

STRUCTURAL ANALYSIS OF KI CRYSTALS PRODUCED IN CARBON NANOSPACES

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Introduction

Carbon nanopores whose width is a few nm order provide strong interaction potential field to molecules introduced in the nanopores compared with the surface. The strong potential fields cause unique structure formations of the introduced molecules, which are different from bulk phase structure. Since a high pressure gas phase reaction occurs even without an application of external high pressure in such nanopores, the effect of nanopores is well known as quasi-high pressure effect. First experimental study on quasi-high pressure effect of carbon nanopores was suggested by J. Imai et al. [1]. They clarified slit-shaped micropores of mean pore width of 0.9 nm of an activated carbon fiber (ACF) worked as a disproportionation reaction field of dimerized NO. Although the disproportionation reaction of $(\text{NO})_2$ to N_2O and NO₂ generally occurs at a high pressure of more than 20 MPa, the high pressure reaction of NO molecules was caused by the confined nanopores. Similar to the disproportionation reaction of NO molecules, CCl_4 molecules adsorbed in ACF with the slit pores of 0.8 nm formed a unique packing structure at 303 K. However, the formation of CCl_4 molecules in ACF with the slit pores of 1.1 nm is close to bulk liquid [2]. The previous study indicates that the CCl_4 molecular packing is more intensely restricted in the narrower pore. The direct observation of packing structures of potassium iodine (KI) in nanopores of single-wall carbon nanotubes (SWCNTs) with the different diameters were achieved by using high-resolution transmission electron microscope (HR-TEM) [3,4]. The KI crystal in SWCNTs with smaller diameter forms imperfect NaCl type structure. On the other hand, alkali-metal halides undergo a structural phase transition from NaCl type to CsCl type at several GPa [5-7]. Since the structural phase transition induces insulator-metal transition by a change of electronic band structure, solid alkali-metal halides under high pressure are of great physical interest. Therefore, we studied here the quasi-high pressure effect of one- or two-dimensional carbon nanopores against KI crystal growth whose structural phase

transition and metallization are induced at 1.9 GPa and over 115 GPa, respectively.

Experimental

Single-wall carbon nanohorn (SWCNH) and activated carbon fiber (ACF) were used as one- or two-dimensional nano-sized crystal growth field, respectively, as shown in Fig. 1. Even though SWCNT is remarkable carbon nanomaterial with one-dimensional pores, many catalytic metals still remain in SWCNTs and it is difficult to remove the metal particles without inducing structural defects. In contrast, SWCNHs are produced without any metal catalysts. SWCNH forms an assembly structure of the large number of horn-shaped single-wall carbon nanotubes with the diameter of 2 – 5 nm [8]. The spherical assembly of SWCNHs with a uniform size of 80 nm has interstitial nanopores can be utilized as nano-sized one-dimensional crystal growth spaces; the KI crystals should form anisotropic crystals aligned along the carbon walls of SWCNHs. On the other hand, ACF with the pore width of 1.1 nm consists mainly of an aggregated structure of micrographites, which form many open-pores on ACF; the pore structure of ACF is suitable geometrical structure that adsorbed molecules easily access into pores.

Highly pure KI was doped in each of SWCNH and ACF by heating mixtures of the each carbon sample and KI at 1073 K for 8h in closed quartz cell. As mentioned above, HR-TEM studies have already indicated the imperfect KI structures in the carbon nanopores. Although the HR-TEM observation is a powerful tool to clarify nanocrystal structures, the HR-TEM often provides information on the local structure. In this study, the detail crystal structures of products in carbon nanopores were determined not only by HR-TEM observation but also by synchrotron x-ray diffraction (XRD) pattern because the XRD profile provides overall information on KI crystals in the confined nanopores. KI-doped SWCNH (SWCNH/KI) and ACF (ACF/KI) were sealed in 0.5 mm Lindemann glass capillary in ambient or N₂ condition whose humidity were ca. 55 % and 14 %, respectively, for the synchrotron XRD measurements.

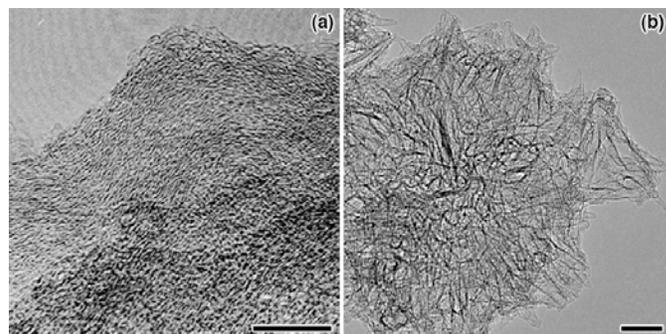


Fig. 1 HR-TEM images of (a) ACF and (b) SWCNH. Scale bar: 10 nm

Results and Discussion

The XRD profile of SWCNH showed huge broad peak and sharp 002 diffraction at $2\theta \sim 17^\circ$ and 10 reflection peak of the turbostratic structures of rotational graphenes of SWCNH and the micrographites is observed at $2\theta \sim 27^\circ$. The bulk phase structure of KI can be easily assigned to NaCl type structure, which is an ordinary structure of alkali-metal halide at ambient condition. On the other hand, a new set of weak diffraction lines was observed together with the XRD patterns of NaCl type structure in SWCNH/KI prepared in the ambient condition.

Fig. 2 shows synchrotron XRD patterns of (a) ACF, (b) ACF/KI prepared in the humidity of 55 % and (c) ACF/KI prepared in the humidity of 14 % and (d) KI at ambient temperature. Since ACFs are formed by micrographite, XRD profile of ACF shows huge broad peaks of 002 and 10 diffraction. Although the XRD pattern of SWCNH/KI suggested presence of the unique structure of KI, which is different from bulk phase structure, KI structure in ACF/KI prepared in the ambient condition is just bulk phase (NaCl-type) structure. Since KI is a representative deliquescent material and the pore structure of ACF is accessible to gas molecules such as vapor around the ACF, deposition of KI crystals synthesized in ACF should occur and be transformed to bulk phase structure. The XRD pattern of ACF/KI sealed in the Lindeman glass capillary under N_2 gas atmosphere shows a new set of very weak diffraction lines with strong diffraction patterns derived from bulk phase structure. The details of structural information on KI crystal in SWCNH/KI and ACF/KI are discussed in more depth at this conference.

Conclusions

The structural phase transition of KI crystal in nanospaces has been studied with the crystal stability of high pressure phase at ambient condition. Synchrotron XRD patterns clearly indicate that KI crystals in nanospaces can form disordered structures aligned to spatial structures. Both nanospaces of SWCNH and ACF produced the unique crystal growth field. However, the structural stability was quite difference by the accessibility of ambient gases to pores. The present study on nanospaces will not lead to understand the phase behavior in confined nanospaces such as CO_2 storage in subsurface geology but also to be applied as the new synthesis field for high pressure reaction.

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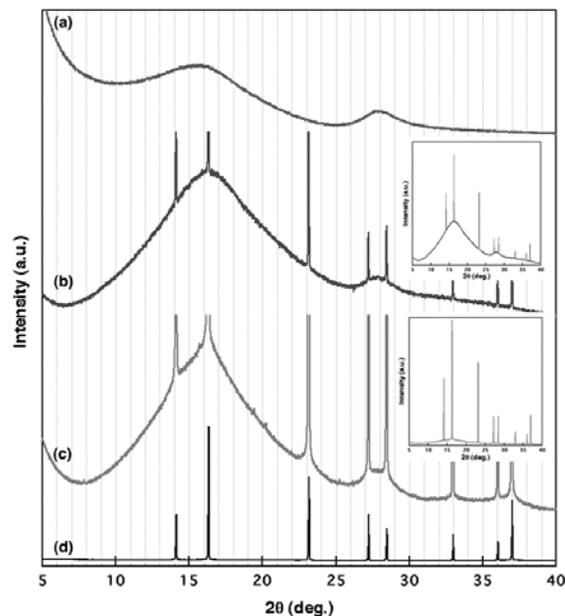


Fig. 2 Synchrotron XRD patterns for (a) ACF, (b) ACF/KI (ambient), (c) ACF/KI (N_2) and (d) KI. Inset: Overall XRD patterns including bulk phase lines from 5 to $40^\circ/2\theta$.

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