graphite (1 0) spots of the exfoliated crystal and also through the $(\sqrt{3} \times \sqrt{3})R30°$ peak of an adsorbed monolayer of krypton. The best fit to the graphite peak is a Lorentzian with 2.3° HWHM. The scattering from the adsorbed Kr monolayers is obviously quite weak. The best fit value of the in-plane Kr mosaic is about 3° HWHM although a Lorentzian fit with width constrained to 2.3° HWHM (shown in Fig. 3) seems to work adequately. Figure 4 is a radial scan through the same krypton Bragg peak. The solid line corresponds to a lineshape analysis of the data which is essentially identical to
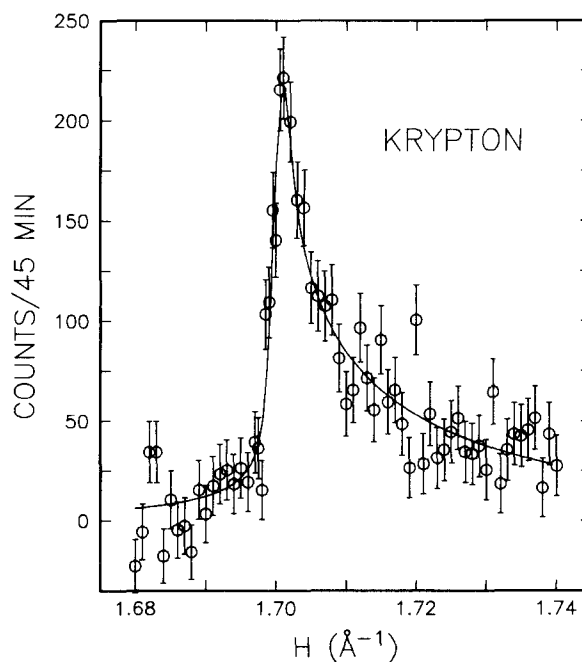

FIG. 2. Krypton adsorption isotherm taken at $T = 77$ K.

FIG. 4. Bragg peak from krytpon monolayer. The solid line is a Warren fit appropriate to 2-d scattering.

that usually carried out for *ZYX* graphite substrates[14] (except that the powder average is replaced by an average over the in-plane mosaic). This fit yields an average step-free surface size of at least 2000 Å and a *c*-axis tilt mosaic of 17° HWHM. The intensity of this scattering suggests that it originates from ~ 1000 separate krypton layers.

In conclusion, $SbCl_5$ seems to be an excellent exfoliant for the preparation of well-oriented natural graphite substrates. The in-plane coherence length (which is comparable to present *ZYX* substrates[15]), together with the good in-plane mosaic, has already made a qualitative improvement in experiments on melting phenomena in adsorbed monolayers.[3] Single crystal exfoliated graphite should facilitate a broad range of surface science experiments where a microscopically smooth, well-oriented substrate is called for.

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