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Effect of pH on the exfoliation of K-THF-GICs

ABSTRACT

Recently, numerous methods for preparing isolated graphene without oxidation have been developed to retain the intrinsic characteristics of graphene such as its excellent electrical conductivity. One such method is the exfoliation of alkali-metal graphite intercalation compounds (GICs) the via addition of solvents. The GICs are exfoliated through via a decomposition reaction between alkali-metal atoms existing in the interlayers and molecules. This process does not result in the oxidation of graphite layers.

In this study, non-oxidized graphene was prepared by the exfoliation of stage-1 K-THF-GICs through addition of various polar solvents. The direction and thickness of the exfoliated products were measured by TEM observation. As result, the exfoliation of the alkali metal GICs was more effective when a polar protic solvent such as alcohol or water were added in the polar solvent. The lengths of the products were on the order of a few micrometers in the planar direction and the thickness were on the order of a few nanometers. However, the products were condensed in exfoliated K-THF-GICs dispersion after sonication. To solve this problem, the effect of pH on the exfoliation of K-THF-GICs is examined based the on measurement of zeta potential in each pH solution.

EXPERIMENTAL

As host materials, natural graphite with grain size of 100 μm (SN-100, SEC Carbon, Ltd.) and 3 μm (SNO-3 SEC Carbon, Ltd.) were used. The XRD parameters of these materials are shown in **Table 1**. Stage-1 K-THF-GICs were synthesized from two above mentioned graphite powders via a solution method under an Ar atmosphere[1, 2]. The obtained K-THF-GICs were filtrated with THF ($40 \times 10^{-3} \text{ dm}^3$). Subsequently, the exfoliation process was conducted using different polar protic solvents (H_2SO_4 aq, deionized water and NH_4OH aq) followed by sonication (43 kHz, 148 - 170 W) for 5 min. The K-THF-GICs suspension was obtained by removing the precipitation from the supernatant solvent completely.

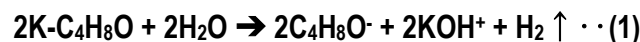
Zeta potential measurements were conducted several times using the diluted K-THF-GICs dispersions. The average values were reported as the zeta potential of the dispersions.

Table1 :XRD parameters of used host carbon.

Host carbon	d_{002} / nm	$L_{c(002)} / \text{nm}$	$L_{c(004)} / \text{nm}$	$L_{a(110)} / \text{nm}$
SN-100	0.3353	271	295	921
SNO-3	0.3356	110	163	476

RESULTS AND DISCUSSION

The structure of the stage-1 K-THF-GICs formed using both starting materials was confirmed by XRD. A large amount of hydrogen gas was generated by the decomposition using alcohol and deionized water through following equation (1).



Equation (1) generates KOH, a strong base which may remove the K present in the interlayers of the GICs. The generated KOH shows strong basic properties and it has the possibility of neutralizing the reaction by inducing

the oxidation of graphite on addition of a strong acid solvent. Few-layered graphene was subsequently prepared in the K-THF-GICs dispersion via equation (1).

For Zeta potential measurements of K-THF-GICs dispersions, the zeta potential on the surface of exfoliated products show a negative minus value without the addition of strong acid solvent into the GICs. The graphite starting material with the small grain size resulted in high dispersibility compared to the graphite with large grain size.

Few-layered graphene was obtained from both the host graphite starting materials in both acidic and basic solvents. The selected-area electron diffraction pattern (SAED) of the product formed in basic solvent indicates that the oxidation of graphite may not occur in a basic solvent. On the other hand, graphene was oxidized in an acid solvent.

The aforementioned result is explained in **Figure 1**. In basic solvent, the exfoliated product might electrostatically resist in a basic solutions including a lots hydroxide ions show negative charge. Thus, its dispersibility may improve in a basic solvent. The addition of basic solvents into the GICs may not induce an intense neutralization reaction between the acidic solvent and KOH produced by equation (1).

In summary, the addition of basic solvents in the exfoliation of K-THF-GICs can prevent graphene oxidation and improve dispersibility.

References

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- [2] M. Inagaki and O. Tanaike, Synth. Met., 73 (1995) 77-81

Figure

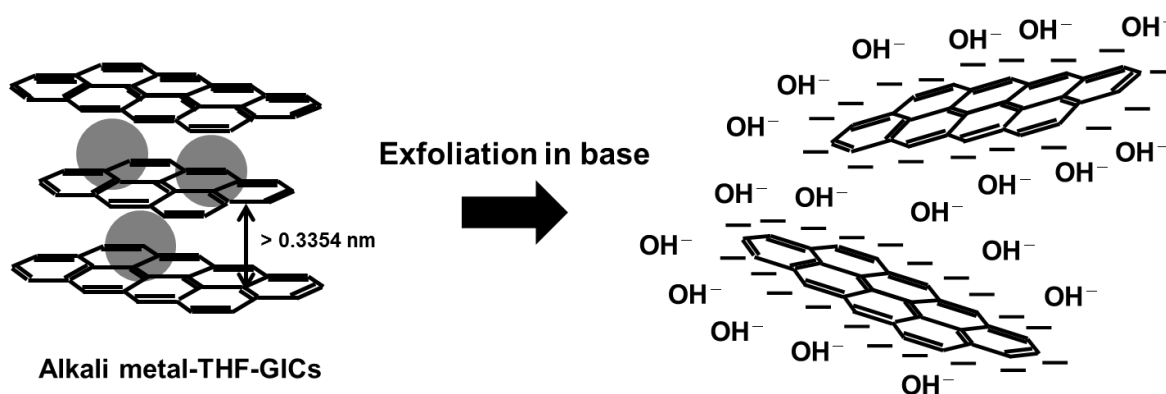


Figure 1: The exfoliation process of stage-1 K-THF-GICs in basic.