A Route toward Digital Manipulation of Water Nanodroplets on Surfaces

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ABSTRACT Manipulation of an isolated water nanodroplet (WN) on certain surfaces is important to various nanofluidic applications but challenging. Here we present a digital nanofluidic system based on a graphene/water/mica sandwich structure. In this architecture, graphene provides a flexible protection layer to isolate WNs from the outside environment, and a monolayer ice-like layer formed on the mica surface acts as a lubricant layer to allow these trapped WNs to move on it freely. In combination with scanning probe microscope techniques, we are able to move, merge, and separate individual water nanodroplets in a controlled manner. The smallest manipulatable water nanodroplet has a volume down to yoctoliter (10⁻²⁴ L) scale.

KEYWORDS: nanofluidic manipulation · atomic force microscope · graphene cover · ice-like layer · molecular dynamics simulation

Manipulation of water at the nanoscale has recently been of great interest in both theoretical and experimental investigations.¹⁻⁶ Much success has been achieved so far through confinement of water in self-assembled nancontainers,⁴⁻⁷,⁸ nanopores, or nanochannels⁵,⁹⁻¹² with a typical volume of an attoliter (10⁻¹⁸ L) or above. In principle, handling individual nanoscale water on certain surfaces, a digital nanofluidic process, could provide more manipulation freedom but face serious difficulties associated with its surface and interface,³,¹³ which must be tailored properly. In this study, we show a new route toward manipulation of individual water nanodroplets (WNs) on a mica surface. These WNs are covered by graphene to avoid direct exposure to the environment. Between the WNs and mica surface, there is a lubricant ice-like buffer layer, which allows these WNs to move freely on it under external forces. In combination with scanning probe manipulation techniques, various processes of merging, separating, and patterning of WNs on the mica surface have been achieved under ambient conditions. The volume of the smallest manipulatable WN in our system is around yoctoliter scale, which is a more than 5 orders of magnitude improvement over the existing micro/nanofluidic manipulation limits.⁴⁻⁶,¹¹,¹²

RESULTS AND DISCUSSION

Samples were prepared by deposition of mechanically cleaved graphene on muscovite mica in a moist atmosphere, a procedure developed previously for trapping water between a mica surface and graphene.¹⁴,¹⁵ Graphite for cleavage is highly oriented pyrolytic graphite (grade ZYA from Materials Quartz, Inc.). Samples were prepared in a glovebox with a relative humidity (RH) of ~80%, but it was not necessary; lower RH also works well. Figure 1a shows an atomic force microscope (AFM) image of a typical sample with several trapped WNs and an ice-like water layer coexisting around them. The height profiles of a nanodroplet and the ice-like layer along the line-cut indicated by the red and blue lines in Figure 1a are shown below, respectively. We can see that the WN has a spherical-cap shape with a basal diameter (D) of ~330 nm and net height (H) of ~7.4 nm, and the 0.4 nm thickness of the ice-like layer is consistent with the monolayer nature of ice.¹⁴,¹⁶,¹⁷ D and H of many WNs covered

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with different layers of graphene were measured and plotted in Figure 1b. For WNs covered by the same layer number of graphene, $D/H$ shows a linear relationship, while WNs with the same $D$ have a decreased $H$ if covered by a thicker graphene layer, which is attributed to the higher in-plane tension of the thicker graphene (Figure 1c). We also calculated the contact angle ($\theta_C$) as a function of $D$ (Figure 1d; see more discussions in the Supporting Information). We can see that the $\theta_C/D$ shows an opposite trend as compared with the case for normal micro/macroscale water droplets.13,18 In our samples, most $\theta_C$ values were distributed in the range 6$^\circ$–18$^\circ$, in contrast to $\sim$22.7$^\circ$ for a WN on mica without graphene covering.19 Note that the $\theta_C$ of WNs confined between graphene and hydrophobic substrates is 5$^\circ$–12$^\circ$ in previous studies,18 which is consistent with our results. This similarity indicates that $\theta_C$ of these trapped WNs should be dominated by the constraint of graphene, rather than the contact line tension.20 More details on the elastic modulus of the WNs are provided in the Supporting Information (Figures S2, S3).

These WNs along with the surrounding ice-like layer trapped under graphene are very stable; no visible changes were observed during a two-month monitoring period when putting such samples in ambient conditions. In this sandwich structure, the covered graphene, an atomically thin material, is flexible, robust, and hydrophobic, allowing the probing and manipulation of the underneath WNs directly. Figure 2a illustrates a process of moving the trapped WNs under graphene when we applied a sufficient external force by an AFM tip. Due to this AFM-based manipulation technique (see more details in Methods), we can pattern randomly distributed WNs into regular arrays (Figure 2b,c), merge two or more isolated WNs into a single one (Figure 2d,e), and separate one WN into two or more WNs (Figure 2f). The blue dashed arrows marked in Figure 2b show the routes of the tip during the manipulation process. Throughout the whole process, we had not observed any damage to the graphene, ice-like layer, or mica surface, revealing the robust nature of this structure. It is also worth mentioning that the nanodroplet can follow the designed route well at a tip speed of $<100$ nm/s, while pulling off of a small WN would occur if the tip speed is $>\sim500$ nm/s. Figure 2f shows the isolation of an ultrasmall WN (in the blue dotted circle) from a large one. This separated WN has a $D = \sim45$ nm and $H = \sim1.7$ nm, equivalent with a volume of $\sim1.2$ yoctoliter ($10^{-24}$ L).4,21 Such a small amount of volume of liquid cannot be produced or even approached by previous systems in which a typical manipulatable volume is around a femtoliter ($10^{-18}$ L).4,21 The isolated WNs in our system could be transported freely to anywhere within a two-dimensional channel enclosed by monolayer ice and graphene, suggesting an advanced nanofluidic process as compared with extensively employed nanofluidic systems based on

Figure 1. Topography of the WNs. (a) AFM image of some WNs trapped between few-layer graphene and mica. The area marked with 0L means graphene contacts with bare mica, and 1L stands for one ice-like layer existing between them. Bottom diagrams give the height profile along the red line and blue line, respectively. (b) Sketch map showing the sandwich structure and the geometry relation of $H$, $D$, and $\theta_C$. (c) $D/H$ relationship measured from more than 50 WNs covered by monolayer (black), bilayer (red), and (green) graphene and (d) their corresponding contact angles as a function of diameter.
nanopores/nanochannels.5,9 This new nanofluidic platform is digital, i.e., dealing with individual WNs.

Control experiments were also carried out to understand the mechanism of the dynamic process of WNs during operation. As shown above, all manipulations for trapped WNs were performed with the ice-like buffer layer around them. In control experiments, we tried to move the WNs without the surrounding ice-like layer (Figure 3a) and found that the WN could not be moved no matter how large the tip indentation force ($f_{\text{tip}}$; see more details in Methods) (Figure 3b). Moreover, we also pushed a WN out of an ice-like layer’s edge (Figure 3c) and found that the WN would be stuck at the edge (Figure 3d). During the moving of the WNs along a certain trace on the ice-like layer, continuous exfoliation of graphene/ice and intercalation of WNs would occur. These control experiments indicate that the WNs intercalating between graphene and the bare mica surface is not favorable, which is attributed to higher interaction of graphene/mica than that of graphene/ice.

We also performed molecular dynamics (MD) simulations on water confined between mica and graphene to elucidate the mobility of WNs, which was related to the surface and interface in this system. The CLAYFF force field and Lennard-Jones (LJ) potential were employed in our simulations (see more details in Methods). With excess water confined between mica and graphene with a separation distance of $d_0 = 10$ Å, a dynamically stable WN and a surrounding ice-like layer could be formed (Figure 4a). This ordered monolayer of water molecules has strong binding to the mica surface by forming hydrogen bonds with oxygen atoms on the mica surface. However, this ice-like layer is rough due to the existence of K$^+$ ions on the mica surface, making it difficult to form hydrogen bonds with the above WNs (Figure 4a,b). A huge difference was found for the calculated interaction energies between WN/ice ($\sim 4.26$ kJ/mol) and mica/ice ($\sim 34.3$ kJ/mol). Thus, this ice-like layer acts as a lubricant layer, which allows the WNs to move on it. In addition, the graphene is also hydrophobic and slippery for WNs.25,26 As a result, both the upper and lower interfaces of the trapped WNs make the nanofluidic process feasible. We further simulated water molecules confined within a mica surface with/without K$^+$ ions and a buckled graphene (Figure 4c) and found similar results. As the buckled graphene was moved toward the mica surface, water molecules could move into the bump of graphene, where the separation between mica and graphene was larger.
In our simulations, the monolayer ice next to mica is very stable (Figure 4). It was noted that stable bilayer and trilayer ice-like structures were reported by previous studies. Therefore, the stability of the second water layer is possibly related to the local confinement between graphene and mica. In order to confirm this, we carried out contact mode AFM imaging of which the tip was large enough to cause significant deformation of the water molecules. In Figure 5, we present a series of images of WNs with varying tip indentation forces. Interestingly, a halo of aqueous layer with a thickness of ~0.7 nm (corresponding to room temperature (see Supporting Information). The result presents an ice-like layer nearly without free OH bonding. The first tetrahedral structure (Si–Al) of mica is shown in gray triangular polyhedra with black circles representing O atoms, and graphene is shown on the top. The top view of the ice-like layer (under the blue dashed line in a) is shown in (b). (c, d) Top and side view of water molecules confined within mica and buckled graphene after a 10 ns equilibration run; for simplification, mica is not shown. There are more water molecules at the bump of graphene.

CONCLUSION

In conclusion, water nanodroplets trapped between the mica surface and graphene are demonstrated to be a new platform for digital nanofluidics. With the assistance of a graphene protection layer and ice-like lubricant monolayer, these water nanodroplets can be moved, merged, separated, and patterned into regular arrays freely within a two-dimensional channel. The smallest manipulatable WN has volume around 1 yoctoliter. We also employed MD simulations on the structure of this sandwiched platform to understand the interaction at the water/ice interface and the mechanism of manipulation. This new route toward digital manipulation of water nanodroplets on a surface may be applicable in various fields including biology, chemical synthesis, and "lab-on-a-chip" technology.

METHODS

Estimation of AFM-Tip Indentation Force ($f_{tip}$). In contact mode characterization, $f_{tip}$ could be controlled by adjusting the set point ($V_{set}$) in the contact mode scanning, which is a voltage signal representing the deflection of the tip. $V_{set}$ is the value inputted before tip engaging, which is ~0.5 V in our experiment.
The $f_{tip}$ can be calculated as $f_{tip} = (V_{tip} - V_{sample})SK_{tip}$ where $S$ and $K_{tip}$ are the sensitivity and spring constant of the tip, respectively. The tip for the experiments presented in Figure 2 is an ESP tip (Bruker Inc. USA) with a spring constant of 0.5 N/m and sensitivity of 0.25 N/m and sensitivity of 0.5 N/m. As an example, for the picture shown in Figure 3a, the $V_{sample}$ is 0 V; thus we estimate the $f_{tip} = (0 - 0.5 V) \times 160 \text{nm/V} \times 0.25 \text{ N/m} = 20 \text{ N}$. The set points for Figure 2b–f are 0.5, 1.5, 2.5, 3.5, and 5.5 V, respectively.

**AFM-Based Manipulation.** All manipulations were performed by applying the nanolithography function of the Multimode III AFM. Tips for tapping mode were used during manipulation, as they are mechanically harsher than other kinds of tips. The script files of Nanoscope software were coded in C++ language. In this script, we could set the parameters such as the depth we pressed the tip into the sample, $X$–$Y$ translation distance, and speed of the tip during manipulation. Notice that both the capturing and nanolithography steps were carried out under tapping mode using TESP tips (Bruker Inc. USA). Morphology AFM images were first captured to locate the WN ready for operation. Second the AFM tip was moved to the center of this WN and pushed down a little bit by a few nanometers; then it was moved horizontally along the preset trace. Note that the feedback should be turned off during manipulation.

**MD Simulation.** Water molecules confined between mica and graphene were simulated. The monocristalline muscovite mica $\text{KAl}_2(\text{SiAl})_2\text{O}_2(\text{OH})_2$ with a $6 \times 6$ unit cell in the $(X-Y)$ dimension and a double aluminosilicate layers in the $Z$-dimension was used in our simulations. The supercell of mica is compressed by 6% to match the $(12 \times 12 \times 3)$ supercell of graphene, where $a$ is the lattice constant of graphene. The final supercell is 29.508 Å × 51.109 Å in the $X$- and $Y$-dimensions, respectively. The $Z$-dimension of the supercell is set to 200 Å, to guarantee a separation between graphene and the image of mica of no less than 150 Å. The MD simulations were carried out using the LAMMPS software package$^{22}$ with the NVT ensemble. In our MD simulations, we used the CLAYFF force field$^{23}$ to characterize the interatomic interactions within mica layers as well as interactions between mica and water. The SPC model$^{32}$ was used for water molecules to match the CLAYFF force field. The SHAKE algorithm is applied to keep water molecules rigid. The interaction between water and graphene is described by the 12–6 Lennard-Jones (LJ) potential.$^{28}$ The contact angle on graphene is about 92°, which is close to the previous results using first-principle simulations.$^{29,30}$ The cutoff distance is 10 Å for LJ potentials and 9 Å for Coulombic potential, respectively. Since the melting temperature of the SPC water model is 191 K,$^{31}$ we simulated water confined within mica and graphene at $T = 200$ K, which corresponds to room temperature in the real case.

**Conflict of Interest:** The authors declare no competing financial interest.

**Supporting Information Available:** The elastic modulus of the WNs in peak force mode and its dependence on WNs’ size; cross section of a water drop in contact mode with different set points. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES AND NOTES**


