

SUPERSTRUCTURES OF GRAPHITE INTERCALATION COMPOUND FORMED BY SODIUM-HYDROXIDE SOLUTION STUDIED BY SCANNING TUNNELING MICROSCOPY

Koji Miyake, Yoshiaki Aiso, Makoto Komiyama¹ and Hidemi Shigekawa*

Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

¹Department of Chemistry and Biotechnology, Faculty of Engineering, University of Tokyo, Japan

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Abstract

Highly oriented pyrolytic graphite (HOPG) treated with sodium hydroxide solution was found to show an X-ray diffraction pattern characteristic of a stage-8 intercalation compound. Superstructures such as 2×2 , $\sqrt{3} \times \sqrt{3}$ and noble orthorhombic lattices were observed on the NaOH-treated graphite surfaces by scanning tunneling microscopy, as was previously observed on stage-1 alkali-metal graphite intercalation compound (GIC) surfaces formed by Li, K, Rb and Cs intercalates. The orthorhombic phase has a periodic structure formed by four bright and two dark rows, which were explained by the intercalant arrangement occupying two different sites, in the GIC.

Key Words: Graphite, scanning tunneling microscopy, intercalation, sodium hydroxide, superstructures.

Introduction

Layer compounds such as graphite and transition-metal dichalcogenide are known to form intercalation compounds which have many interesting properties differing from those of host materials, e.g., superconductivity and low-dimensional conductivity. Among them, graphite intercalation compounds (GICs) have attracted considerable attention because graphite is intercalated by a wide variety of atoms. In X-ray diffraction measurements, GICs show periodic stacking structures. When intercalated materials, i.e., intercalants, exist between every n and $n+1$ layer of the host highly oriented pyrolytic graphite (HOPG), the structure is called a stage- n -type one. However, since the stage structure changes reversibly according to temperature, Daumas and Herold [2] proposed a model where intercalants exist between every layer and periodic stage structures are formed by intercalant domains periodically arranged in the direction perpendicular to the sample surfaces.

Alkali-metal GICs (M-GICs) have been studied widely because of their simplicity in analysis. Among the various stages formed by alkali-metal GICs, low-stage structures ($n = 1, 2$) in particular have been investigated in detail experimentally [9] and theoretically [8]. Recently, surface structures of binary and ternary alkali-metal GICs were studied by scanning tunneling microscopy (STM) [3-5], and superstructures such as 2×2 and $\sqrt{3} \times \sqrt{3}$ commensurate with the graphite host lattice were observed on the stage-1 M-GIC ($M = \text{Li, K, Rb, Cs}$) surfaces as was expected from the results of X-ray diffraction measurements. In contrast, for higher stages of these compounds, little is known about the structures. A 2×2 diffraction pattern was obtained for a Na-GIC which has high-stage structures ($n = 6, 8$) [1, 6]; however, no STM study has been reported for this surface.

Recently, we found HOPG treated with NaOH solutions to have an X-ray diffraction pattern characteristic of a new stage-8 structure. In this paper, we report the results of STM observation performed on this high-stage intercalated compound.

*Address for correspondence:
Hidemi Shigekawa,
Institute of Materials Science,
University of Tsukuba,
Tsukuba 305, Japan.

Telephone number: 81-298-53-5276
FAX number: 81-298-55-7440
email: hidemi@mat.ims.tsukuba.ac.jp

Experimental

Samples were prepared by dropping NaOH aqueous solution (concentration 0.1 N) onto freshly cleaved HOPG surfaces or dipping HOPG crystals into NaOH aqueous solution. X-ray diffraction patterns of the treated samples showed a stage-8 structure. Samples were cleaved to provide fresh surfaces and studied by STM (Burleigh ISTM and Digital Instruments Nano-scope III) in air using a PtIr tip. All STM images in this paper were taken in the constant height mode.

Results and Discussion

Figure 1 shows an X-ray diffraction pattern obtained for a graphite surface treated with NaOH aqueous solution. Obtained peaks agree well with the stage-8 Na-GIC structure previously observed [7].

Figure 2b shows the 2×2 superstructure of a this sample (at tip bias voltage, $V_t = -20$ mV; and tunneling current, $I_t = 2.0$ nA). The cross-section along a-b in Figure 2b is drawn in Figure 3a. A honeycomb structure was obtained; however, the distance between the protrusions was about 0.49 nm, which is two times as large as that of HOPG (Fig. 2a). The two-dimensional structure of the intercalated Na atoms in the Na-GIC, previously determined by X-ray diffraction [7], was a 2×2 superstructure commensurate with the host graphite, which is in good agreement with the STM image shown in Figure 2b. Its structural model is shown on the right side of Figure 2b.

Another superstructure differing from the 2×2 was observed at a different area on the same sample. Figure 2c shows an example ($V_t = -25$ mV, $I_t = 1.7$ nA). The cross-section along c-d in Figure 2c is drawn in Figure 3b. The distance between the protrusions was about 0.41 nm, which is in good agreement with a $\sqrt{3} \times \sqrt{3}$ superstructure. Its structural model is shown on the right side of Figure 2c. Recently, a similar $\sqrt{3} \times \sqrt{3}$ structure was found to exist in the low stage K-GIC in addition to the 2×2 superstructure which had been observed by the X-ray diffraction [5]. Since X-ray diffraction measurements seem to result in the 2×2 superstructures similarly for both high and low stages, the $\sqrt{3} \times \sqrt{3}$ structures in alkali-metal GICs may be less stable compared to the 2×2 structures. In fact, the 2×2 structure was observed more often in our experiment. Details are under consideration.

From I-V curves (tunneling current - bias voltage curves) measured on the NaOH-treated HOPG sample, an increase in the charge density near the Fermi level after NaOH treatment was observed, indicating that charge transfer occurs from the intercalate to the host graphite, as has been observed for other alkali-metal

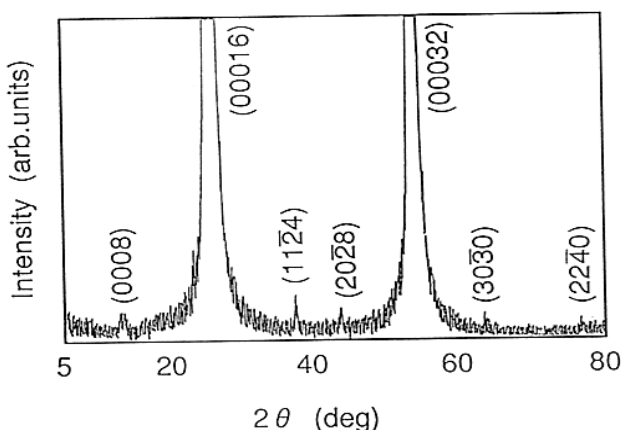


Figure 1. X-ray diffraction pattern for a HOPG sample treated with NaOH solution.

GICs. Detailed analysis of the charge transfer in the both phases has not yet been completed. However, the protrusions observed in the 2×2 surface (Fig. 2b) is broader than that in the $\sqrt{3} \times \sqrt{3}$ surface (Fig. 2c), indicating the more extensive unoccupied states in the 2×2 phase. Transferred electron density in the 2×2 structure is considered to be less than that in the $\sqrt{3} \times \sqrt{3}$ structure.

Because of the fact that the similar structures were observed after each cleavage of the samples, intercalants are considered to exist between every layer of the host HOPG. In order to confirm this, NaOH solution was dropped onto the central area of the sample surfaces, and they were cleaved from the edges of the samples where intercalants are considered to have little influence on the cleavages. Therefore, the structural model proposed by Daumas and Herold [2] is more applicable in explaining the observed structures, rather than the ideal stage structural model proposed originally in which intercalants exist between every n and $n + 1$ layer of the host HOPG.

In addition to the 2×2 and $\sqrt{3} \times \sqrt{3}$ structures, we also found a non-hexagonal superstructure as shown in Figure 4a ($V_t = -20$ mV, $I_t = 2.0$ nA). The structure is similar to that observed for the RbCs-GIC surface as a charge density wave (CDW) phase [4, 5]. The new phase has a periodic structure formed by four bright and two dark rows, as is shown in Figure 4a. Distance between the observed rows was ~ 0.25 nm. A possible model to explain the observed structure is shown in Figure 4b. When the intercalants are placed on the two different sites of an HOPG plane as shown in Figure 4b, on interatomic or atomic sites of the HOPG hexagonal lattice, the periodicity of the rows indicated by solid and dotted lines in Figure 4b can be calculated (as 0.28 nm

Superstructures of graphite intercalation compound

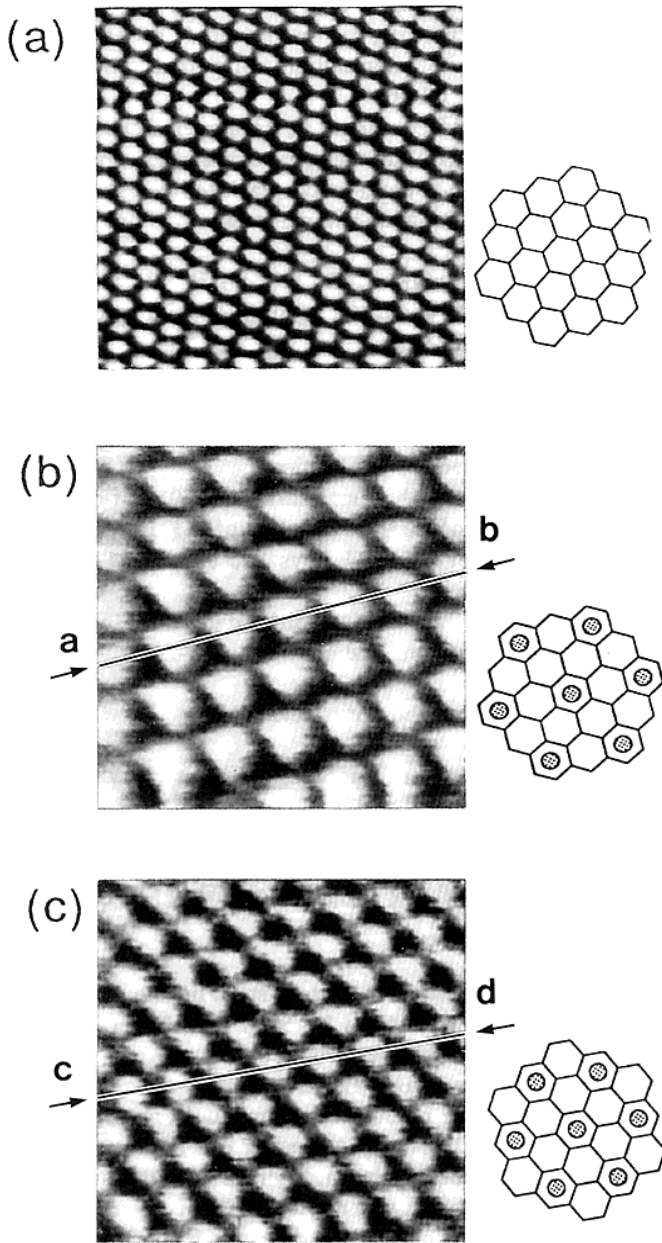


Figure 2. STM images and their structural models of (a) HOPG ($V_t = -30$ mV, $I_s = 2.2$ nA, 3 nm X 3 nm), (b) 2×2 superstructure on a NaOH-treated HOPG surface ($V_t = -20$ mV, $I_s = 2.0$ nA, 3 nm X 3 nm) and (c) $\sqrt{3} \times \sqrt{3}$ superstructure on a NaOH-treated HOPG surface ($V_t = -25$ mV, $I_s = 1.7$ nA, 3 nm X 3 nm).

Figure 4 (at right). STM image (a) and its structural model (b) of non-hexagonal superstructure on a NaOH-treated HOPG surface ($V_t = -20$ mV, $I_s = 2.0$ nA, 8 nm X 8 nm).

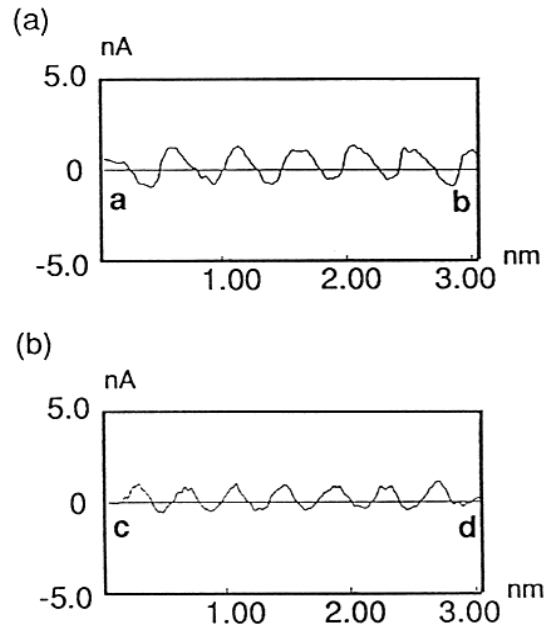
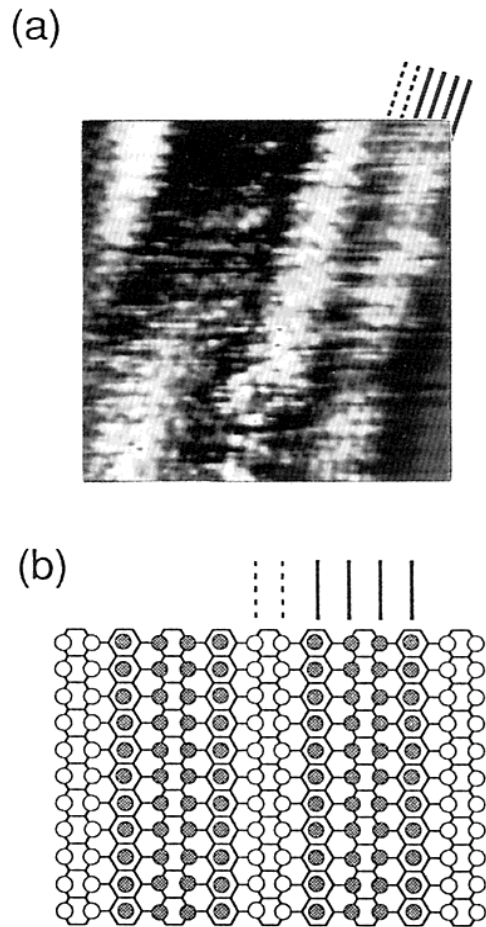


Figure 3. Cross-sections along (a) a-b in Figure 2(b) and (b) c-d in Figure 2(c).



using the HOPG lattice constant), which agrees well with the observed value (~ 0.25 nm). The observed bright and dark rows in Figure 4a correspond to the intercalant rows represented by the closed and open circles in Figure 4b, respectively.

In order to systematically study the properties of the intercalation compounds treated with alkali-metal hydroxide solutions, further experiments are in progress. In the case of NaOH-treated MoS₂ samples, island structure was formed by the intercalants, details of which will be presented elsewhere [7].

Conclusions

HOPG treated with NaOH solution was found to form a stage-8 structure. In addition to the 2 X 2 structure, similar to that previously found by X-ray diffraction analysis for Na-GIC, a $\sqrt{3}$ X $\sqrt{3}$ superstructure was also observed by STM on this high-stage GIC surface. These structures were observed after each cleavage of the samples, thereby supporting the Daumas and Hérold model [2] in which intercalants are assumed to exist between every host layer. Charge density near the Fermi level was increased by intercalation as has been observed for other alkali-metal GICs. In addition, we found a non-hexagonal one-dimensionally ordered long-range superstructure as was observed previously for RbCs-GIC as a CDW phase.

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References

1. Asher RC (1959) A lamellar compound of sodium and graphite. *J Inorg Nucl Chem* **10**, 238-249.
2. Daumas N, Hérold A (1969) Sur les relations entre la notion de stade et les mécanismes réactionnels dans les composés d'insertion de graphite (On the relation between phases and reactions mechanisms in graphite composites). *C R Acad Sci Ser* **C268**, 373-375.
3. Ketly SP, Lieber CM (1991) Scanning tunneling microscopy investigations of the surface structure and electronic properties of ternary graphite intercalation compounds. *J Vac Sci Technol* **B9**, 1068-1071.
4. Lang HP, Thommen-Geiser V, Wiesendanger R, (1992) Scanning tunneling microscopy study of ternary alkali-metal graphite intercalation compounds. *Ultra-microscopy* **42-44**, 624-629.
5. Lang HP, Wiesendanger R, Thommen-Geiser V, Güntherodt H-J (1992) Atomic-resolution surface studies of binary and ternary alkali-metal-graphite intercalation compounds by scanning tunneling microscopy. *Phys Rev B* **45**, 1829-1837.
6. Métrot A, Guérard D, Billaud D, Hérold A (1980) New results about the sodium-graphite system. *Synth Met* **1**, 363-369.
7. Miyake K, Shigekawa H (1995) Surface structure of layer compounds treated with alkali-metal hydroxide solutions studied by scanning tunneling microscopy. *Synth Met* (accepted for publication).
8. Ohno T, Nakao K, Kamimura H (1979) Self-consistent calculation of the band structure of C₈K including the charge transfer effect. *J Phys Soc Jpn* **47**, 1125-1133.
9. Rüdorff W (1959) Graphite intercalation compounds. *Adv Inor Chem Radiochem* **1**, 223-266.

Discussion with Reviewers

Reviewer IV: You are operating STM at close distances. Is it possible that what you are actually seeing is multiple tip effect.

Authors: No, it is not possible because we checked the structures of stage 8, 2 X 2 and $\sqrt{3}$ X $\sqrt{3}$, using X-ray diffraction (Figure 1).

C.J. Sparks: Would not a more systematic and extensive survey of the structures by STM give better evidence of the more common structures?

Authors: Yes, we agree. We are trying to understand the properties of the intercalation compounds more systematically and extensively by using other materials. For example, preliminary recent findings show that similar superstructures formed on GIC by KOH treatment. On The other hand, ordered structure does not form in MoS₂ substrate. We plan to publish complete results with more common structures later.