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Highly stable, flexible ISFET pH sensor using sorted semiconducting SWNTs in aqueous solution

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Abstract

Flexible sensors enable gathering of information from nonplanar surfaces, which facilitates huge data collection tasks. Monitoring of pH levels in industrial wastewater is one example. For this purpose, stable, reliable flexible pH sensors are required to monitor pH in pipes or containers. Carbon nanotube field-effect transistors (CNT-FETs) are attractive transducers for flexible sensors because of their multiple functionalities, such as good electrical properties and mechanical flexibility. However, semiconducting single-walled carbon nanotubes (s-SWNTs) must be separated from metallic SWNTs of high purity for channel materials to be used in CNT-FETs. Here, we developed a simple method to sort s-SWNTs in an aqueous system using only dispersion and centrifugation. This sorting method is much less expensive than other techniques, such as density gradient ultracentrifugation, agarose-gel chromatography, or selective sorting by conjugated polymers. These sorted s-SWNTs result in high-performance CNT-FETs with electrical hysteresis reduced to almost zero and improved bias stability. Importantly, this method demonstrates the importance of the solubility parameter between polymers and water for CNT-FET hysteresis. The resulting carbon nanotubes also have high uniformity of characteristics, making them valuable as transducers for flexible sensors. Furthermore, real-time pH monitoring using ion-sensitive, field-effect transistors (ISFETs) based on CNT-FET is demonstrated in a drainage pipe.

Introduction

Sensors for real-time monitoring are increasingly important in health management and industrial applications¹. In industry, continuous monitoring of water quality parameters such as pH is required to prevent discharge of inadequately treated wastewater². To monitor pH changes in industrial wastewater accurately and continuously, it is necessary to install pH sensors in pipes with small radii. For this purpose, sensor bodies should be mechanically flexible enough to be attached to various small structures and at low cost. Conventional glass-based pH sensors are fragile and lack flexibility, which limits their use in industrial monitoring systems. To overcome these drawbacks, flexible pH sensors using polymer-based, H⁺ ion sensitive membranes have been reported³, and these sensors can monitor solution pH even under bending. However, to realize the “IoT/trillion sensor” concept, it is ideal to create edge systems that integrate flexible sensors and circuits. Readout circuits should be simplified as much as possible. Nothing meeting these specifications has yet been demonstrated.

An alternative approach to pH sensors employs ion-sensitive, field-effect transistors (ISFETs), in which the gate is covered with an ion-sensitive layer and the current flowing between source (S) and drain (D) is controlled by the electrostatic field generated by the gate⁴. This way, instead of measuring the potential difference between glass-based electrodes, the S/D current of FET is recorded. Since inflexible Si devices are often used for ISFETs, it is necessary to use flexible materials for transistors in order to make ISFETs with high conformability. For this strategy, flexible ISFETs have been studied previously. However, most flexible ISFETs still suffer from current drift and hysteresis, which are important for practical applications.

To address these inadequacies, in this study, we demonstrate a flexible ISFET based on single-walled carbon nanotubes (SWNTs). Toward hysteresis-free and drift-free CNT-based FETs, a purification method of SWNTs and passivation materials are proposed. As a channel material for FETs, semiconducting SWNTs (s-SWNTs) of high purity have high field-effect mobility in general, and can be fabricated with a solution process⁵. Among channel materials, s-SWNTs must be sorted from raw SWNTs to achieve high purity. Several methods for sorting s-SWNTs have recently been developed, such as density gradient ultracentrifugation (DGU)⁶, agarose-gel filtration⁷, and aqueous two-phase extraction⁸. Conventional purification methods require a s-SWNTs sorting process separate from dispersing and centrifuging processes. This incurs significant costs for s-SWNT sorting materials and processing equipment. On the other hand, selective dispersion of s-SWNTs, which only necessitates dispersing and centrifuging, has been proposed as an alternative strategy for sorting⁹. Recently, several groups have reported dispersants for sorting s-SWNTs. Many of these are conjugated polymers (CPs)¹⁰. Although CPs can sort s-SWNTs with extremely high purity, with few exceptions¹⁰⁻¹¹, dispersants are expensive, and sorting can only be done in non-polar organic solvents, such as toluene or xylene. These organic solvents damage flexible substrates such as PET, so the other solvents must be used.

For the first time, this study proposes selective dispersion of s-SWNTs using water as a solvent, which does not damage flexible substrates. Furthermore, using selected s-SWNTs, stable operative CNT-FETs are investigated as ISFETs in terms of hysteresis, uniformity, and bias stability. The CNT-FET configuration is optimized mainly by the s-SWNTs network as a channel material for the FET and passivation layers over CNTs. In addition, flexible ISFETs, which are fabricated by composing CNT-FETs with a pH-sensitive membrane formed of Al₂O₃ on a polyimide film, show the drain current response in solution pH change. Finally, an ISFET-based pH sensor with industrial applicability is affixed to a pipe with a small curvature to monitor pH changes of flowing water (Figure 1).

Results and Discussion

Selective dispersion of s-SWNTs

Figure 2a shows the process of sorting s-SWNTs. First, raw SWNT powder (diameter, 0.8–1.1 nm) and a dispersant in ultrapure water (UPW) were mixed. The dispersant is a hydrophilic acrylic polymer (detailed in the experimental section and the structure of the polymer is shown in Figure S1) that selectively disperses s-SWNTs. After the mixture was dispersed using an ultrasonic homogenizer, the dispersion was centrifuged to remove large bundles of SWNTs. The resulting greenish supernatant indicated that highly concentrated

semiconductor components were sorted from raw SWNTs having a diameter of ~ 1 nm (Ref.12). The absorption spectrum of sorted s-SWNT with absolute scale is shown in Figure S2. First, to check SWNT purity in the supernatant, Raman spectra ($\lambda_{\text{ex}} = 633$ nm) were taken (Figure S3). The relative intensity of the D-band ($1300\text{--}1350\text{ cm}^{-1}$) and G-band (1590 cm^{-1}) was $I_D / I_G < 0.01$, indicating that the D-band was clearly small compared to the G-band. This result indicates that the supernatant had sufficiently high SWNT purity for FET operation. To confirm the purity of s-SWNTs, optical absorption and Raman spectra were examined. Optical absorption spectra of both sorted and unsorted SWNTs, which were normalized at 730 nm (the absorption peak of S11) were measured (Figure 2b). For HiPco SWNTs, absorption peaks around 450–550 nm represent optical transitions of metallic SWNTs (M11), and absorption peaks from 650–900 nm (S22) and 900–1300 nm (S11) are derived from optical transitions of s-SWNT¹². Compared to the absorption spectrum of unsorted SWNTs, metallic M11 peaks were significantly reduced in absorption spectra of sorted s-SWNTs, indicating that semiconductor purity increased. Figure 2c shows the Raman spectra of sorted and unsorted SWNTs. In Raman spectroscopy, the ratio of metallic SWNTs (m-SWNTs) and s-SWNTs is calculated by evaluating radial breathing mode (RBM) Raman spectra¹³. For SWNTs with a diameter of ~ 1 nm, both M11 and S22 bands resonate at 633 nm excitation¹³. RBM peaks are divided into two resonance groups, those in the S22 band ($250\text{--}300\text{ cm}^{-1}$), and those in the M11 band ($190\text{--}220\text{ cm}^{-1}$). Compared to the RBM of unsorted SWNTs, metallic M11 peaks (200 cm^{-1}) were clearly reduced among sorted s-SWNTs. For ratio evaluation, the ratio of m-SWNT to s-SWNT in unsorted SWNT samples was assumed to be 1:2. Although we could not confirm the specific purity of s-SWNTs, based on channel length dependence of CNT-FETs discussed later, it likely realizes high purity. Compared to conventional sorting methods in aqueous systems^{13, 14}, this proposed method achieved equal or higher semiconductor purity. To examine the effect of molecular weight of the polymer on sorting s-SWNTs, polymers with MW = 12,000, 25,000, and 36,000 were synthesized. Absorption spectra of s-SWNTs sorted by polymers with different MWs are shown in Figure S4. This result indicates that sorting of s-SWNTs did not depend on polymer molecular weight in the range of MW = *ca.* 10,000–40,000. Thus, strict control of molecular weight is unnecessary for s-SWNT sorting. Moreover, including dispersion and centrifugation, the process requires less than 1 h, providing high purity s-SWNTs easily and quickly. Note that the hydrophilic acrylic polymer is much less expensive than CPs that have been used previously^{11, 15}. Starting materials of this polymer and a typical CP are compared in Table S1. It is likely that CPs cost around 100 times more than this polymer, consisting of monomers similar to those used in mass-produced acrylic polymers.

Figures 2d and 2e are atomic force microscopy (AFM) images of s-SWNT networks formed by the sorted s-SWNT dispersion solution at low and high concentrations, respectively. Even though SWNTs formed dense networks, most were individual and formed fewer bundled networks. As can be seen in the height profiles of SWNT networks (Figure 2f), the degree of stacking of SWNT networks was controlled by soaking with different SWNT concentrations. The s-SWNT dispersion sorted in this study succeeded in forming dense SWNT networks with few bundles, for thin-films of FETs. Dispersants of SWNT are one of the factors that determine the state of SWNT networks¹⁶⁻¹⁷, and these results indicate that the dispersant not only has the ability to sort s-SWNTs to achieve high purity, but also to form ideal SWNT-network thin films for CNT-FETs.

Optimization of CNT-FETs

To prove that sorted s-SWNTs are suitable as a channel material, CNT-FETs on Si / SiO₂ wafers were characterized. SiO₂ (thickness, 200 nm) was used as a global back-gate dielectric, and Ti / Au electrodes were deposited on the SWNT networks as S/D electrodes. First, dependence on layer thickness was studied by measuring I_{DS}–V_{GS} curves of CNT-FETs with single- and multi-layer s-SWNT networks (Figure S5). CNT-FETs with multi-layers-SWNT networks required a gate voltage of +80 V to reach the off-state, whereas the CNT-FET with a single-layer achieved the off-state at +10 V. It is probably difficult to apply a gate voltage across a multi-layer network of s-SWNTs and a large gate voltage is required to turn off the drain current. Notably, even multi-layer s-SWNT FETs achieved the off-state at a higher gate voltage (Figure S5), suggesting that there is almost no metallic SWNT layer caused by bundling of CNTs, unlike other CNT network layers reported previously¹⁷. This is a significant advantage to this dispersion method for reliable high I_{ON}/I_{OFF} state CNT-FETs. Another important parameter is channel dependence. Based on previous reports using >95 % purified s-SWNT solution, channel length <20 μm of CNT-FETs shows a decrease of the ON/OFF ratio due to a metallic CNT effect between S/D electrodes¹⁸. In contrast, this study clearly indicates that the ON/OFF ratio remains >10⁵ even at a 5-μm channel length (Figure S6), which indicates that the CNT network has the higher purity of s-SWNTs. This is an advantage to our proposed method for sorting s-SWNTs.

Next, effects of a passivation layer over the s-SWNT network layer are discussed by comparing fundamental I_{DS}–V_{GS} characteristics for CNT-FETs with and without passivation (Figure 3a). Hysteresis of CNT-FETs with passivation, especially with passivation of CYTOP and polymethyl methacrylate (PMMA) is smaller than that without passivation. Furthermore, it was evident that the smaller fedors solubility parameter (SP) of the passivating polymer results in reduced hysteresis (Figure 3b). The fedors SP value is described as:

$$\delta = (\sum E_{coh} / \sum V)^{1/2} (1)$$

where E_{coh} and V are the cohesive energy density and molar volume for a substituent group, respectively¹⁹. The fedors SP value for water is estimated to be higher than that of alcohols, such as methanol (δ = 13.8). Hence, polymers such as polyvinyl alcohol (PVA) with high SP values have good solubilities in water, while polymers with low SP values, such as CYTOP, have poor water solubilities. These results indicate that hysteresis can be suppressed by using a polymer with low aqueous solubility. In previous reports, water adsorption to the s-SWNT channel degrades hysteresis in CNT-FETs properties, and passivation has been considered an effective method to suppress hysteresis²⁰⁻²¹. However, there are no reports that systematically indicate the importance of the solubility parameter between passivating polymers and water.

While hysteresis could be decreased by applying a low SP passivation layer, a threshold voltage shift was clearly observed between V_{DS} = –1 V and –20 V (Figure 3c). We hypothesized that this V_{GS} shift is due to charge trapping at the channel/dielectric interface near the drain electrode with large bias stress at V_{DS} = –20 V (Ref. 22). To reduce V_{GS} shift, S/D electrode materials were investigated. We tried to increase adhesion between SWNT networks and S/D electrodes by increasing the thickness of the Ti electrode in order to eliminate the trapped charge. However, there was almost no improvement (Figure 3d). In a study by Wang *et al.*²³, metal

deposition on s-SWNT networks increased their conductivity, and Cr (0) (6 valence electrons) atoms form bis-hexahapto complexes at SWNT sidewalls. This bridges adjacent CNTs and reduces inter-nanotube junction resistance. We speculated that Cr removes trapped charges and improves S/D-electrode contact with SWNTs. To confirm this speculation, I_{DS} - V_{GS} characteristics of CNT-FETs with Cr / Au S/D electrodes were analyzed. The results showed that the V_{GS} shift was significantly improved between $V_{DS} = -1$ V and -20 V (Figure 3e). To optimize this effect, the thickness of the Cr electrode was increased from 1 to 30 nm. The best suppression of the V_{GS} shift was achieved at >2.5 -nm thickness of Cr S/D electrodes (Figure 3f). Although large work function metals such as Pd are preferred as electrode materials for p-type CNT-FETs²⁴, Cr electrodes with a relatively low work function provide bias stability. Details of the Cr electrode effect should be clarified in the future. Another important parameter for FET development is uniformity. In Figures 3g–3j, histograms at linear transfer show mobility of $6.53 \pm 0.32 \text{ cm}^2 / \text{Vs}$, $\log(I_{ON} / I_{OFF})$ of 6.07 ± 0.42 , hysteresis at $I_{DS} = 100 \text{ nA}$ of $1.41 \pm 0.15 \text{ V}$, and threshold voltage (V_{GS}) at $I_{DS} = 100 \text{ nA}$ of $-2.97 \pm 0.40 \text{ V}$, whereas those at saturation transfer show mobility of $6.95 \pm 0.30 \text{ cm}^2 / \text{Vs}$, $\log(I_{ON} / I_{OFF})$ of 7.17 ± 0.47 , hysteresis at $I_{DS} = 100 \text{ nA}$ of $0.95 \pm 0.09 \text{ V}$, and V_{GS} at $I_{DS} = 100 \text{ nA}$ of $-1.55 \pm 0.48 \text{ V}$. The field-effect mobility at linear transfer and saturation transfer is calculated using Equations (2) and (3), respectively.

$$\mu = \frac{dI_{DS}}{dV_{GS}} \frac{L}{W} \frac{1}{C_{ox} V_{DS}} \quad (2)$$

$$\mu = \frac{1}{2} \left(\frac{dI_{DS}}{dV_{GS}} \right)^2 \frac{L}{W} \frac{1}{C_{ox} I_{DS}} \quad (3)$$

where L is the channel length ($L = 100 \text{ }\mu\text{m}$) and W is the channel width ($W = 300 \text{ }\mu\text{m}$), and C_{ox} is parallel plate capacitance of the transistor ($C_{ox} = 17.7 \text{ nF/cm}^2$). The histogram indicates that CNT-FETs are relatively uniform in various characteristics. This high uniformity is attributed to the uniform, thin-film formed by s-SWNT dispersion. I_{DS} - V_{GS} characteristics of CNT-FETs at different temperatures are shown in Figure S7. Based on the results, I_{DS} increases at higher temperature, suggesting that this has a negative temperature coefficient of resistance.

CNT-FETs on flexible substrates

A flexible ISFET-based pH sensor with an extended gate structure was developed. The Al_2O_3 layer (thickness, 50 nm) was chosen for both the gate insulator and the pH membrane, in which the Al_2O_3 layer is the high- k gate-dielectric material and a good material for pH membranes in previous studies²⁵. Figures 4a-b show flexible ISFETs on a polyimide (PI) film and an optical micrograph of ISFET components. CYTOP passivation was applied over a wide area, except for the electrode pads and the pH-sensing membrane so as to improve CNT-FET characteristics and eliminate strain under bending of the device. Representative I_{DS} - V_{GS} and I_{DS} - V_{DS} characteristics of the flexible CNT-FETs are shown in Figures 4c-d. Mobilities at $V_{DS} = -0.2$ and 3 V were 4.55 and $4.68 \text{ cm}^2/\text{Vs}$, respectively. There was small hysteresis of $\sim 0.07 \text{ V}$ and V_{GS} shifts between linear and saturation transfers of $\sim 0.1 \text{ V}$. Constant current was evident in the saturation region (Figure 4d). Furthermore,

even at constant gate and drain bias ($V_{GS} = -2$ V, $V_{DS} = -1$ V), flexible CNT-FETs maintain steady-state drain current with small I_{DS} drift (Figure 4e). This current stability is due to CYTOP passivation with small hysteresis, and the Cr S/D electrodes, which suppress the V_{GS} shift for CNT-FETs.

Because this develops stable flexible ISFETs, mechanical flexibility was examined by measuring I_{DS} – V_{GS} curves as a function of the bending radius down to 1 cm (Figure 4f). These results reveal that FET behaviors are almost identical over a wide range of bending radii, resulting in almost constant performance of $\log(I_{ON}/I_{OFF})$ and mobility (Figures 4g and 4h). Next, to check durability, a cycle test at 2 cm bending radius was conducted (Figure 4i). After 1,500 bending cycles, the threshold gate voltage was slightly shifted to negative voltage, while performance of mobility and $\log(I_{ON}/I_{OFF})$ were well maintained (Figure 4j and 4k). The results indicate that these flexible CNT-FETs are useful for large curved surfaces and flexible uses.

pH detection

I_{DS} – V_{ref} characteristics at different pHs were investigated (Figure 5a). Although small hysteresis was observed, indicating that these ISFETs have low charge-trapping, a relatively stable threshold gate voltage shift was observed as a function of pH. Focusing on characteristic changes in solutions of different pH, the threshold voltage was negatively shifted from pH 9.18 to pH 1.68. This behavior of ISFETs is consistent with previous reports^{4, 25}. Figure 5b shows that the ΔV_{ref} shift at $I_{DS} = 10$ nA, which is calculated as $\Delta V_{ref} = 0$ V at pH 6.86, changed linearly at a rate of 62.4 mV / pH, indicating a good correlation between V_{ref} shift and hydrogen ion concentration. These results are in good agreement with Nernst theory, according to which theoretical pH sensitivity is 59.2 mV / pH at 298K. Similar verification with another device showed a linearity of 59.1 mV / pH in Figure S8. The results indicate that pH sensitivity of the CNT-ISFETs had high uniformity. Next, real-time pH monitoring and continuous I_{DS} monitoring with constant $V_{ref} = -2$ V and $V_{DS} = -1$ V was performed in solutions of various pHs. The drain current changed in response to pH changes (pH 9.18, 6.86, and 4.01), showing instant and consistent changes on immersion in different pH solutions and stable current levels (Figure 5c). The I_{DS} showed almost the same values for each pH, indicating that the system was able to respond appropriately as pH changed repeatedly up and down. There were small I_{DS} drifts caused by diffusion in the solution when another pH solution was added to the one being measured. This suggests that this ISFET has relatively high response speed. This ISFET-based pH sensor, with its stable drain current change corresponding to the pH change and quick pH response, is expected to measure pH change in environments with flow velocity.

Finally, as a proof-of-concept of the flexible, CNT-FET-based, extended-gate ISFET pH sensor for industrial applications, the device was attached to the inside wall of a polyvinyl chloride (PVC) pipe (bending radius, 5 cm), and the pH of tap water (flow rate, 100 mL/min) was measured continuously in real-time (Figure 5d). Tap water was forced to flow constantly over the pH membrane and Ag / AgCl electrode, and the response of the ISFETs was measured by dropping acidic or basic solutions into the running water. The ISFETs affixed along the shape of the PVC pipe had continuous stable drain current even with tap water running. After 0.1 mL of 0.1 M HCl was added to the running water, the drain current immediately decreased significantly and then returned to its original value (Figure 5e). Next, a large volume of 0.1 M HCl solution (1 mL) was added, and the drain

current immediately decreased as well, returning to the original current value more slowly than before. After the acidic solutions, 0.01 M NaOH solution was also added to the running water and drain current changes were confirmed. A drop of basic solution caused the I_{DS} to increase, and a larger quantity of base made the change larger. This suggests that pH can be measured in flowing water. By installing sensors in pipes, it is possible to comprehensively manage pH changes in wastewater.

Conclusion

This study developed a simple, high-purity s-SWNT dispersion method in an aqueous system and highly stable and reliable flexible CNT-FETs for pH monitoring. With aqueous selective dispersion, the sorting time of s-SWNT can be greatly shortened, and the aqueous dispersion is less damaging to flexible substrates. The characteristics of CNT-FETs fabricated using this dispersion method showed good performance in terms of hysteresis, bias stability, and bending resistance. The importance of the solubility parameter between polymers and water was systematically demonstrated. The thin film formed by dispersion of s-SWNT achieved high uniformity of CNT-FET characteristics. Furthermore, these results indicated that this pH sensor is able to detect real-time changes in pH in flowing water. Although there are still several challenges such as achieving low-cost fabrication using printing methods and demonstrations of practical use in water quality improvement systems, this proposed sensor has great potential for pH monitoring in industrial applications.

Experimental Section

Dispersant for sorting s-SWNTs

15 g of ethanol were prepared in a reaction vessel, and the reaction atmosphere was replaced with nitrogen while stirring. Then the temperature of the oil bath was increased to 80 °C. Solution (A) was prepared for dropping funnel 1, in which 50 g of a polymerization monomer, methoxy polyethylene glycol (9) methacrylate, and 0.17 g of a chain transfer agent, 3- mercapto-1,2-propanediol, were dissolved in 16 g of ethanol. Solution (B) was prepared for dropping funnel 2, in which 0.13 g of a polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile), were dissolved in 44 g of ethanol. Solutions (A) and (B) were simultaneously added dropwise to the reaction vessel through the respective dropping funnels over a period of 1 h. After completion of reagent additions, the mixture was aged for 1 h with stirring until the reaction was finished. Subsequently, ethanol was removed with a rotary evaporator, so that a dispersant was produced. The MW of the synthesized polymer was 36,000, based upon GPC measurements.

Sorting s-SWNTs.

To sort s-SWNTs, 150 mg of hydrophilic acrylic polymer and 30 mg of raw SWNTs (HiPco SWNT purchased from NOPO Nanotechnologies) were mixed in 30 mL of UPW and ultrasonicated for 10 min at an amplitude of 30% (Branson, 450D) at 20 °C. The dispersed solution was centrifuged at 20,000 rpm (12,700 × g) (Hitachi Koki, CS100FNX) for 10 min to remove most undispersed residues. Then the supernatant (*ca.* 25

mL) was collected as an s-SWNT dispersion.

CNT-FETs on Si/SiO₂ wafers

1% aminopropyl triethoxysilane (APTES, Sigma-Aldrich) in IPA was applied to highly doped n-Si wafers (thickness, 200 nm) at 150 °C. An s-SWNT dispersion (1.45 µg / mL) was dispersed on the APTES-treated wafer for 1 h, followed by DI rinse. Deposited wafers were annealed at 180 °C for 30 min. S/D electrodes of Ti / Au (5 nm/100 nm) or Cr / Au (5 nm/30 nm) were deposited (W = 1000 µm, L = 100 µm, Figures 3a–3f, and W = 300 µm, L = 100 µm in Figures 3g–3j). Finally, CYTOP was deposited by spin coating, and CNT-FETs were annealed for 1 h at 180 °C.

CNT-FETs on Flexible PI film

The fabrication process is described in Figure S9 in Supporting Information. For the flexible ISFET substrate, a polyimide (PI) precursor solution of poly (pyromellitic dianhydride-co-4,4'-oxidianiline), amic acid (Sigma-Aldrich) was spin-coated on a handling Si wafer and cured at 350 °C to form the PI film. To improve adhesion between the PI film and metal layers, a SiO_x layer (10 nm) was deposited with electron-beam (EB) evaporation. Local Al back-gate electrodes (100 nm) were sputtered and patterned using a wet etching method, after which, to form a contact on the Al gate electrode, Cr / Au (5 nm/ 30 nm) was deposited as electrode pads. Subsequently, a 50-nm Al₂O₃ dielectric layer was deposited by atomic layer deposition (ALD) at 200 °C. Via holes were created in the Al₂O₃ dielectric layer by etching with buffered hydrogen fluoride (BHF), enabling contact with the gate electrode. After treatment of the dielectric layer with 1% aminopropyl triethoxysilane in IPA for 10 min at 150 °C, the substrate was immersed in 1.45 µg / mL s-SWNT dispersion solution for 1 h, followed by a DI rinse. The channel was patterned using O₂ plasma treatment. Cr / Au (5 nm/ 30 nm) S/D electrodes were deposited and treated using a lift-off process to pattern the electrodes. Next, CYTOP (CTL-809A, AGC) was dropped on the channel as a passivation layer, followed by annealing at 180 °C for 1 h. An Ag / AgCl reference electrode was printed and cured at 80 °C for 5 min. The PI substrate was then detached from the handling wafer.

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Conflict of Interest

MA and AH are the inventors of a patent filed for the CNT sorting method.

Data Availability Statement

Data that support findings of this study are available from the corresponding author upon request.

Keywords

carbon nanotube, field-effect transistor, flexible device, pH sensor

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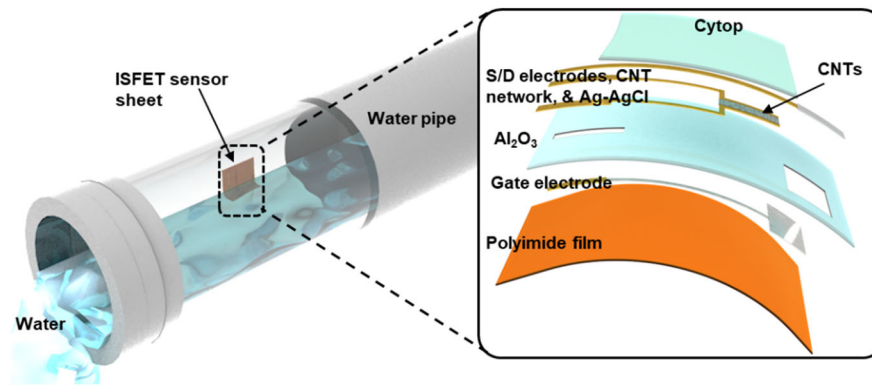


Figure 1. Schematic of a flexible CNT-based ISFET application for monitoring pH in flowing wastewater.

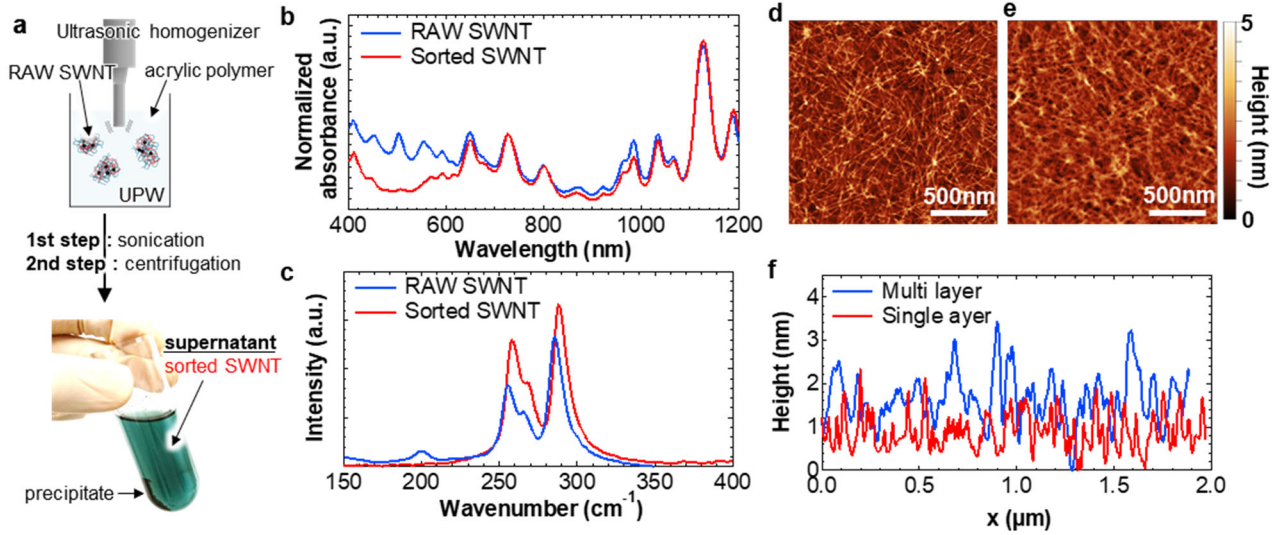


Figure 2. (a) Sorting of s-SWNTs and a photo of the supernatant including sorted s-SWNTs. (b) Optical absorption spectra and (c) Raman spectra of sorted s-SWNTs and raw SWNTs. AFM images of sorted s-SWNT networks formed by the sorted s-SWNT dispersion at (d) low and (e) high concentration. (f) Height profiles of SWNT networks extracted from AFM images shown in (d-e).

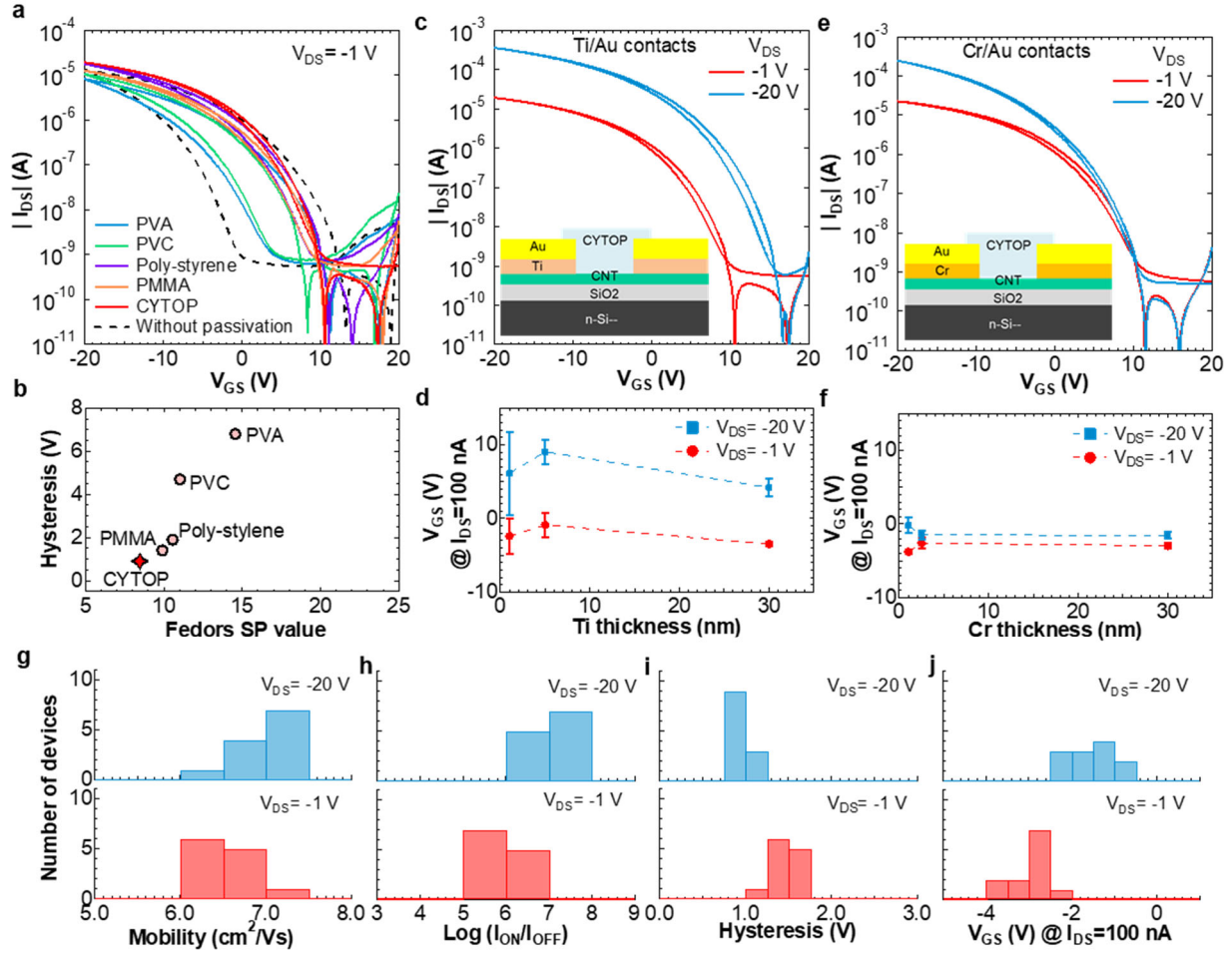


Figure 3. (a) I_{DS} - V_{GS} characteristics of CNT-FETs with/without passivation. (b) Measured hysteresis at $I_{DS} = 100$ nA vs. the Fedors SP value of polymers used for the passivation layer of CNT-FETs. (c) I_{DS} - V_{GS} characteristics of CNT-FETs with Ti / Au SD electrodes. (d) Gate voltage at $I_{DS} = 100$ nA for different thicknesses of Ti electrodes. (e) I_{DS} - V_{GS} characteristics of CNT-FETs with Cr / Au SD electrodes. (f) Gate voltage at $I_{DS} = 100$ nA for different thicknesses of Cr electrodes. Plots of (g) mobility, (h) $\text{Log}(I_{ON}/I_{OFF})$, (i) hysteresis at $I_{DS} = 100$ nA, and (j) V_{GS} at $I_{DS} = 100$ nA for 12 CNT-FETs at $V_{DS} = -1$ V and -20 V.

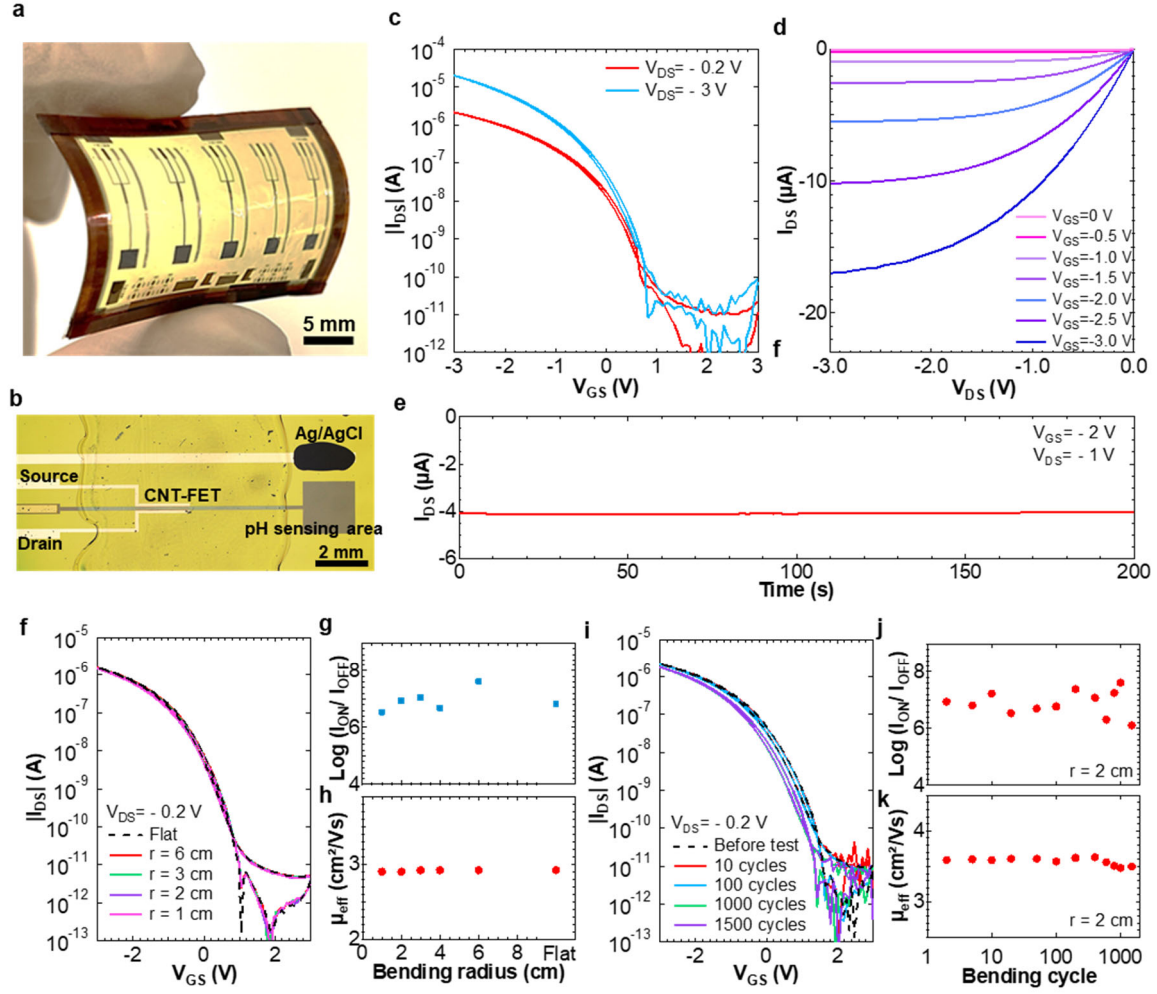


Figure 4. (a) Photograph of fabricated flexible ISFETs. (b) Optical micrograph of the ISFET. (c) I_{DS} - V_{GS} and (d) I_{DS} - V_{DS} characteristics of the flexible CNT-FETs. (e) On current bias stability at $V_{GS} = -2$ V and $V_{DS} = -1$ V. (f) I_{DS} - V_{GS} curves at different bending radii. (g) I_{ON}/I_{OFF} and (h) field-effect mobility as a function of the bending radius extracted from (f). (i) I_{DS} - V_{GS} curves after multiple bending cycles at a 2-cm radius. (j) I_{ON}/I_{OFF} and (k) field-effect mobility as a function of bending cycle extracted from (i).

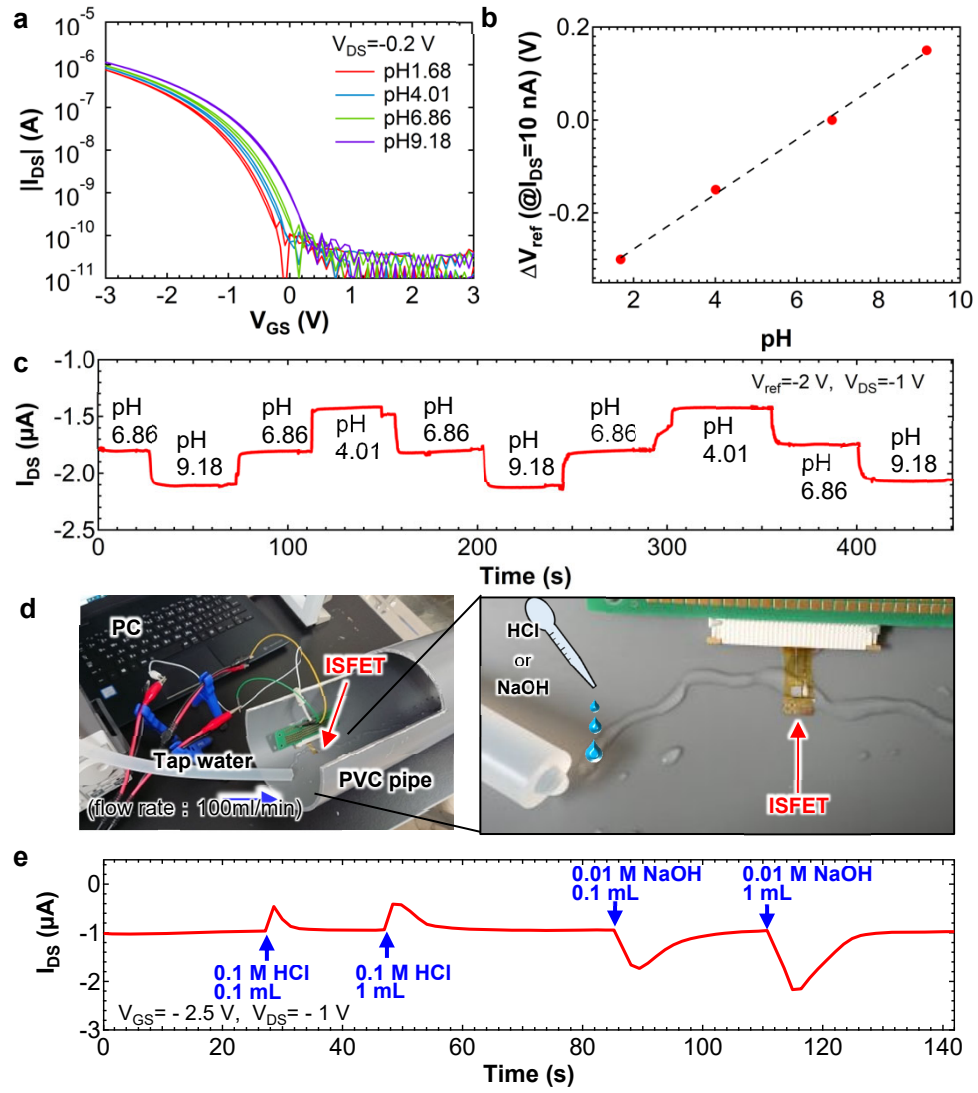


Figure 5. (a) I_{DS} - V_{ref} characteristics of the ISFET at $V_{DS} = -0.2$ V in solutions of different pH. (b) V_{ref} at $I_{DS} = 10$ nA as a function of pH extracted from (a). (c) Real-time I_{DS} measurement of solutions with different pH. (d) Photos of real-time pH monitoring of flowing water in pipes. (e) Real-time pH measurement of flowing tap water adding acid and base solution.

ToC

Small hysteresis carbon nanotube field-effect transistors (CNT-FETs) are studied by developing sorting method of CNTs and modifying the surface of CNT network. Using high quality CNT-FETs, a flexible pH sensor based on ion-sensitive FET mechanism is studied for industrial application is demonstrated for industrial drainpipe monitoring.

