ABSTRACT: The detonation nanodiamonds form the aggregate having interparticle voids, giving a marked hygroscopic property. As the relationship between pore structure and water adsorption of aggregated nanodiamonds is not well understood yet, adsorption isotherms of N2 at 77 K and of water vapor at 298 K of the well-characterized aggregated nanodiamonds were measured. HR-TEM and X-ray diffraction showed that the nanodiamonds were highly crystalline and their average crystallite size was 4.5 nm. The presence of the graphitic layers on the nanodiamond particle surface was confirmed by the EELS examination. The pore size distribution analysis showed that nanodiamonds had a few ultramicropores with predominant mesopores of 4.5 nm in average size. The water vapor adsorption isotherm of IUPAC Type V indicates the hydrophobicity of the nanodiamond aggregates, with the presence of hydrophilic sites. Then the hygroscopic nature of nanodiamonds should be associated with the surface functionalities of the graphitic shell and the ultramicropores on the mesopore walls.

INTRODUCTION
Diamond nanoparticle (nanodiamond) s were first discovered in the 1960s as a product of detonation processes.1,2 Nanodiamonds are also found in nature as part of protoplanetary disks of certain types of stars.3,4 Nowadays, nanodiamonds are produced by several routes such as plasma-assisted chemical vapor deposition (CVD),5 autoclave synthesis from supercritical fluids,6 electron irradiation of carbon "onions",7 ion irradiation of graphite,8 chlorination of carbides,9 ultrasound cavitation,10 laser ablation,11 and high-energy ball milling of high-pressure and high-temperature (HPHT) diamond crystals.12 The most popular nanodiamonds are the ones prepared by the detonation method.1 This is because of the multistep oxidation-purification procedure, which has been actively studied for detonation soots consisting of diamond particles (up to wt. 75%), other carbon allotropes, metal impurities, and oxides.13–15 Osawa et al. succeeded to obtain highly pure detonation nanodiamonds.13

Although the properties of nanodiamonds depend on the production method, precursors, and applied conditions, nanodiamonds can be generally described as polyhedral particles of sp³ hybridized carbon atoms, which can be obtained as colloidal individual particles as small as 4−5 nm in diameter.1,2,13 Such materials have chemically active surfaces, while its core remains inert. Nanodiamonds present a unique
surface structure coming from the mixture of diamond-like sp³ and graphitic sp² carbon atoms. The graphitic or amorphous carbon layers, consisting of sp² hybridized carbon, wrap the surface of each nanodiamond particle. Nano-diamond particles tend to aggregate at the nanometer scale of 50–500 nm due to their high surface energy. The aggregates have intergranular gaps, which accounts mainly for mesoporosity. Moreover, exceptional properties of nanodiamonds are reported as mechanical and optical properties, fluorescence, high thermal conductivity and electrical resistivity, chemical stability, and resistance to harsh environments and biocompatibility. In addition, water adsorption on the surfaces of diamonds and detonation nanodiamonds induces negative electron affinity and giant electric permittivity, respectively. Nanodiamonds are expected to be mechanical enhancers and highly sensitive photodetectors. Furthermore, nanodiamonds are described as the most biocompatible materials among all the carbon-based materials because of their low toxicity, and thereby, the nanodiamonds are excellent candidates in biochemical and medical fields.

Wettability well defines the hydrophilic (or hydrophobic) character of a material. The water wettability is described by contact angle for liquid water. The air–water contact angles of polished diamond faces of a single crystal are 75.9° (for the diamond face [111]) and 71.0° (for the diamond face [110]). Therefore, the surfaces of the diamond are not hydrophilic, but rather hydrophobic. Although the wettability of nanodiamonds has not been fully explored, the water contact angle of a nanodiamond film was 73 ± 3° in air at room temperature. Besides, low water affinity of nanodiamond powders is reported. The contact angles of nanodiamonds synthesized by chemical vapor deposition are 32° after oxidation and 93° after reduction. Nanodiamond surfaces without oxidation treatment are also hydrophobic. However, no reports were found on the contact angle of detonation nanodiamonds due to difficult measurements through the hygroscopic nature. Accordingly, water adsorption studies were carried out to evaluate the affinity of the detonation nanodiamonds for water, giving no clear understanding yet. For example, powder of detonation nanodiamonds containing a small amount of large mesopores (>15 nm) was able to adsorb a small amount (<4%) of water from the air and ultradispersed diamond powder, without and with modification under air, adsorbed water being associated mainly to the surface chemical functionalities. However, none of these discussed the role of both porosity (micropores, mesopores) and presence of surface functionalities to describe the interaction of nanodiamonds with water. This study reports a new insight on the affinity of detonation nanodiamonds for water from the relationship between water adsorptivity and nanoporosity and surface functionalities.

### EXPERIMENTAL SECTION

**Materials and Methods.** Nanodiamond hard hydrogels obtained from Nano-Carbon Research Institute, Ltd., Japan (density of 2.2 × 10³ particles g⁻¹) were used after grinding and sieving using a 0.7 μm sieve without further purification.

**Characterization of Nanodiamonds.** The morphology of nanodiamonds was examined on powdered nanodiamonds by means of field-emission scanning electron microscopy (FE-SEM; JEOL, JSM-7000F). A high-resolution transmission electron microscope (HR-TEM) was used to observe the nanodiamond crystals. This measurement was carried out on fine powder samples collocated on a Cu grid by using a 2100F microscope (JEOL, Japan) operated at 200 kV. Electron energy loss spectroscopy (EELS) was carried out with a scanning transmission electron microscope (STEM) ARM200CF at 80 kV to describe the electronic structure of carbon present in the nanodiamond particles. X-ray diffraction pattern (XRD) of nanodiamonds was measured at room temperature using the X-ray diffractometer (SmartLab X-ray, Rigaku Co.) with Cu Kα (40 kV and 30 mA). The profiles of temperature-programmed desorption (TPD) of the as-received nanodiamonds were measured in the temperature range of 373 to 1273 K under He flow of 300 mL min⁻¹, with a heating rate of 10 K min⁻¹ using the TG-DTA-Photoionization Mass Spectrometer (Rigaku Co.). Nanodiamond samples were degassed at 393 K for 2 h under vacuum prior to the measurement. The pore structure of the nanodiamond powder sample was determined volumetrically by N₂ adsorption isotherm at 77 K using an apparatus Autosorb iQ; Quantachrome after preheating at 423 K and 10⁻⁴ Pa for 2 h. Quenched solid density functional theory (QSDFT) analysis was applied to determine the pore size distribution from the N₂ adsorption isotherm. Water vapor adsorption isotherm of nanodiamonds was measured at 298 K using a volumetric equipment Quantachrome-Hydrosorb after pretreating at 423 K and 2 mPa for 2 h.

### MODELING AND SIMULATION SECTION

**Modeling of Nanodiamond and Simulation of Water Adsorption Isotherm.** The 4 nm nanodiamond was generated using a novel heuristic three-step approach. In the first step, we generated a 4 nm carbon sphere by cutting a perfect diamond supercell using spherical coordinates. The cubic diamond supercell was built by replication of the unit cell in Mercury Visualization Package from the Cambridge Structural Database System. In the second step, we optimized the energy of carbon atoms inside a sphere using Monte Carlo (MC) quench simulations in NVT ensemble. A three-body environmental-dependent interatomic potential (EDIP) was used for computing carbon—carbon interactions. As previously, the temperature decreases linearly from 3000 K down to 30 K, with a step of 10 K. For each temperature, 1000 MC displacement steps were performed using the Metropolis algorithm. The displacement of carbon atoms was adjusted every 1000 MC steps to maintain the acceptance ratio of 0.4. In the final step, the energy of a quenched 4 nm nanodiamond was minimized in the general utility lattice program (GULP) implemented with EDIP potential. We use a constant volume optimization with conjugate gradients. The Grand Canonical Molecular Dynamics (GCMD) method proposed by Eslami and Müller-Plathe was applied to simulate a water isotherm. The GCMD algorithm by Eslami and Müller-Plathe is almost fully deterministic. The only stochastic term is the choice of the initial velocity of the scaling factor. The GCMD simulations of water adsorption were done with the self-made code; a TIP4P/2005 model was used for the description of water particles. Simulations were done with the use of typical parameters and procedures. Time step was set to 2 fs and the temperature to 298.2 K. The nanodiamond structure was kept rigid (no movement of structure atoms was considered). A RATTLE method was used to keep all bonds in the water molecules constrained. The total time of each simulation varied from a few up to more than 80 ns until no substantial change in the number of molecules was observed. Final adjusted parameters describing the behavior of the structure are listed in Table S1. The modeling of nanodiamond and simulation procedures will be published in another journal.
Figure 1. HR-TEM images of (a) aggregates of nanodiamond crystals and (b) nanodiamond twin crystal. The diamond crystal cores are wrapped with nondiamond carbon shell.

Figure 2. STEM-EELS mapping images of nanodiamonds at (a) 2 and (b) 5 nm distance to the edge.
RESULTS AND DISCUSSION

Detonation nanodiamonds used in this study are well depicted by TEM images shown in Figure 1; analysis of such images gives information on the particle size of nanodiamonds, as well as on the aggregation structure of crystalline particles. The TEM images in Figure 1 evidence aggregation of nanodiamond particles of an average particle diameter of 4.5 ± 0.7 nm (Figure S1); primary nanodiamond crystals are interconnected to each other, providing intergranular gaps of small mesopore and micropore dimensions. These nanodiamonds are highly crystalline, and even twins of an explicit facet structure are often observed, as shown in Figure 1b.

Additionally, the STEM mapping images on Figure 2 show that there are many structures surrounding the particles of nanodiamonds as a shell-like structure, as seen on Figure S2. The EELS spectrum of the shell structure region indicates clearly the presence of graphitic sp² carbon through the peak at 284 eV due to the π* states. The peak derived from sp³ orbital is confirmed on the surface layer, while the sp³ signal becomes stronger as moving to the core of the nanodiamond (mapping images at 2 and 5 nm, respectively). These EELS findings agree with previous observations of nanodiamonds surrounded by graphitic shells, typically found for nontreated detonation nanodiamond samples.26,43

The crystal structure of nanodiamonds was analyzed by means of XRD. As shown in the profile of Figure 3, [220] = 4.3 nm, and [311] = 4.6 nm).36 The crystallite sizes are close to the average particle size from HR-TEM observation, indicating that these nanodiamonds are highly crystalline.

Thermogravimetric analysis under He gas flow in Figure 4a shows the decomposition of nanodiamonds; about 3% of a weight loss is observed up to 523 K, which stems from the evolution of CO₂ and CO, as seen in Figure 4b, referring to the temperature-programmed desorption analysis. The evolved gases of m/z = 28 and 44 are assigned to CO and CO₂, respectively, which are derived from oxygen-containing carbon groups or amorphous carbon situated on the graphitic surface. Since carboxyl, carboxyl anhydrous, and lactone groups decompose as CO₂,47 the evolution of the CO₂ gas must indicate the presence of such functionalities on the nanodiamond shell. Evolution of water vapor is observed mainly up to 523 K; desorbed water should come from water strongly adsorbed in the narrow pore spaces in the nanodiamond aggregates, even after degassing at 393 K prior to the measurement.

The aggregated structure of nanodiamonds is clearly confirmed by SEM observations, as shown in Figure 5. The SEM image shows the aggregates of units of about 20 nm agreeing with the TEM image in Figure 1.

Nitrogen adsorption isotherm at 77 K gives an average information on the aggregated structure of nanodiamonds. Figure 6 shows the N₂ adsorption isotherm of powdered nanodiamonds and the pore size distribution derived from the adsorption isotherm.

The N₂ adsorption isotherm of nanodiamonds, is close to IUPAC Type IV, being indicative of mesoporous materials. A pronounced adsorption hysteresis from P/P₀ = 0.5–0.8 supports the presence of predominant mesopores.48,49 The N₂ adsorption isotherm in terms of the logarithm of relative pressure shows the presence of micropores in addition to mesopores, as seen in Figure 6b. The BET surface area is 300 m² g⁻¹. The pore size distribution is obtained using the QS-DFT method, assuming a slit-pore shape model, as it was stated to be the best-fit model for carbon onions found as aggregates of 4–6 nm in average primary particle diameter.30,51 Additionally, Figure S3 shows the high resolution αₛ plots of the N₂ adsorption isotherm. This αₛ plot presents an upward deviation of filling swing below αₛ = 0.5, indicating the presence of micropores and ultramicropores as part of the hierarchical porosity in the nanodiamond aggregates.52 Then, the slit-shaped pore model fits better for the porosity of nanodiamonds observed by TEM, as shown in Figure S4. The pore size distribution of nanodiamond aggregates is shown in Figure 6c. The nanodiamonds have a high amount of uniform size distribution mesopores of 4.4 nm on average and a small amount of micropores whose width is in the range of 1–2 nm, as seen in Figure S3 as well. The pore structural parameters are listed in Table 1.

The average mesopore size agrees well with the average crystal size, suggesting that the observed mesopores originate from a colloidal aggregation structure of uniform diamond crystals. As the primary nanodiamond crystal is wrapped with an ultrathin graphitic layer, as mentioned above (see also Figure S2), the micropores stem from interstices in nanocrystal contacts and incomplete wrapping with graphitic layers.

Phenomenologically, it is well-known that a hierarchical structure of micropores and small mesopores induce an unusual sorption property for water.53–55

Figure 3. X-ray diffraction pattern of powdered nanodiamonds. Inset: Deconvoluted diffraction pattern of the [111] reflection. Solid and dotted lines indicate the experimental and deconvoluted peaks, respectively.
Water Adsorption Property and Hygroscopic Nature. Figure 7 shows the water vapor adsorption isotherm of nanodiamonds, which is characteristic of IUPAC Type V, suggesting hydrophobicity. The whole feature of water adsorption isotherm indicates that nanodiamonds exhibit a weak hydrophobicity, as shown in Figure 7a. Nevertheless, the slight adsorption of vapor water in the low-pressure range shown in Figure 7b suggests the presence of hydrophilic sites on nanodiamonds, likely surface functional groups on the graphitic shells, which is shown by the TPD results, similar to the theoretical work by Gubbins et al. (1998), which clearly showed the importance of the hydrophilic sites in water adsorption.

Nanodiamond aggregates are hierarchically porous materials, as shown above. Micropores from the outer graphitic shell with surface functional groups donate local hydrophilicity to the mesopore walls consisting of nanodiamond-aggregated structures. As the mesopore volume is about 7× larger than the micropore volume, adsorbed water should be close to liquid-like water. Correspondingly, the density of adsorbed water from

<table>
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<tr>
<th>total pore vol at $P/P_0 = 0.97$ cm$^3$ g$^{-1}$</th>
<th>$S_{BET}$ m$^2$ g$^{-1}$</th>
<th>micropore vol$_{DFT}$ ($&lt;2$ nm) cm$^3$ g$^{-1}$</th>
<th>mesopore vol$_{DFT}$ ($2−6$ nm) cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37</td>
<td>300</td>
<td>0.043</td>
<td>0.300</td>
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Table 1. Pore Structural Parameters of Powdered Nanodiamonds

Figure 4. (a) TG analysis of nanodiamonds under He; weight loss (-----) and derivative of TG curve (····). (b) Evolved gases on the course of TG measurement of nanodiamonds; CO (black line, $m/z = 28$), CO$_2$ (gray line, $m/z = 44$), and H$_2$O (dotted line, $m/z = 18$).

Figure 5. SEM image of nanodiamonds.

Figure 6. N$_2$ adsorption isotherms of powdered nanodiamonds at 77 K in (a) linear scale and (b) logarithmic scale; (c) QS-DFT derived pore size distribution. Solid and open symbols in (a) and (b) denote adsorption and desorption branches, respectively.
adsorbed amount and pore volume is around 1 g cm$^{-3}$. Consequently, these mesopores of large pore volume can accept liquid water, exhibiting a marked hygroscopic property, as shown in Figure 8, which shows a photo describing the water droplet on pelletized graphite and nanodiamonds after 20 s upon adding a water droplet. We cannot see the water droplet on the nanodiamonds, while the water droplet is stable on the graphite. The nanodiamonds with high hygroscopic property absorb very quickly all the water droplet.

While hydrophobicity is a surface phenomenon that refers to the weak attraction or repulsive interaction of water molecules to the surface, hygroscopic property explains the ability of the material to absorb liquid water in its interior structures. The water adsorption isotherm shows a weak hydrophobicity of nanodiamonds and the presence of a few hydrophilic sites located at the external surface. Such hydrophilic sites induce adsorption of water molecules on them in the low $P/P_0$ range, accompanied with predominant adsorption of water in mesopores at higher $P/P_0$ range. This adsorption mechanism should be associated with the observed hygroscopic nature of

Figure 7. (a) Water vapor adsorption isotherm of powdered nanodiamonds at 298 K. (b) Closer look at the water adsorption isotherm in the low relative pressure range. Solid and open symbols indicate adsorption and desorption branches, respectively.

Figure 8. Water droplet on pelletized graphite and nanodiamonds on dropping a water droplet; photograph was taken 20 s after droplet deposition.

Figure 9. (a) Change in the number of adsorbed water molecules ($n$) at saturated vapor pressure ($P_0$) in GCMD simulation. (b) Experimental water adsorption (open squares)−desorption (closed squares) isotherms ($T = 298$ K). Green circles show the GCMD simulated adsorption isotherm (snapshots corresponding to blue arrows are shown in Figure 10).
nanodiamonds, which was measured by determining the change of the height of the water droplet on the sample.\textsuperscript{5,56,57}

We created the structure model of a nanodiamond crystal and simulated the water adsorption isotherm using the nanodiamond model. Figure 9 shows the GCMD simulated water vapor adsorption isotherm. Figure 9a shows the time course of adsorption of water molecules on the nanodiamond model at $P/P_0 = 1$. The time-change of adsorption provides the equilibrium adsorption amount for each pressure and then we can determine the adsorption isotherm. Figure 9b shows a comparison of the experimental and simulated adsorption isotherms; the simulated adsorption isotherm coincides well with experimental desorption branch where the desorption branch describes the equilibrium adsorption.\textsuperscript{58}

Thus, the nanodiamond model expresses well the characteristic structure of the nanodiamonds in particular for water adsorption; the initial uptake and the kink at $P/P_0 = 0.7$ are well described. We can obtain the molecular level understanding of water adsorption on nanodiamonds. The snapshots of adsorption of water molecules at the four $P/P_0$ denoted by arrows in Figure 9b are shown in Figure 10. Water molecules are adsorbed only on hydrophilic sites on the graphitic shell of nanodiamonds at $P/P_0 = 0.16$, then water clusters grow to form a continuous water layer with an elevation of $P/P_0$ finally inducing condensation in the mesopore.\textsuperscript{59,60} The nanodiamond with graphitic shell and their aggregated model can describe the experimental water vapor adsorption, as shown above. The modeling-aided approach should deepen the understanding of the hygroscopic nature of nanodiamonds in the future.

Figure 10. Snapshots from the simulation box for selected relative pressures pointed by arrows in Figure 9. The inset shows a typical water cluster formed at a hydrophilic site (C atoms marked in green) and $P/P_0 = 0.16$.

So far, experiments and simulations support a novel mechanism on the hygroscopic property of nanodiamond aggregates. This work demonstrates that hydrophilic sites and ultramicropores give rise to the water adsorption. The outermost surface of nanodiamonds consists of sp\textsuperscript{2} hybridized carbon similar to other porous carbons. The water adsorption mechanism of nanodiamonds is similar to that of ordinary carbons consisting of sp\textsuperscript{3} hybridized carbon atoms. However, nanodiamonds shows a larger uptake in low relative pressure and exhibit a remarkable hygroscopic property under an ambient condition, which is completely different from porous carbons. Nanodiamonds can capture efficiently liquid water under an ambient condition, as it was shown here. Such hygroscopic property was explained with the relevance of ultramicroporosity, surface functionalities, and the hierarchical porosity in the nanodiamond aggregates. The remarkable hygroscopic nature of nanodiamonds could be useful to their biomedical applications.

\section*{CONCLUSIONS}

The detonation nanodiamonds are aggregates of highly crystalline particles of 4.5 nm in average size, which have graphitic outer layers of surface functionalities. The nanodiamond colloidal aggregates have small mesopores exhibiting hydrophobic behavior for water vapor adsorption. However, the surface functionalities on the graphitic outer layers of the nanodiamond and ultramicropores in the aggregate interstices can work as hydrophilic sites; those should accept liquid-like water in the mesopores, inducing the observed hygroscopic nature. Experimental and modeling studies support the above mechanism on the hygroscopic property of the detonation nanodiamonds. However, we need to evaluate quantitatively this property in order to clarify exactly the remarkable hygroscopic property of detonation nanodiamonds in future studies.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b02046.

Table S1 and Figures S1–S (PDF).

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