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Transmission Electron Microscopy of Gas-Supersaturated Water Encapsulated in Graphene Liquid Cells

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Dissolution of gas molecules (such as N_2 and O_2) in water is an important and fundamental phenomenon. Since gas molecules may remain in a supersaturated state in water without forming gas bubbles, one wonder whether gas molecules aggregate into clusters or form any microscopic structure under supersaturation conditions. To answer this question, it is essential to have a method to observe the structures of dissolved gas in water with a spatial resolution of several nanometers down to atomic level. In recent years, transmission electron microscopy (TEM) of graphene liquid cells allows observation of liquid encapsulated between graphene layers with sub-nanometer resolution [1,2]. Thus we encapsulated gas-supersaturated water between two laminated graphene layers suspended over holes of TEM grids.

In preparation of gas-supersaturated water, a glass bottle containing deionized water (resistivity of 18.2 MΩ·cm) was placed in a pressure tank (TNKB1-3; Misumi). The tank was first pumped to ~0.1 atm for about 1 hr and then pressurized to 3-4 atm with high-purity (99.999%) of gas. Six gases, including N_2, O_2, Ar, Xe, CO_2, SF_6, were used. The water was stored in the pressurized tank for about two days and opened right before preparation of graphene liquid cells. To prepare the graphene liquid cells, two graphene-covered copper TEM grids were first heated to 180°C to remove moisture and contaminants on graphene. The loading of water into graphene liquid cells followed a procedure reported in Ref. [2]. All graphene liquid cell samples were imaged using a field-emission type TEM (JEM-2100F) with an acceleration voltage of 100 kV. All experiments were carried out at room temperature.

Fig. 1 shows TEM images of polycrystalline nitrogen nano-precipitates in a graphene liquid cell. The precipitates had a lateral size of several to ~100 nanometers. The crystalline lattice structures varied over times probably due to electron irradiation or rotation of the precipitates. Coalescence of neighboring precipitates into a larger precipitate was also observed. We also acquired electron energy loss spectra (EELS). Spectra around nitrogen k-edge (~400 eV) were obtained on some large precipitates and spectra around oxygen K-edge (~540 eV) were obtained throughout the entire liquid pockets, indicating that water containing nitrogen was encapsulated in the graphene liquid cell. The observation of polycrystalline nano-precipitates with dark contrast indicates that nitrogen molecules can form a condensed phase in the graphene liquid cell. This is surprising because nitrogen molecules are typically in the vapor phase under ambient conditions. Formation of a condensed phase of nanometer scale for nitrogen molecules (and other gas molecules) in water was proposed in previous studies [3,4]. The current observation confirms such a picture, but the observation of polycrystalline structure has never been proposed or predicted previously.

We also observed another interesting phase in other water pockets (Fig. 2). A high density of tiny void-like structures was observed at underfocus (Fig. 2a), but the contrast changed under different focusing conditions (Fig. 2b,c). We have seen such a phase for water supersaturated with other gases (O_2, Ar, Xe, CO_2, or SF_6). They all showed contrast reversal when the imaging condition was switched between underfocus and overfocus. The spacing between the void-like structures was typically several

nanometers. The detailed patterns of this type of structures changed rapidly when imaged under high electron dose rates. The liquid in the water pockets might even drain out when imaged at very high magnifications for a few minutes.

The above two types of structures were not observed when fresh deionized water (without gas treatment) was encapsulated in graphene liquid cells. In addition, these two types of structures were not present in the same water pockets, suggesting that they belong to different states for gas-supersaturated water in graphene liquid cells. Further study is needed to understand whether these states are also present in bulk water or they might be present only when the water is confined in graphene liquid cells.

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[5] The authors acknowledge funding from the Ministry of Science and Technology of Taiwan, and Academia Sinica.

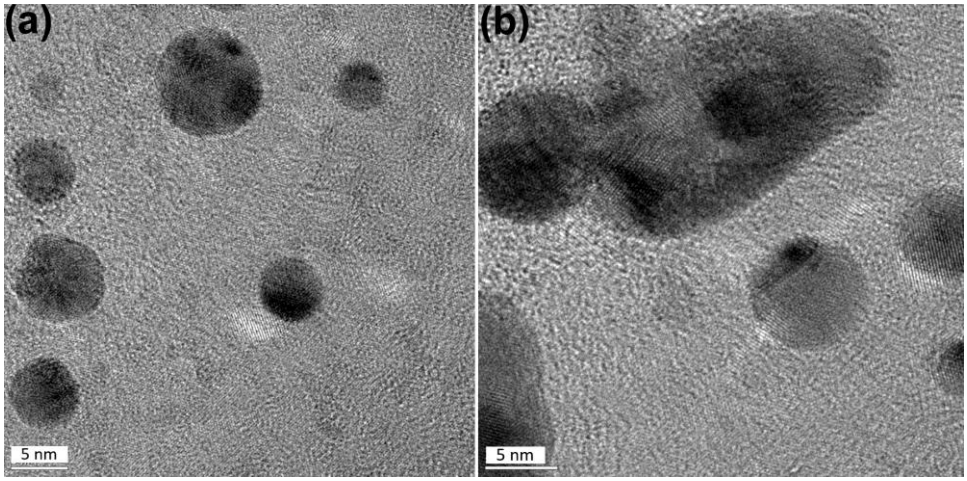

Figure 1. TEM image of N_2-supersaturated water encapsulated in a graphene liquid cell.

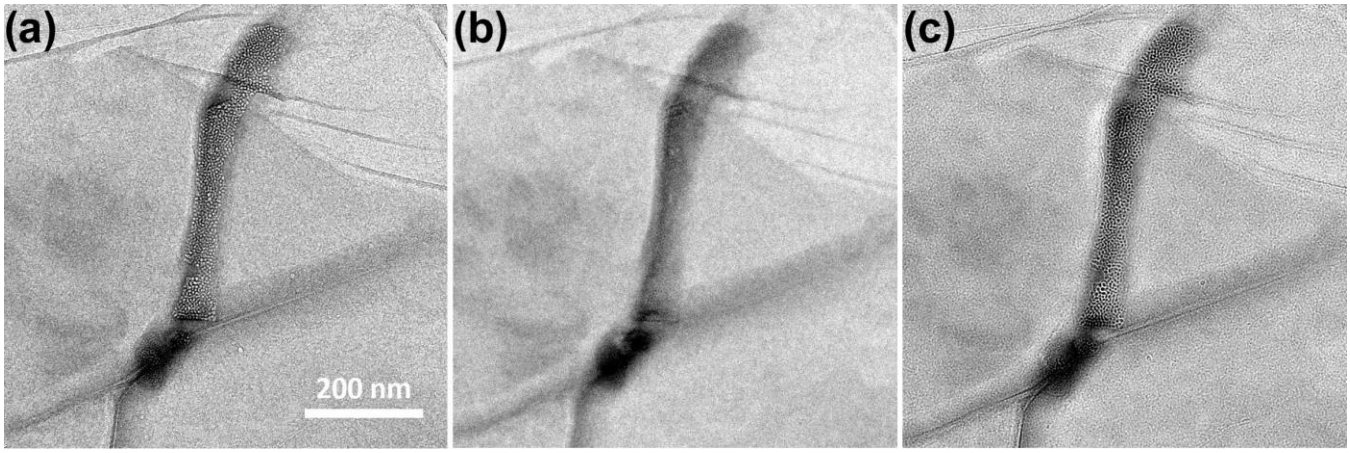

Figure 2. Images of another state for N_2-supersaturated water encapsulated in a graphene liquid cell acquired with various focusing conditions. (a) Underfocus -1400 nm. (b) On focus. (c) Overfocus 2500 nm.

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