

Hygroscopic Micro/Nanolenses along Carbon Nanotube Ion Channels

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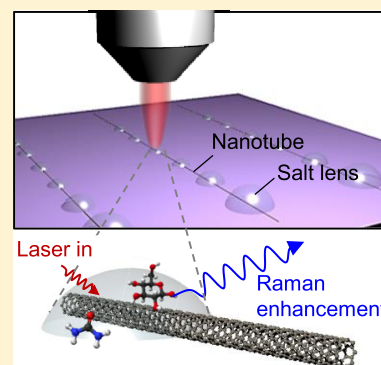
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Supporting Information

ABSTRACT: Nanolenses of alkali metal halides can be a unique optical element due to their hygroscopicity, optical transparency, and high mobility of constituent ions. It has been challenging, however, to form and place such lenses in a controlled manner. Here, we report micro/nanolenses of various alkali metal halides arranged as a one-dimensional (1D) array, using the exterior of single-walled carbon nanotubes (SWNTs) as a template for forming the lenses. Applying an electrical bias to an aqueous solution of alkali metal halides placed at the end of an SWNT array causes ionic transport along the exterior of SWNTs and the subsequent formation of salt micro/nanocrystals. The crystals serve as micro/nanolenses that optically visualize individual SWNTs and amplify their Raman scattering by orders of magnitude. Molecules dissolved in the ionic solution can be electrokinetically transported along the nanotubes, captured within the lenses, and analyzed by Raman spectroscopy, which we demonstrate by detecting ~12 attomoles of glucose and 2 femtomoles of urea. The hygroscopic salt nanolenses are robust under various ambient conditions indefinitely, by transitioning to liquid droplets above their deliquescence relative humidity, yet can be removed nondestructively by water. Our approach could have broad implications in the optical visualization of 1D nanostructures, molecular transport or chemical reactions in 1D space, and molecular spectroscopy in salty environments.

KEYWORDS: Carbon nanotubes, hygroscopic nanolens, optical visualization, Raman spectroscopy, ionic transport



INTRODUCTION

Micro/nanolenses have played an important role in nanotechnology through enabling subdiffraction-limit microscopy,^{1–4} light-harvesting in solar cells,⁵ and spectral amplification.^{6–9} The majority of existing micro/nanolenses are solid-state objects^{1,10,11} that are mechanically robust¹² and fixed in size, location, and composition. Removal of those lenses, however, often requires acid treatments and thus can be destructive to the specimens. Liquid-phase lenses^{3,4} have advantages of being removable by solvent and also deformable, but their long-term stability is not guaranteed due to evaporation.¹⁰ Therefore, micro/nanolenses composed of alkali metal halides¹³ provide new opportunities in optics and spectroscopy because of their hygroscopicity, optical transparency, solubility in water, and the high mobility of the constituent ions under an electric field. However, forming such lenses and arranging them in a well-defined manner have not been demonstrated.

Single-walled carbon nanotubes (SWNTs) have a one-dimensional (1D) tubular structure with both the interior and the exterior available for the transport of alkali metal halides and various molecular species. Recent studies have focused on the interior of SWNTs, demonstrating transport of individual

ionic and molecular species such as cations of alkali metals,¹⁴ methanol,¹⁵ amino acids,¹⁶ and DNA.¹⁷ The exterior channels of SWNTs are unique in that they can be modified and characterized more easily, allow higher flux of ions, and are more responsive to the ambient conditions than the interior. We have previously demonstrated that such distinctive characteristics of the SWNT exterior result in novel phenomena, cation-preferring transport of ions, and accumulation of ionic species as salt crystals along the nanotubes.¹⁸ Hence, the ion conduction along the SWNT exterior is an emerging research topic that requires further exploration.

In this work, we demonstrate hygroscopic micro/nanolenses of alkali metal halides arranged as parallel 1D arrays, using the ion channels of aligned SWNTs as a template for forming the salt lenses. Our approach is distinct from existing ones, because the lenses are formed by the transport phenomena occurring selectively along the exterior of SWNTs. The lenses, being much larger than the diameter of SWNTs, optically visualize the location of individual SWNTs and amplify Raman

Received: April 30, 2019

Revised: September 30, 2019

Published: October 31, 2019

scattering of molecular species captured within the lenses by the electrokinetic transport. The salt lenses are hygroscopic and thus preserve such capabilities indefinitely, by undergoing phase transition in response to the ambient humidity, yet they can be removed nondestructively by rinsing with water. The 1D array of hygroscopic micro/nanolenses could find broad applications in the optical visualization and spectroscopic characterization of various 1D nanostructures, the study of molecular transport and chemical reactions in 1D space, as well as the detection of various Raman-active molecules in a salty environment.

RESULTS AND DISCUSSION

Arrays of salt micro/nanocrystals were formed along SWNTs by modifying the experimental platform that we previously reported.¹⁸ Centimeter-length horizontally aligned SWNTs were grown by chemical vapor deposition (CVD) on a silicon substrate with thermal oxides (Figure 1a, left). A metal cover was deposited on one side of the SWNTs, and then a droplet of 3 M NaCl was placed on the other side, as illustrated in Figure 1a (right). With application of an electric field across the nanotubes using Pt wires, (+) to the solution and (−) to the metal cover, transport of ions occurred along the exterior of the nanotubes.¹⁸ The procedure decorated the nanotubes with arrays of salt crystals within 10 min. Figure 1b shows an optical micrograph of the crystals formed along the nanotubes between the metal cover and the solution, which optically visualized over 80% of the total nanotubes (Figure S1). The result suggested the formation of crystals on both metallic and semiconducting nanotubes. The red arrows in Figure 1a,b indicate the direction of the ionic transport. For some samples, we shortened the nanotubes using photolithography and oxygen plasma etching prior to ionic transport. This optional step helped to define the meniscus of the droplet by endowing the etched region with hydrophilicity, but it did not affect the efficiency of crystal formation.

Our approach was applicable to nanotubes having larger diameters (e.g., double-walled carbon nanotubes) (Figure S2) as well as to nanotubes on a bare silicon substrate (Figure S3). Scanning electron microscopy (SEM) and Raman spectroscopy of the nanotubes before and after crystal formation confirmed that no damage to the nanotubes occurred (Figure S4) and that the salt crystals can be removed nondestructively by simple rinsing with water (Figure S5). The shape and size of the crystals did not change during baking of the substrate at 100 °C, collection of SEM images under a vacuum, or storage in various ambient conditions for 28 d (Figure S6), which confirmed the robustness of the crystals on carbon nanotubes. We also emphasize that our approach for forming salt structures by the ionic transport is not limited to aligned carbon nanotubes but is applicable to a variety of 1D nanostructures, including a random network of SWNTs (Figure S7), silver nanowires (Figure S8), and graphene nanoribbons (Figure S9).

Figure 1c and Figure S10 show images of the array of NaCl crystals along a nanotube collected in situ under an optical microscope. The images shown were collected at 12, 116, 222, and 365 s. The length of the array increased linearly with time at a rate of $\sim 30 \mu\text{m}/\text{min}$. When the duration of ionic transport was fixed at 400 s, the use of a higher electric field (10 V/mm) resulted in longer crystal arrays than the use of a lower field (5 V/mm), as shown in Figure 1c (inset) and Figure S11. The logarithmic normal distribution of the crystal diameters was

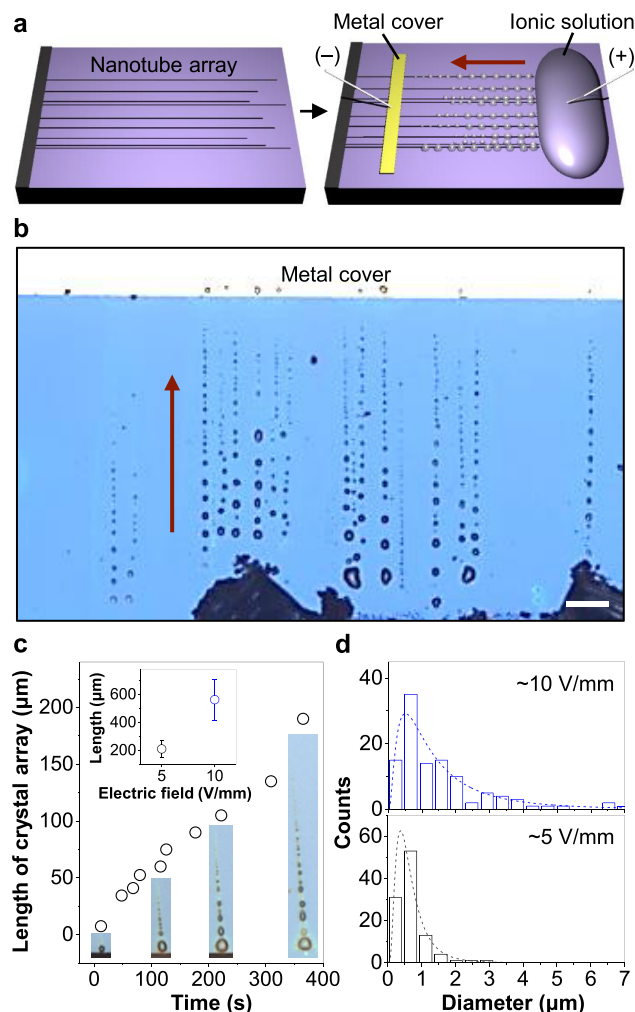


Figure 1. Formation of salt micro/nanocrystals along SWNTs via exterior transport. (a) Experimental platform for forming the array of micro/nanocrystals along the nanotube. (b) Optical image of NaCl micro/nanocrystals formed along nanotubes after application of a bias. Scale bar: 50 μm . (c) In situ monitoring of the formation of NaCl micro/nanocrystals along a nanotube. (inset) The length of the NaCl crystal array at two different electric fields after 400 s. (d) Distributions of the diameter (bars) and logarithmic fits (lines) of salt crystals formed along nanotubes using an electric field of $\sim 10 \text{ V/mm}$ (top) and $\sim 5 \text{ V/mm}$ (bottom).

shifted to the right (i.e., larger crystals) at the stronger electric field (Figure 1d). By adjusting the duration and the intensity of the electric field as well as the relative humidity (Figure S12), a rough control of the crystal size and the distance between crystals can be achieved, although accurate control of individual crystals is still challenging as described in the formation of metal oxides,^{11,19} condensed water vapor,²⁰ and ice crystals²¹ on nanotubes. Further increasing the electric field ($>12 \text{ V/mm}$) caused formation of continuous narrow bands of NaCl solution by the electrowetting²² of the nanotubes (Figure S13). The formation of salt structures on the nanotube can be explained by the Rayleigh-Plateau instability.²³ During the ionic transport along the nanotube, a thin film of ionic solution formed along the nanotube surface turns into an array of liquid droplets to minimize surface energy, followed by transition to salt crystals upon evaporation of water. Here, the ionic transport along the nanotubes was driven mainly by the repulsion between the cations accumulated near the edge of

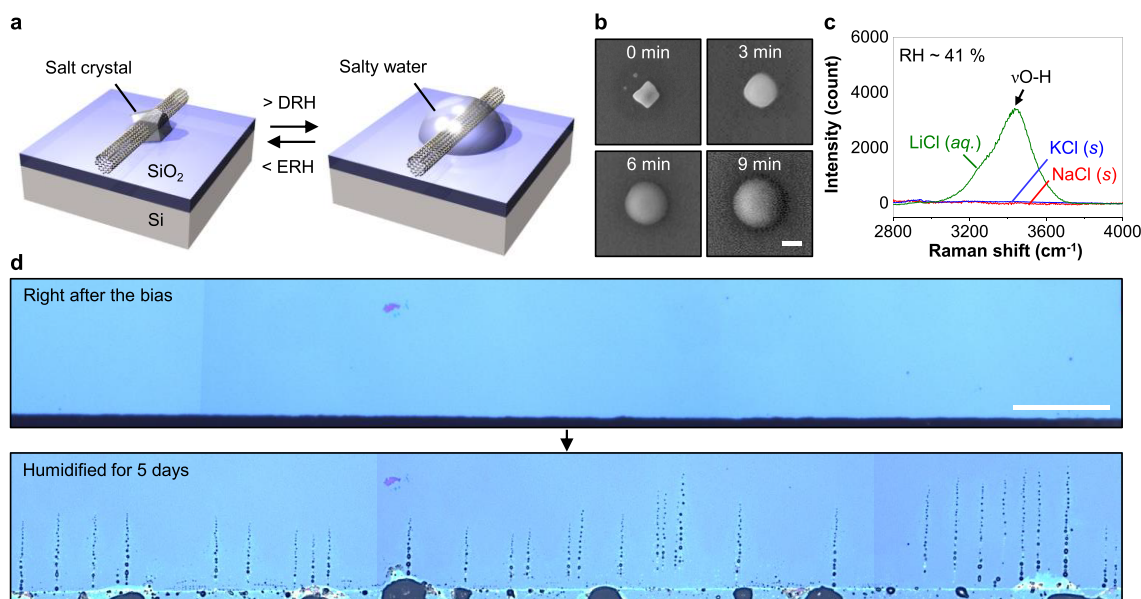


Figure 2. Phase transition of salt micro/nanocrystals based on RH. (a) Schematic of the salt crystal transition based on the DRH and ERH. (b) Environmental SEM images of the transition of a NaCl crystal into an aqueous saline droplet via the absorption of water vapor at 90% RH. Scale bar: 1 μm . (c) Raman spectra of microcrystals of various alkali metal halides at RH of 41%. (d) Optical images right after the transport of KI solution (0.16 M) for 1 min at 40 V/mm (top) and after storage in humidified conditions for 5 d without applying bias (bottom). Scale bar: 300 μm

the droplet under an electric field. Thus, we expect that the crystals along the nanotubes were enriched with cations, as has been reported in electrospray,²⁴ electrohydrodynamic jet printing,²⁵ and our previous study.¹⁸

A unique feature of our approach is the use of hygroscopic salt crystals whose phase is determined by the relative humidity (RH) of the ambient air. As illustrated in Figure 2a, the salt crystals transition to liquid droplets by spontaneously absorbing water from the air when the humidity is raised above the deliquescence relative humidity (DRH).²⁶ When the humidity is lowered, the droplet shrinks, due to dehydration, and eventually crystallizes below the efflorescence relative humidity (ERH). The ERH is usually lower than DRH, resulting in hysteresis in the phase transition and thus making it difficult to accurately determine the phase, especially at humidity values between DRH and ERH, without knowing the history of the humidity. For NaCl crystals larger than 40 nm, the DRH and ERH values are 75% and 45%, respectively.²⁶ The environmental SEM images of a NaCl crystal in Figure 2b clearly show the deliquescence of the NaCl crystal at 90% RH (>DRH). Raman spectroscopy was used to further confirm the physical state. Figure 2c shows Raman spectra of NaCl, KCl, and LiCl collected at 41% RH, which is above the DRH of LiCl (11.3%)²⁷ and below the ERH of NaCl (45%) and KCl (56%).²⁸ On the basis of the fact that the O–H stretching mode (3000–3600 cm^{-1}) of water molecules was only detected for LiCl, we determined that LiCl was present as aqueous saline droplets, whereas NaCl and KCl were solid crystals. Below the ERH, the metal halides should be in the solid state and show no O–H stretching in their spectra.

In humidified conditions, trace amounts of the salts that are not immediately visible under an optical microscope gradually grow into larger liquid droplets, thereby allowing the optical visualization of individual nanotubes. Note that the optical visualization of nanotubes, like in the previous studies,^{19,20} means being able to indirectly locate the nanotubes, in this

study by utilizing the salt structures that are large enough to be visible under an optical microscope. During the transport of 0.16 M potassium iodide (KI) solution along the nanotubes by applying 40 V/mm for 1 min at 54% RH, for instance, no crystals were visible in the optical micrograph, and the nanotubes could not be located (Figure 2d, top). After the sample was stored in humidified conditions ($72 \pm 13\%$ RH) without applying bias for 1 d, above the DRH of KI (59%), we observed the formation of KI liquid droplets along 27 nanotubes within the region of interest (Figure S14). After 5 d of humidification, the visualized portion of the nanotubes was extended approximately four times, and nanotubes that did not appear on day 1 were also visualized (Figure 2d, bottom). The results strongly supported the presence of small KI crystals along the entire tube length due to the exterior transport of ions.¹⁸ The visualization process monitored for 5 d in Figure 2d can be easily accelerated by increasing the electric field and the ambient humidity. The use of salt crystals to visualize carbon nanotubes is advantageous over existing approaches, such as nanoparticles of metals^{19,29} or proteins,³⁰ condensed vapor,²⁰ or organic crystals³¹ that are either temporary or destructive to the nanotubes. Water vapor evaporates quickly and allows for only short-term visualization of the individual SWNTs.²⁰ Nanoparticles of metals^{11,29,32} or metal oxides¹⁹ enable optical visualization and/or surface-enhanced Raman, but their removal requires etchants that may alter the properties of the nanotubes. The salt crystals, which were formed exclusively along the nanotubes, were stable indefinitely under ambient conditions, due to the hygroscopicity of the alkali metal halides, and can be rinsed off easily using water while preserving the properties of the nanotubes.

The NaCl crystals having a refractive index (n) of 1.54 and a plano-convex shape (Figure S15) serve as micro/nanolenses to amplify the Raman scattering of the underlying specimen. Figure 3a shows the NaCl crystals along the SWNT (top) and a map of the G-peak intensity of the Raman spectra (bottom)

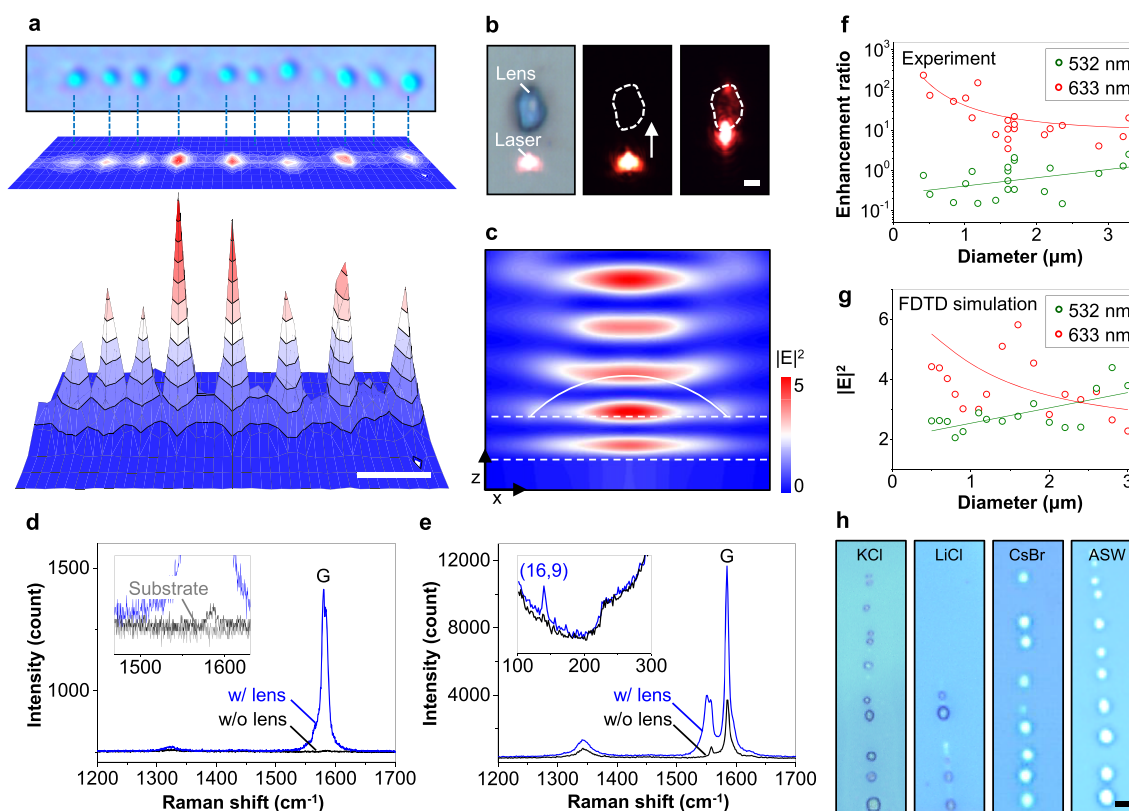


Figure 3. Salt crystals as a micro/nanolenses. (a) Optical micrograph of a lens array on an SWNT (top) and a corresponding G-peak intensity map (bottom), confirming the enhancement effect of the lenses. Scale bar: 5 μm . (b) Optical micrographs showing illumination of the edge of a microlens mapped in (a), which excited the entire lens via total internal reflection. Scale bar: 2 μm . (c) FDTD simulation, showing the electromagnetic wave enhancement (633 nm) of the lens ($n = 1.33$, $d = 1.4 \mu\text{m}$, contact angle = 40°). The solid and the dotted lines indicate the lens and the Si/SiO₂ substrate, respectively. (d) Raman spectra of a single SWNT under 633 nm excitation and the SWNT enhanced by the nanolens in solid state ($d \approx 420 \text{ nm}$). (inset) A magnified view of the tangential mode (G-peak). (e) Single-tube Raman spectra as (16,9), based on the radial breathing mode (RBM, inset), which was detected only with the lens ($d = 3.3 \mu\text{m}$). Here the lens is in solid state. (f) Enhancement ratio of the lens vs the diameter of the lens at different excitation wavelengths. Solid lines represent the best fit to the data. (g) Maximum intensity of electric field, calculated by FDTD, vs diameter of the lenses at different excitation wavelengths. Solid lines represent the best fit the simulation results. (h) Micro/nanolenses of KCl, LiCl, CsBr, and ASW along a nanotube at RH of 41%. Scale bar: 3 μm .

under 633 nm excitation, which was obtained by scanning the laser illumination over the sample at 0.5 μm resolution. The sharp peaks in the intensity map at the locations of the crystals confirmed that the 1D array of NaCl crystals was responsible for the enhanced Raman scattering. The varied degrees of enhancement were attributed to the nonuniform size of the crystals and the different location of the nanotube within the crystals. Being hygroscopic, the salt lenses transition between liquid and solid phases in response to the ambient humidity, but their capability of amplifying Raman scattering is preserved regardless of their phase (Figure S16). Note in Figure 3a that the Raman spectra of the high-aspect-ratio nanostructure was detected from the entire lens area, making it easy to spectroscopically characterize a single nanotube by removing the need for precisely illuminating the 1D nanostructure. The results can be explained by optical micrographs in Figure 3b. Shown on the left are one of the lenses mapped in Figure 3a and the laser spot. Turning off the white light leaves only the laser spot visible (right), with the dotted line indicating the lens. Moving the laser spot to the lower edge of the lens illuminates the entire lens (right) by total internal reflection³³ as supported by the ray tracing for the lens (Figure S17). Raman spectra from another lens clearly show amplified Raman scattering of an SWNT even upon illumination at the

edge (Figure S18). A finite difference time domain (FDTD) simulation suggested that the enhancement was achieved in part by the focusing of the incident electromagnetic wave by the lens, as shown in Figure 3c for a lens ($n = 1.33$) with a diameter of 1.4 μm and contact angle of 40° (Figure S19). The presence of an SWNT, which is only 1–2 nm in diameter, did not affect the FDTD simulations and thus was not considered in the calculation. Because of the 1D structure of the nanotubes, their spectral intensity is strongly polarization-dependent and exhibits a maximum when the excitation laser is polarized in parallel to the tube axis.³⁴ After decoration with salt lenses, even the nanotubes that exhibited no Raman signal at perpendicular excitation could be characterized by Raman spectroscopy (Figure S20). The results above suggest that the salt micro/nanolenses enable the Raman spectroscopy of carbon nanotubes, which can be challenging or inconvenient to perform without lenses.

Deposition of the lenses enhanced the single-tube Raman spectra by up to 2 orders of magnitude, enabling the detection of both the tangential mode (G-peak) (Figure 3d) and the RBM of the nanotubes (Figure 3e), even when the electronic transition was off-resonance from the excitation laser. We examined the variation of this enhancement with the diameter of the lenses and the wavelength of the excitation laser. For

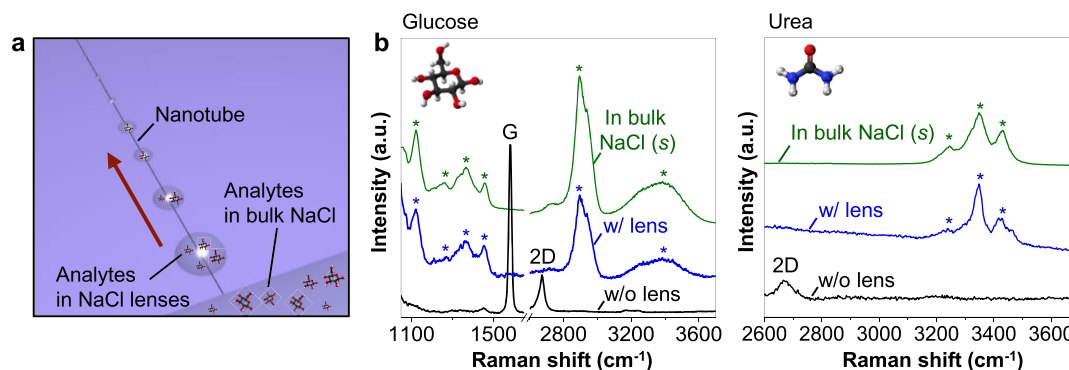


Figure 4. Use of the salt micro/nanolens for probing Raman-active molecular species. (a) Schematic of the transport of a Raman-active molecular species along the nanotube and its capture within the lenses. (b) Raman spectra at 532 nm excitation after the transport of glucose (left, 41% RH) and urea (right, 49% RH), collected from a bulk NaCl crystal in the reservoir (green), an NaCl lens on the nanotube (with lens, blue), and the bare nanotube between lenses (without lens, black). Characteristic Raman modes of glucose or urea are marked with asterisks, and all the spectra were shifted vertically for easy comparison.

each spectrum, we adjusted the location of the laser spot, as well as the distance between the microscope objective and the specimen, to maximize the G-peak of SWNT. Figure 3f shows the enhancement ratio (ER) of the G-peak, which is defined as the G-peak intensity with the lens divided by the intensity without the lens, versus the diameter of the salt crystals at an excitation wavelength of 532 nm (green) and 633 nm (red). By collecting spectra from each lens at different wavelengths, we were able to examine the dependence of the Raman spectra of an SWNT on the wavelength of the excitation laser independently of the shape and size of the lenses. At 532 nm, the signal enhancement by the lens was small ($ER = 0.8 \pm 0.7$), and the enhancement ratio increased marginally as the lens size was increased. At 633 nm, the signal was highly enhanced, with an average enhancement of 38 ± 58 times and a maximum enhancement of up to 230 times; the enhancement ratio decreased overall as the lenses became larger. These dependences on the wavelength and lens diameter were supported by FDTD simulation. Similarly to the experiments in Figure 3f, where the G-peak was maximized, we plotted based on the FDTD simulations the maximum intensity of electromagnetic wave within each lens versus the lens diameter (Figure 3g). If we assume that the SWNT is always located on the substrate and at the center of the lens, the results of FDTD simulations do not match with the experimental results (Figure S21). As the lens diameter increased, the intensity maxima of electromagnetic waves moved out of the lens at 633 nm (Figure S22) but into the lenses at 532 nm (Figure S23). Although at 532 nm the Raman intensity is reduced by the lens ($ER < 1$) in most diameter range, the spectra in Figure 3e collected using a lens with diameter of $3.3 \mu\text{m}$, the largest diameter we tested, showed a strong enhancement. For off-resonant nanotubes whose Raman features could not be detected without the lens, obtaining the enhancement ratio was not feasible. Therefore, the enhancement ratio in Figure 3f is an underestimate, and the true ER may actually be comparable to that of surface-enhanced Raman spectroscopy (SERS),¹¹ which reported average and maximum ER of 97 and 629, respectively. Such capability of the lenses that amplifies Raman scattering also enabled detection of the presence of carbonaceous species (Figure S24) or a low degree of covalent functionalization (Figure S25) on the sidewall of a single SWNT, whose characterization is otherwise difficult. Being able to choose the refractive index of the lens is another

important issue for optical applications, as light propagation is strongly affected by the refractive index of a medium. By using solutions of various alkali metal halides, we were able to form salt crystals having different refractive indices along the nanotubes. Figure 3h shows salt structures formed by transporting KCl ($n = 1.48$), LiCl ($n = 1.66$), and CsBr ($n = 1.69$) at 3 M, as well as artificial seawater³⁵ (ASW, $n = 1.49$).³⁶ LiCl is in liquid state, and all the others are solid crystals. We also found it possible to form lenses using NaCl solution at a much lower concentration (5 mM), artificial tear fluid, and two kinds of cell culture media (Dulbecco's Modified Eagle's Medium (DMEM), RPMI 1640) as shown in Figure S26. The above results suggest that the micro/nanolenses along the SWNTs serve as versatile optical components.

The salt lenses in this report are distinct from existing ones, as they are formed by the transport phenomena of ions. Therefore, if the ionic solution contains molecular species, these molecules should also transport electrokinetically along the exterior of the nanotubes and become captured within the salt lenses. In this manner, a small amount of Raman-active molecules can be extracted from a bulk solution and probed using the 1D array of salt micro/nanolenses. Figure 4a shows a schematic of the electrokinetic transport and capture of molecules by NaCl lenses on an SWNT. Here, we used glucose or urea as the analyte. The lenses were formed by transporting a 1 M solution of D-(+)-glucose or urea in 3 M NaCl. Figure 4b shows the Raman spectra collected from different spots on nanotubes transporting glucose (left) and urea (right) at 532 nm excitation. As a reference, spectra were collected from NaCl crystals in the reservoir (green); the fingerprint Raman modes of glucose and urea are marked with asterisks (Figure S27). No analyte signal was detected from the nanotube portions between lenses (black). In contrast, all the fingerprint modes of the analytes were observed at the locations where lenses were present (blue), likely due to the collection of sufficient analytes and the spectral amplification effect of the lenses. The spectrum was obtained from a location within the lens at which G and 2D peaks from SWNT did not appear (Figure S28). All the lenses used in Figure 4b were in solid state as supported by the presence of NaCl crystals in the reservoir. Assuming a hemispherical lens with diameter of $2 \mu\text{m}$ and no enrichment or depletion of analytes within the lens, our result corresponds to the detection of ~ 2 femtomoles of glucose or urea. The detection of glucose by the lens was

possible at much lower concentrations down to 10 mM, which corresponds to detection of ~ 140 attomoles for a $3.8\ \mu\text{m}$ droplet (Figure S29). When considering the confocal volume of $\sim 1.2\ \mu\text{m}^3$, the volume being illuminated by the laser, the amount is estimated to be ~ 12 attomoles. This value is 10 times greater than the 1.18 attomole glucose detection that has been achieved using an SERS substrate.³⁷ Accumulation of the transported analytes into a salt lens is a unique and strong feature of our approach that enables detection of trace amount of analytes. Our results thus demonstrate the great promise of utilizing these salt lenses for extracting and probing analytes with high salt content, for instance, in the body fluids of animals, cell culture media, and marine environments.

In Figure 4b, the spectra from bulk NaCl crystals (green spectra) were collected from dried salts, which contained analytes that were highly concentrated by evaporation of water. The signal therefore was much stronger in the bulk than in the lenses. To make a fair comparison between the bulk and the lenses, we collected Raman scattering from two different glucose samples in liquid state: microdroplets having plano-convex shape versus a bulk droplet. We filled an array of rectangular poly(dimethylsiloxane) (PDMS) microwells with glucose solution, followed by transferring the solution onto a SiO_2/Si substrate, which resulted in formation of liquid-phase microlenses ($d = 10\ \mu\text{m}$) with plano-convex shape by surface tension (Figure S30). The intensity of C–H stretching mode of glucose ($2800\text{--}3000\ \text{cm}^{-1}$) was then compared between the microlenses and a bulk droplet (0.2 mL) of glucose, which were 279 ± 12 and 212 ± 13 , respectively (Figure S31). The Raman signal of a thick transparent sample originates from an extended region, which can be more than $5\ \mu\text{m}$ away from the focal plane.^{38,39} In a bulk solution of glucose, for example, the Raman signal reached a maximum at $15.2\ \mu\text{m}$ from the air–solution interface (Figure S32). Lenses that are $10\ \mu\text{m}$ in diameter cannot fully benefit from the extended region compared to the bulk droplet. Also, there can be potential absorption and loss of glucose by PDMS microwells.⁴⁰ Therefore, the enhancement by $\sim 32\%$ supports that the plano-convex shape of the microlenses indeed amplifies the Raman scattering of analytes within the lens.

In conclusion, we demonstrate 1D array of salt micro/nanolenses formed selectively along the exterior of single-walled carbon nanotubes by the ionic transport. The hygroscopicity of the salts guarantees the long-term stability of the lenses under various environmental conditions. The lenses are promising for use in both the visualization and spectroscopy of underlying nanomaterials, as well as for detecting trace amounts of surface-bound or soluble molecular species that are not easily detectable using existing approaches. These salt micro/nanolenses, which are robust and non-destructively removable, will find applications in optical or spectroscopic studies in 1D space, including electrokinetic separation of molecules, chemical reactions, and molecular detection in a highly saline environment. Since our approach is based on 1D transport phenomena that are still largely unexplored, further studies are necessary to understand how the crystal formation is affected by the properties of the nanotubes (i.e., their diameter, chirality, and metallicity).

■ EXPERIMENTAL SECTION

Decoration of the Salt Micro/Nanolens Arrays along the SWNTs by Exterior Transport. The aligned arrays of centimeter-long SWNTs were synthesized via CVD, as

reported elsewhere.^{14,41} A metal cover ($500\ \mu\text{m}$ width, $70\ \text{nm}$ (Au) or $30\ \text{nm}$ (Pt) thickness) was patterned perpendicular to the nanotubes. A millimeter-wide strip of photoresist was then patterned on the metal cover such that the strip was parallel to the metal cover. The nanotubes unprotected by the photoresist were etched using reactive ion etching (RIE) at $20\ \text{sccm O}_2$ and $100\ \text{mTorr}$ for 1 min, followed by removal of the photoresist in acetone. A droplet of $3\ \text{M NaCl}$ solution was then placed on an etched area. The silanol groups created by RIE had made this area hydrophilic, thus ensuring that the droplet was in contact with the nanotubes. One Pt wire from the (+) side was dipped into the ionic droplet, and another Pt wire from the (–) side was in contact with the metal cover. An electrical bias was then applied using a semiconductor parameter analyzer (Agilent E5272A) or a direct-current (DC) power supply (GWINSTEK, GPR-30H10D). The salt crystals formed along the nanotube were characterized by SEM (Hitachi S-4800), and their cross-section was prepared and imaged using a focused ion beam (FIB, Helios 450 HP).

Raman Spectroscopy and Mapping. Raman spectroscopy was performed using a Horiba LabRAM HR or WITec Alpha 300 equipped with 532 and $633\ \text{nm}$ excitation lasers. The estimated spot size of the laser was $721\ \text{nm}$ through the $100\times$ objective (Olympus MplanFL N, NA 0.9). All the spectra in this work were collected with the laser polarized in parallel to the nanotube axis unless otherwise specified. The chirality and diameter of the nanotubes were determined based on the Kataura plot⁴² and the relationship, $d\ (\text{nm}) = 248/\text{RBM}\ (\text{cm}^{-1})$.⁴³

FDTD Simulation and Ray Tracing. The software Lumerical was used to perform the three-dimensional (3D) FDTD simulation. The intensity of the electromagnetic wave was calculated as the wave propagated through a micro/nanolens on a silicon substrate with a $300\ \text{nm}$ thick SiO_2 layer. The material properties were taken from Palik's optical constants handbook.⁴⁴ The incident laser had a wavelength of 532 or $633\ \text{nm}$ with a beam amplitude of $1\ \text{V/m}$, and the distance from the substrate was fixed at 2 times the excitation wavelength. A perfectly matched layer (PML) absorbing boundary was employed to minimize reflection of the light waves. Ray tracing simulation was performed using LightTools software to show total internal reflection within the lens.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.nanolett.9b01767](https://doi.org/10.1021/acs.nanolett.9b01767).

Formation of salt crystals on nanotubes with different diameters and on a bare silicon substrate, evidence of no damage in nanotubes by the crystals, robustness of the salt crystals in various environments, formation of salt crystals on various nanostructures (SWNT random network, silver nanowires, and graphene nanoribbons), real-time monitoring of the crystal formation on SWNTs, the effect of humidification on the salt lenses, the effect of electric field on the crystal formation, cross-sectional images of salt lenses, ray-tracing simulation within the lens, polarized Raman spectroscopy of SWNTs underneath salt lenses, FDTD simulations at varied lens diameters and excitation lasers, lens-assisted

detection of light functionalization or carbonaceous species on SWNTs, salt lenses formed by various ionic species (low-concentration NaCl solution, artificial tear fluid, and cell culture media), Raman spectra of glucose and urea, detection of glucose at lower concentrations (10–500 mM), and Raman spectra from bulk solution versus microlens (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) (NRF-2017R1A2B4008226 and NRF-2016R1C1B-1013524), the Nano Material Technology Development Program (2016M3A7B4910635), and the Korea Institute of Energy Technology Evaluation and Planning and the Ministry of Trade, Industry & Energy of the Republic of Korea (No. 20174030201470). The study contains results obtained at the Ulsan National Institute of Science and Technology Central Research Facilities. The authors thank Prof. J. Lee at UNIST for assistance with the FDTD simulations.

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