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Efficient preparation of graphene liquid cell utilizing direct transfer with large-area well-stitched graphene

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ABSTRACT

By utilizing graphene-sandwiched structures recently developed in this laboratory, we are able to visualize small droplets of liquids in nanometer scale. We have found that small water droplets as small as several tens of nanometers sandwiched by two single-layer graphene are frequently observed by TEM. Due to the electron beam irradiation during the TEM observation, these sandwiched droplets are frequently moving from one place to another and are subjected to create small bubbles inside. The synthesis of a large area single-domain graphene of high-quality is essential to prepare the graphene sandwiched cell which safely encapsulates the droplets in nanometer size.

1. Introduction

Electron microscope observation of solution and solution-based processes is one of the important issues in nanometer-scale science. For example, the direct structural observation of biomolecules, such as proteins, in water provides crucial information to understand how the protein works in living systems [1–4] and how physical changes occur in solution such as dissolution, precipitation and dispersion [5–7]. Until now, great research efforts have been devoted to elucidate the microscopic structure and dynamics of solution, in which various spectroscopic techniques have been widely employed to obtain information on various phenomena in solutions [8–11].

Observation of solutions using transmission electron microscopy (TEM) can, in principle, provides direct information on microstructure of solution at atomic level [12–18]. Recent advancement on TEM has enabled us to observe structure of matters with spatial and time resolution down to 0.05 nm and 1 ms, respectively [19,20]. In addition, development of low-acceleration voltage technique has greatly expanded versatility of TEM, enabling us to observe bio-organic fragile materials at atomic resolution [21]. High-resolution TEM simultaneously gives us information on electronic structure and bonding state [22]. If TEM can equally be applied to observe solution, it must be one of the most powerful characterization techniques to provide direct and high-resolution structural information on solution.

TEM observation of solutions have achieved by using environmental cell [23,24]. Recently we demonstrate graphene liquid cells: liquids sandwiched by two single-layer graphene sheets for visualization of metal particles in solution with atomic resolution [16,17,25]. Graphene is the one-atom-thick carbon sheet, and due to the thinnest structure composed of a light element, graphene is almost transparent to electron beam [26,27]. In addition, graphene is a mechanically and chemically stable conductor [28–30], and high-contrast and stable TEM observation can be done using graphene as a sample support [31–33]. In addition, even a single-layer graphene has the perfect impermeability, and if various solutions can be sandwiched between two graphene layers, the solution can be supported stably even under an UHV condition, which provides TEM observations of microstructure of solutions [17,34].

There are, however, some unsavory points corresponding to reproducibility and yield of graphene liquid cells because of vulnerability of low-crystalline graphene sheets. It is important to utilize high-quality graphene to ease the fabrication of the graphene liquid cells as well as of graphene nano-ribbons [34–36].

Here, we have development a simple technique for preparation of the graphene liquid cell by utilizing direct transfer process with large-area and high-quality graphene grown on copper. The large area high-quality graphene was based on the chemical vapor deposition (CVD) on copper foils, which has been developed by

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Ruoff and coworkers [37,38]. The pretreatment of copper foils with atmospheric pressure of pure hydrogen gas provides well-stitched and large-area graphene within a relatively short reaction time. By using such a well-stitched graphene and direct transfer process, we are able to prepare the graphene liquid cell in high yield.

2. Materials and methods

We used copper foils as substrates for graphene growth. A copper foil (nilaco, 99.9%, 10 × 100 × 0.02 mm) was placed in a quartz tube and annealed at 1323 K under 500 sccm flow of 100% hydrogen for 50 min [37,39,40]. After the pre-anneal treatment, copper (111) surface preferentially appears. Graphene growth was then performed under 250 sccm flow of $Ar/H_2/CH_4$ (Ar: 97%, H_2: 3%, CH_4: 0.0002%) at the same temperature. The typical growth time of a mm size graphene is ca. 16 hours.

Graphene grown on a copper foil was transferred onto a TEM grid (SiN membrane film with 2 μm pore) using the direct transfer method. To remove copper substrates, a copper foil with a continuous film of graphene grown on the surface was placed on aqueous solution of ammonium peroxodisulfate (1 mol/L) for 12 h (see supplementary information). This process can remove the copper foil almost completely, leading to the graphene film floating on the etching solution, the graphene film was picked up by a SiN TEM grid, and the picked-up graphene was then carefully placed onto aqueous solution of hydrochloric acid to remove copper residues. Before fabrication of a graphene liquid cell, the so-washed graphene on the TEM grid was further cleaned with hydrogen plasma treatment [31,41].

The TEM observation was made with either a field-emission type JEM-2100F or JEM-2010 with an acceleration voltage of 80 kV. Typical exposure time and current density were 0.3 s and 96 A/cm^2, respectively.

3. Results and discussion

Our strategy to prepare the graphene liquid cell is a simple and direct preparation of a sandwiched structure using a high-quality large-area CVD-grown graphene. Figure 1 shows the preparation scheme of the graphene liquid cell. First, a CVD-grown graphene is transferred onto a SiN membrane grid with 2 μm holes penetrating through the membrane. Second, using a mist generator, various solutions are then sprayed onto another graphene specimen floating on etching solution. Third, to form a graphene sandwiched liquid cell, the deposited micro-size droplets of solutions are covered by the originally-transferred graphene on TEM grid. In the preparation of the graphene liquid cell, incorporation of large-area and seamless graphene layers is essential to realize successful encapsulation of solutions. To achieve high-yield preparation of the graphene liquid cell, we have developed a growth technique for high-quality large-area graphene.

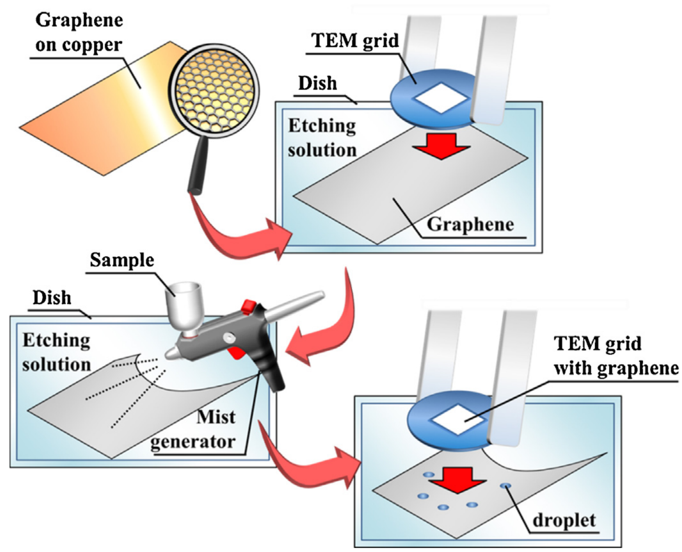

Figure 1. Preparation scheme of the graphene sandwiched structure. Graphene on the solution can be observed by careful irradiation of proper fluorescent light.

Graphene has been synthesized with chemical vapor deposition (CVD) using methane and a cupper foil as the carbon source and the substrate, respectively. The CVD growth of graphene is strongly influenced by the substrate, and (111) plane of cupper has been known as the suitable surface to grow high-quality graphene [42,43]. To prepare the (111) plane, we have utilized high-temperature pretreatment of cupper foil under pure H_2 flow. After the pretreatment, almost all surfaces of the cupper foil have turned into to form (111) plane and grain boundaries in cupper foil have

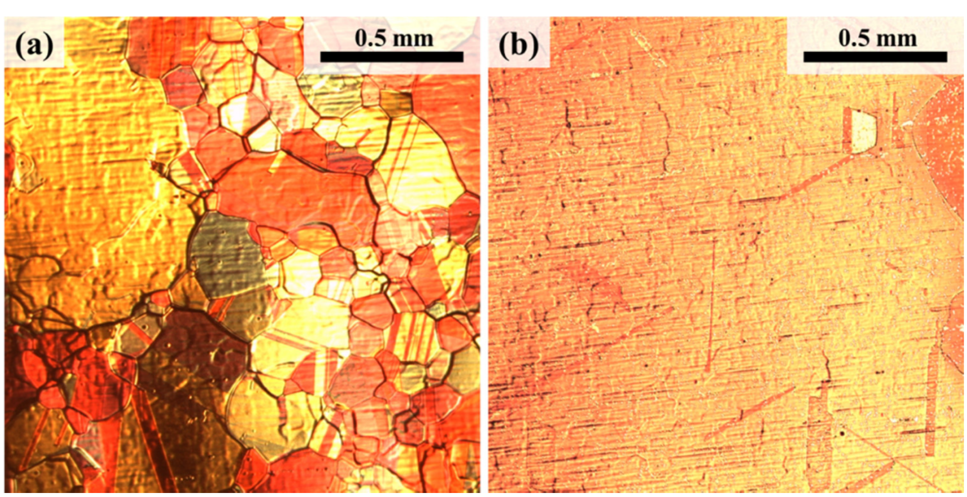

Figure 2. Optical images of copper surface after pretreatment with Ar/H_2 (a) and pure H_2 at high temperatures (b). Both copper surfaces were oxidized by annealing at approximately 500 K to visualize the copper domains and surface orientation via the color variations. Pretreatment for one hour with Ar/H_2 and H_2 at 1327 K results in two quite different surfaces of the copper substrate, as can be seen in (a) and (b): the Ar/H_2 annealed surface has colorful and small copper domains, whereas the pure H_2 annealed surface is simply a flat surface. Because the domain boundaries of the copper surfaces act as nucleation sites for graphene, we never obtain boundary-less graphene sheets for preparing the graphene liquid cells.