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Selective deposition of monolayer graphene oxide (GO) on hexagonal boron nitride (h-BN) and restoration of GO using catalytic properties of h-BN

Graphene shows a variety kind of intriguing properties and has been expected as a new material for future electronics. The properties of graphene are strongly affected by the substrate, especially, hexagonal boron nitride (h-BN) was found to be an optimal substrate[1]. Graphene on h-BN shows ultra-high mobility because of the absence of charged impurities at the interface[2]. Therefore, graphene on h-BN is a potential candidate as a good platform for both basic research and industrial application, and a high-throughput synthesis method for this structure is strongly required. Currently, the exfoliation method is used to fabricate this structure; although this method makes it possible to yield high quality samples, the productivity is quite low. A new facile preparation method should be developed. From the viewpoint of the productivity, Graphene oxide (GO) has been expected as a precursor of graphene for high throughput synthesis. A plenty of GO sheets can be deposited on various types of substrates controlling the thickness and coverage. Furthermore, the size and shape of GO sheets are also controllable. However, graphene made from GO has a serious drawback: unacceptable low crystallinity. Thermal annealing and treatment using chemical agents have been conducted to reduce GO for a long time. Although most of the functional groups of GO are eliminated after reduction, some of them and disordered area remain even after the strong reduction. This imperfection kept the properties of reduced GO (rGO) far from that of graphene. Under this circumstance, we have developed a new method that changes GO into high crystalline graphene using CH_4/ H_2 plasma and Cu catalyst [3,4]. This method yields quite high-quality graphene; mobility reached about 1000 cm2/Vs. This restoration and reduction of GO proceeds on any substrates. We applied this method to fabricate the structure of graphene/h-BN in this presentation.

At first, h-BN was deposited on SiO_2 (300 nm)/Si by the exfoliation method at 100 °C to obtain a large h-BN single crystal[5]. Then, we annealed the specimen at 400 °C in a vacuum to eliminate the contamination. Next, we deposited GO sheets using spin coating. GO was synthesized by modified Hummers method from graphite powder. To obtain a large GO, we skipped ultra-sonication process and synthesized large GO sheets of larger than 50 μm × 50 μm. GO was preferably deposited on h-BN instead of SiO_2. After that, we treated this specimen of thick GO sheets with ultrasonication in water for 10 seconds. This short ultrasonication process eliminated all GO sheets except monolayer GO sheets attaching h-BN (Fig. 1a). We succeeded in fabricating monolayer GO on h-BN with quite a high coverage. Then, we treated this specimen with the plasma: RF plasma power 10 W, total pressure 9.7-9.8 Pa, flow rate CH_4 35 sccm, H_2 35 sccm, temperature 500 °C, treatment time 1 hour. Fig. 1b, 1c shows the Raman spectra of GO on h-BN before/after treatment. Lowering I_D/I_G and increasing I_{2D}/I_D indicate high crystalline graphene growth. In the case of the treatment on SiO_2, Cu catalyst is indispensable to obtain high crystalline graphene. On the other hand, no catalyst is required in the case of the treatment on h-BN. This means that h-BN has some catalytic properties for the restoration of GO. We measured Raman mapping to elucidate the origin of the catalytic properties. Fig. 2 illustrates the mapping of I_D/I_G and I_{2D}/I_G. According to this mapping, all spots in GO indicated as A showed lower I_D/I_G than all spots in GO indicated as B. It implies that the orientation angle between GO and h-BN relates with the catalytic properties.

We succeeded in fabricating graphene/h-BN structure with the facile method using the plasma treatment. This method enables us to apply this structure to industrial applications.

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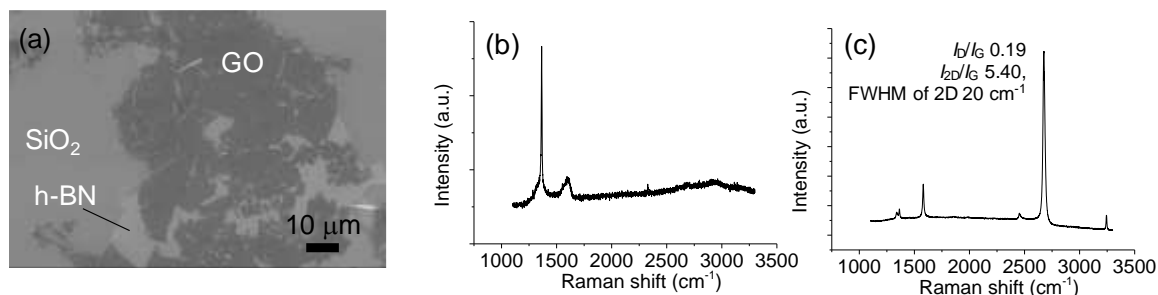
Figures

Figure 1: (a) SEM images of GO/h-BN/SiO$_2$ after ultrasonication. Raman spectra of GO (b) before and (c) after the plasma treatment.
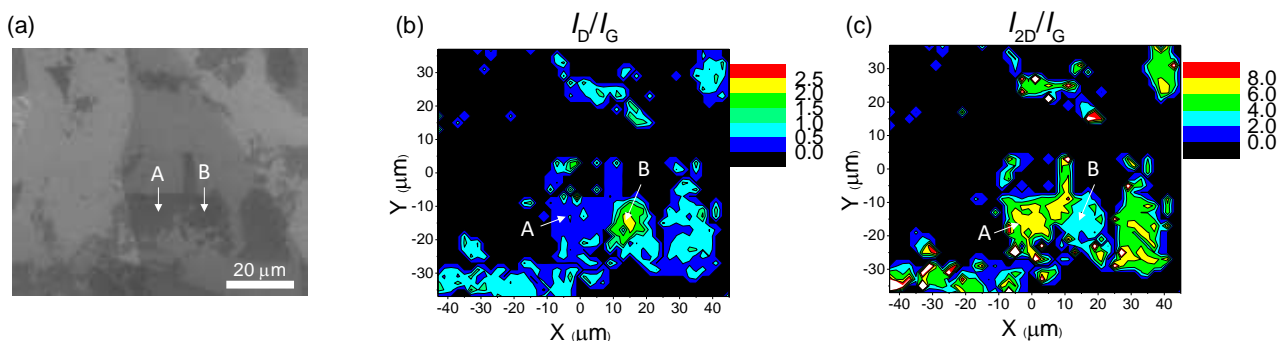

Figure 2: (a) SEM images of GO/h-BN/SiO$_2$ for the Raman mapping. A and B indicate GO single sheets. Raman mapping of (b) I$_D$/I$_G$ and (c) I$_{2D}$/I$_G$.