

Structure Analysis of Conducting Nanosheet Crystallites

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Introduction

Conducting nanosheet crystallites derived from exfoliation of electroconductive layered compounds including graphite and layered ruthenates^{1,2} have stimulated huge quantities of researches as to applications associated with energy harvesting and storage technology because their unique dimension and structure often trigger unexpected physicochemical properties. Understanding of their crystal structure, therefore, is of significantly importance in order to utilize and control their properties. In this study, we investigated two-dimensional periodic structure of several conducting nanosheets by means of grazing-incidence X-ray diffraction analysis.

Experimental

Layered ruthenates, $\text{KRuO}_{2.1}$ and NaRuO_2 , were delaminated into elemental host layer, i.e. ruthenium oxide nanosheet called K-type¹ and Na-type², respectively, in this study. Graphite oxide was obtained via chemical reaction of graphite with *conc.* H_2SO_4 solution including KMnO_4 and NaNO_3 and then dispersed into TBAOH aqueous solution, yielding a suspension of graphite oxide nanosheets. Sub-monolayer films in which these anionic nanosheets lay flat to Si substrate were fabricated through electrostatic adsorption with cationic polymer used as a binder. Graphene-restacked film on SiO_2 substrate was obtained by simple dry-cast method of the suspension of the graphite oxide nanosheets and subsequent reduction process induced by heating at 900°C for 1h under 10% hydrogen gas flow. In-plane diffraction pattern of these nanosheet films was measured by a four-axis diffractometer equipped with NaI scintillation counter at the BL-6C in Photon Factory.

Results and Discussion

Synchrotron radiation in-plane XRD pattern for the self-assembled monolayer film of K-type and Na-type ruthenate nanosheets were displayed in Fig. 1a and b, respectively. The K-type nanosheet film exhibited many sharp in-plane diffractions in the d^{-1} region from 3 to 10 nm^{-1} . All of the observed peaks are indexed to hk reflections of a 2D oblique cell.¹ The refined cell parameters were $a = 0.5610(8)\text{ nm}$, $b = 0.5121(6)\text{ nm}$ and $\gamma = 109.4(2)^\circ$. As for Na-type nanosheet, only three peaks were identified in the d^{-1} region. These peaks can be assignable to hk reflections of a 2D hexagonal cell with cell parameter of $a = 0.2929(6)\text{ nm}$.²

Unlike the case with ruthenate nanosheets, we hardly detected any diffraction signal from sub-monolayer film of graphite oxide nanosheet and its reduced form, graphene, owing to very weak interaction of constituent carbon atoms with hard X-ray ($\sim 0.11\text{ nm}$) and much low concentration. To gain information on two-dimensional periodicity of carbon atoms, graphene-restacked film including a large amount of graphene was used. It should be noted here that incidence X-ray easy to penetrate into even this thicker film was totally reflected by the substrate surface and some of them should be diffracted in the direction parallel to the substrate. Successfully obtained in-plane diffraction pattern of the graphene-restacked film was shown in Fig. 1c. Distinctive two peaks gave refined cell parameter of $a = 0.2434(2)\text{ nm}$ in hexagonal symmetry. Interestingly, its C-C bond distance calculated from the a -axis, $\sim 0.1406\text{ nm}$, became definitely smaller than that of graphite presumably because of release from π - π stacking. These experimental data would be helpful not only for their fundamental study but also for various applications.

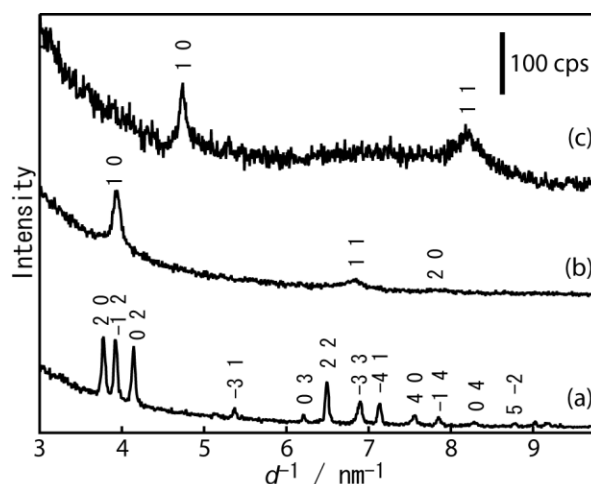


Figure 1 In-plane diffraction patterns for (a) K-type and (b) Na-type ruthenate nanosheet films and (c) graphene-restacked film.

References

- [1]K. Fukuda et al., J. Solid State Chem. 182, 2997 (2009).
- [2]K. Fukuda et al., Inorg. Chem. 49, 4391 (2010).

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