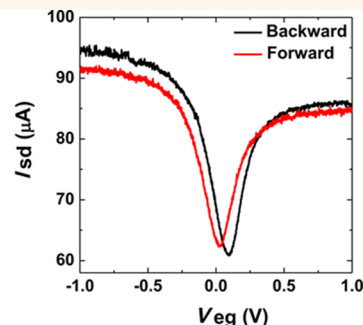
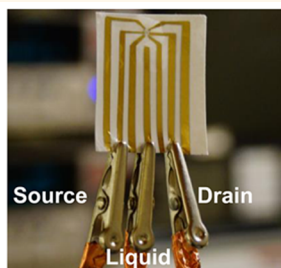
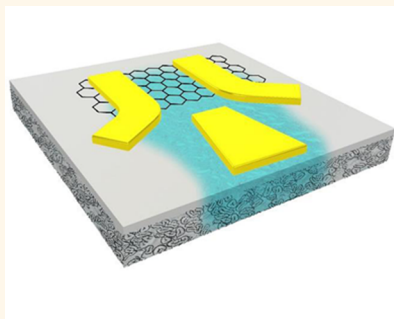


Aqueous Gating of van der Waals Materials on Bilayer Nanopaper

Wenzhong Bao,[†] Zhiqiang Fang,[†] Jiayu Wan,[†] Jiaqi Dai, Hongli Zhu, Xiaogang Han, Xiaofeng Yang, Colin Preston, and Liangbing Hu^{*}

Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742-4111, United States. [†]These authors contributed equally to this work.

ABSTRACT



In this work, we report transistors made of van der Waals materials on a mesoporous paper with a smooth nanoscale surface. The aqueous transistor has a novel planar structure with source, drain, and gate electrodes on the same surface of the paper, while the mesoporous paper is used as an electrolyte reservoir. These transistors are enabled by an all-cellulose paper with nanofibrillated cellulose (NFC) on the top surface that leads to an excellent surface smoothness, while the rest of the micro-sized cellulose fibers can absorb electrolyte effectively. Based on two-dimensional van der Waals materials, including MoS₂ and graphene, we demonstrate high-performance transistors with a large on–off ratio and low subthreshold swing. Such planar transistors with absorbed electrolyte gating can be used as sensors integrated with other components to form paper microfluidic systems. This study is significant for future paper-based electronics and biosensors.

KEYWORDS: liquid-gated transistor · mesoporous paper · paper sensors · MoS₂ · graphene · microfluidics

Paper electronics are particularly promising for low-cost diagnostics, since these devices can be potentially fabricated with scalable roll-to-roll processes.^{1–5} The mesoporous structure allows loading analyte directly inside paper, rich surface treatment, and new device configurations. These functionalities can enable a range of biosensing applications which are impossible to achieve on other substrates such as plastics. There are a few recent reports of transistors on paper,^{6–8} and extensive surface functionalization was conducted to achieve a smooth surface that is compatible with electronic devices; however, surface functionalization removes the mesoporous structure in paper rendering it unsuitable for microfluidic devices. Transparent paper based on nanofibrillated cellulose (NFC) has recently been demonstrated.^{9–11} These reports demonstrate a nanoscale smooth surface and

compatibility with electronics,^{6,7,12} however, such transparent paper is not porous enough to host liquid solutions effectively for microfluidic type sensing devices. Two-dimensional (2D) van der Waals materials such as graphene and MoS₂ have inspired enlightening investigations on their attractive physical and chemical properties^{13–18} and show wide applications in high-performance electronics and optoelectronics.^{19–21} 2D layered materials are usually mechanically deposited on various dielectric substrates and atomically flat layered insulators.^{22–27} Interactions between 2D materials and substrates greatly impact the mechanical and electrical performance of 2D material devices; *e.g.*, layered boron nitride (BN) substrate can improve the electrical mobility of graphene up to 1000000 cm⁻¹ V⁻¹ s⁻¹,²⁸ a 10-fold increase compared to the device made on SiO₂.²⁹ However, the complex

* Address correspondence to binghu@umd.edu.

Received for review July 25, 2014 and accepted October 5, 2014.

Published online October 06, 2014
10.1021/nn504125b

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and high-cost fabrication processes of these substrates continue to limit the larger scale application of 2D materials for electrical devices.

In this work, we report the first demonstration of a bilayer mesoporous nanopaper that reduces the surface roughness to nanoscale for 2D materials and is porous enough to contain liquid solutions. This bilayer nanopaper allows us to host high-performance liquid–electrolyte-based transistors with 2D materials deposited on the smooth surface of the bilayer nanopaper and the electrolyte absorbed in the porous side. Unlike traditional thin-film transistors (TFT) where source/drain and gate electrodes are separated on opposite sides of the dielectrics, all metal electrodes are now on the smooth surface of the bilayer mesoporous nanopaper. This simplified design can greatly reduce the fabrication process and cost. In our work, both graphene and MoS₂ transistors are demonstrated with high performance. A proof-of-concept pH sensor is also demonstrated on the basis of graphene transistor.

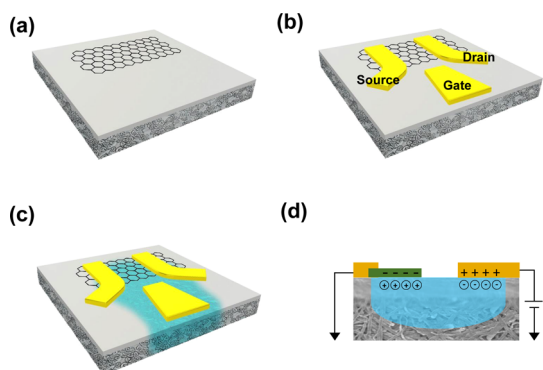


Figure 1. (a) Schematic of 2D materials exfoliated on a piece of bilayer mesoporous nanopaper, followed by (b) contact electrodes fabrication. (c) Liquid can be absorbed by the porous side. (d) Side view of a 2D material device on bilayer mesoporous nanopaper with charge and ion-distribution details.

These paper-based devices are potentially low-cost and fully biocompatible. Along with a simple but effective single-side transistor design, we take a crucial step toward paper-based microfluidic electronics for diagnostics, bioassays, and other functionalities.

RESULTS AND DISCUSSION

Our goal is to deposit van der Waals 2D materials on a piece of ultrasmooth paper, followed by fabricating metal contacts (Figure 1a,b). The smoothness of the paper surface is an important factor in achieving strong adhesion between 2D materials and surfaces of paper, as well as high electronic mobility. Meanwhile, one of the most promising applications of paper substrate is the liquid absorption capability that benefits from its mesoporous nature and excellent hydrophilicity. Therefore, we expect that 2D materials can be deposited on one side of paper, while the other side can also absorb liquid that directly contacts the 2D materials at the interface (Figure 1c), but the challenge here is that the ultrasmoothness and excellent water absorbency are two compulsory properties of regular paper. However, thanks to the hierarchical structure of wood fiber, the properties of paper can be tailored by combining micro- and nanoscale cellulose fibers to fulfill the two specific needs.

Morphology of the Bilayer Nanopaper. By combining the excellent liquid absorption ability of hardwood fibrous network with the superior surface roughness of NFC film, a bilayer structure of paper prepared by a two-step vacuum filtration was rationally designed to fit these stringent requirements (Figure 2a). In such bilayer nanopaper, a very thin layer of pure NFC is used to reduce the surface roughness, and a thick layer of unbeaten hardwood fibers network is used to provide superior liquid absorption capacity. Note that nanopaper is only a network of cellulose nanofibers possessing nanoscale pores that sharply reduce the liquid flow

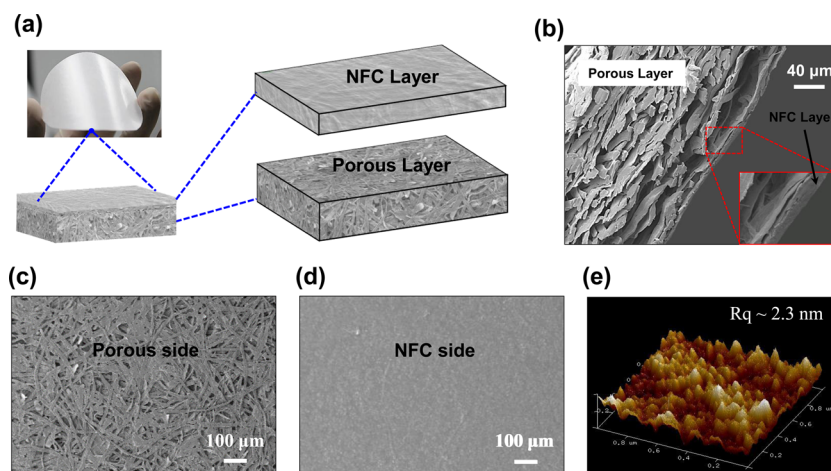


Figure 2. (a) Schematic bilayer structure of paper for ionic liquid-gated transistor; (b) photo of our paper with the smooth side toward viewer; (c) SEM image of rough side of paper showing the porous structure; (d) cross-sectional and (e) smooth-side SEM image of our paper; (f) AFM height image of smooth side of our paper (Roughness $R_q \approx 2.3$ nm, scanning area: $1 \mu\text{m} \times 1 \mu\text{m}$).

TABLE 1. Basic Information for Our Paper and Filter Paper

		grammage (g/m ²)	density (g/cm ³)
our paper	porous layer	70.4	0.34
	NFC layer	3.5	1.16
filter paper		71.0	0.48

rate inside paper. The thickness of NFC film in the bilayer nanopaper was thus tailored at a value of 2–4 μm to ensure the superior smoothness for the deposition of 2D materials and also to enable the permeation of liquids. The image in Figure 2a displays a rationally designed bilayer nanopaper with the smooth NFC side facing the observer, which appears shiny due to the specular reflection of light resulting from excellent surface smoothness. A scanning electron microscope (SEM) was applied to image the microscopic structure of the cross section, rough side, and smooth side of paper. As shown in Figure 2b, the bilayer configuration of the paper is clearly depicted. The NFC film was firmly attached to the micro-sized fibrous network, which is illustrated in the inset of Figure 2b. A highly porous structure is achieved by using unbeaten hardwood fibers, which ensures the prominent liquid absorbent capability of this paper (Figure 2c). Through this design, the paper not only possesses superior liquid absorbency but also has an ultrasmooth surface (Figure 2d) that fulfills the need of mechanical exfoliation of 2D material sheets on the smooth surface. Surface roughness is a crucial parameter for the deposition of 2D materials sheets on substrates. An atomic force microscope (AFM) was used to characterize the surface roughness of the smooth side of paper, and the AFM height image of smooth surface of the bilayer nanopaper is shown in Figure 2f. We see here a root-mean-square roughness (R_q) of 2.3 nm.

Liquid Absorbency. The 3D porous fibrous network enables liquid to wick in both lateral and thickness directions of paper under capillary force, which has been utilized to develop paper-based microfluidic devices for diagnostic purposes.^{30,31} We designed and prepared a paper with high water absorption capability for liquid-electrolyte-based transistors. First, the paper was cut into a rectangular shape (1.5 cm wide and 7 cm long) and then vertically dipped into deionized water for 1 min to allow water to diffuse along the paper under capillary force until a balance was reached between capillary force and weight of absorbed water in paper. The bilayer nanopaper has a higher porosity than filter paper (Table 1) due to the use of hardwood pulp that presents a stronger capillary force and a higher capacity of holding water within the paper. Therefore, our paper can absorb more water than filter paper (VWR International, LLC, diameter: 9.0 cm) in the same period and presents higher suction height during the measurement (Figure 3a).

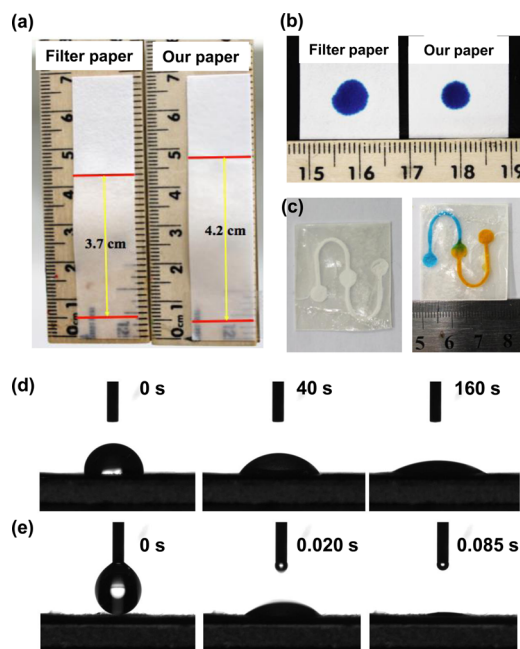


Figure 3. (a) Capillary suction height of filter paper and our paper (absorption time: 1 min); (b) lateral diffusion of water based dye on filter paper and our paper; (c) patterned paper before (left) and after (right) absorbing blue (20 μL) and yellow dye (20 μL) by capillary action; water intake capacity of (d) smooth side and (e) rough side of bilayer structural paper.

Water-based dye droplets with a volume of 3 μL were separately dripped onto the surface of filter paper and the mesoporous side of our paper using a pipet. Both paper samples rapidly absorbed the dye droplets in less than one second (see Figure 3b). Notice, however, that filter paper has large surface roughness (in micrometers), which is not compatible with fabrication of electronic devices at all. Our bilayer nanopaper also manifests the ability to control the lateral diffusion of liquid that guarantees sufficient liquid passing from the rough side to the smooth side of paper. Limited lateral diffusion of liquid in paper also facilitates the preparation of patterns with high resolution, which indicates that our paper also has the potential to fabricate paper-based microfluidic devices. Figure 3c shows a patterned bilayer nanopaper with absorbed dyes confined in the pattern which is defined by photolithography.^{30,32,33} A volume of 20 μL for blue and yellow aqueous dye solutions was added from left to right of the reservoir with respect to the image and distributed uniformly in the channel for 5 min by capillary force.

In this study, the penetration of liquids in the perpendicular direction of paper is also desirable for the liquid-gated transistor. Five microliters of water was dripped onto the smooth and rough side separately. As shown in Figure 3d, the volume of water droplet on the smooth side of paper decreases with the increasing time; it takes 180 s for paper to absorb most of the water. When the same volume of water was in

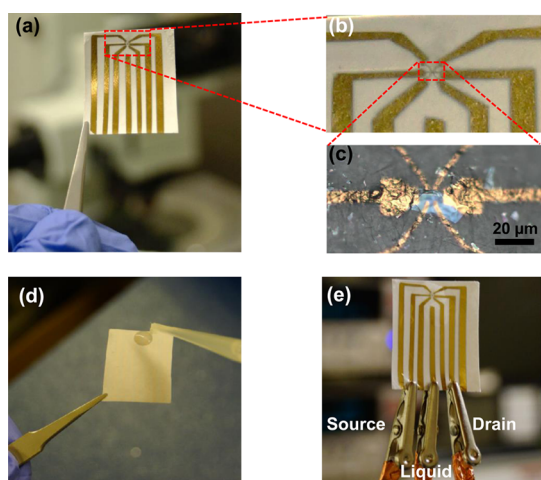


Figure 4. (a–c) Zoom-ins of an 8 nm thick graphene device fabricated on a piece of paper, the gold contacts extend to the bottom of paper for further electrical measurement. (d) Liquid can be absorbed into the highly porous back side. (e) Transistor measurement setup. The center electrode contacts the liquid absorbed.

contact with the rough mesoporous side of the paper, it was fully absorbed by paper in less than 1 s (Figure 3e). Therefore, the mesoporous side could be used as a reservoir to quickly absorb liquid and allow it to slowly penetrate through the smooth side to contact the target device.

Therefore, the excellent water absorption capability and superior surface smoothness of our bilayer nanopaper has the potential to combine the low cost, simplicity, portability of paper-strip tests with the traditional electrochemical detection of analyte.

Transistors on Paper. Mesoporous bilayer nanopaper with a surface roughness reduced to the nanoscale on one side is perfectly compatible with electronic devices. We prepared various ultrathin 2D materials on the smooth NFC side of the paper, fabricated devices from them, and studied their electrical properties (Figure 4a–c). In Figure 4c, an 8 nm thick few-layer graphene (FLG) sheet is mechanically cleaved¹³ on the NFC side, followed by a direct deposition of 50 nm thick gold electrodes with Hall-bar geometry using a unique shadow mask method.³⁴ Since the fabrication process is completely free of lithography and resists contamination, the cellulose paper remains in its original condition and the 2D material is also left uncontaminated. The liquid is then absorbed by the highly porous side and penetrates through the NFC layer to contact the 2D material while the whole device structure remains complete. Figure 4e shows a typical measurement setup of our “paper device.”

The charge carrier density is a key parameter to tune electrical properties of 2D materials. Usually, the controlling of surface carrier density can be achieved by electric-field tuning through carrier accumulation or depletion in a metal oxide semiconductor field effect transistor (MOSFET). For graphene and other

2D materials, regular dielectric materials are thermally grown SiO₂ or layered hexagonal boron nitride (h-BN). Recently, a different approach using ionic liquid or special electrolyte has been developed for 2D materials.^{35–38} The mechanism of this type of FET is based on an electrochemical concept. By controlling the gate electrode, the moving ions can form an electric double layer (EDL) at the electrolyte/channel interface. This new method is compatible to our “paper devices” perfectly by taking advantage of paper’s excellent hydroscopicity, and here, we first demonstrate working graphene/MoS₂ transistors on the paper gated by the polymer electrolyte absorbed inside the highly porous side of our paper.

In this study, the polymer electrolyte applied for “paper transistor” is lithium perchlorate (LiClO₄) dissolved in poly(ethylene oxide) (PEO), mixed with methanol. Using a standard two-probe measurement, the room-temperature source–drain current I_{sd} was measured for graphene/MoS₂ devices as a function of the electrolyte gate V_{eg} , which controls the carrier density n and type of charge carriers. A pronounced hysteresis is observed in these $I_{sd} - V_{eg}$ curves, which can be mainly attributed to the low ionic conductivity (*i.e.*, a slow polarization relaxation) of the electrolyte and the interfacial trapped charges. However, the transfer characteristics are reproducible as long as the sweep rate and direction of the electrolyte gate voltage are kept constant. A 6 nm thick graphene device displays prominent hole and electron-doped regimes in Figure 5a, with a minimum I_{sd} at the Dirac point, indicating continuous carrier modulation ability of V_{eg} under ambient conditions. In Figure 5b,c, MoS₂ devices display a thickness dependence: a relatively thin (15 nm thick) device (Figure 5b) displays an n-type unipolar behavior indicated by turning on of I_{sd} at positive V_{eg} while staying off at a window of negative V_{eg} . The 35 nm thick device (Figure 5c) shows good ambipolar behavior with a smaller window of the off-state that separates the electron and hole regions. The subthreshold swing S , defined by $dV_g/d(\log I_{sd})$ at the largest slope, is estimated to be about 90–150 mV/dec at room temperature for our typical MoS₂ devices, which is close to the theoretical limit of $kT(\ln 10)/e \approx 60$ mV/dec for the ideal MOSFET. The thinner MoS₂ device also exhibits a large on–off ratio ($>10^5$), which is as high as values obtained on SiO₂/Al₂O₃ substrates.^{15,39} Such values are much better than those achieved by organic semiconductors,⁷ indicating 2D materials on the ultrasmooth and porous bilayer nanopaper could be a promising platform for studying various 2D materials and future device applications.

Our “paper transistor” has promising liquid-based applications, and here we demonstrate its ability of pH testing. Acid solutions were made by addition of dilute H₂SO₄ solution in deionized (DI) water, and basic solutions were made by dissolving NaOH in DI water.

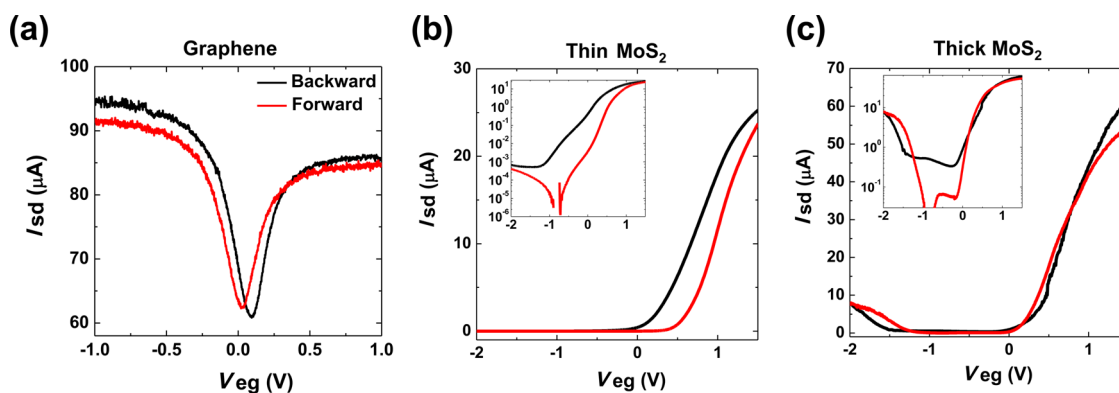


Figure 5. (a) Source–drain current (I_{sd}) vs electrolyte gate voltage (V_{eg}) for an 6 nm thick graphene device, (b) a 15 nm thick MoS_2 device, and (c) a 33 nm thick MoS_2 device. The source–drain voltage is 0.1 V for all devices. All measurements are performed at room temperature.

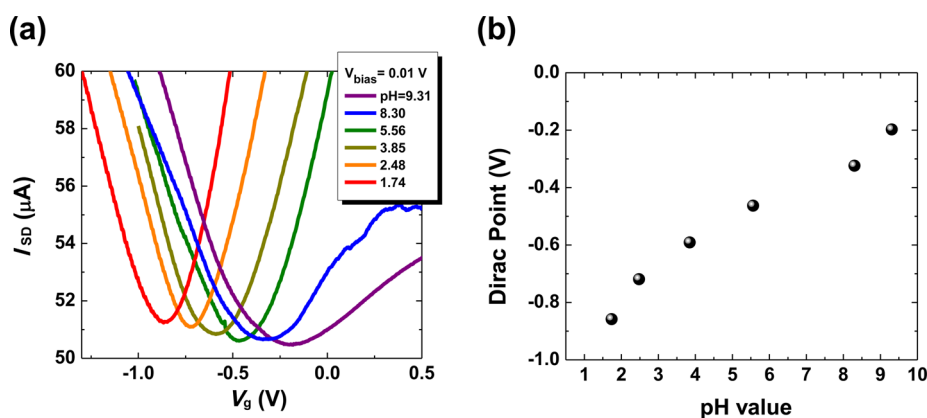


Figure 6. (a) Source–drain current (I_{sd}) as a function of V_{eg} , at pH values of 1.74, 2.48, 3.85, 5.56, 8.30, and 9.31. (b) V_{eg} value at the Dirac point as a function of pH value.

The pH value of each solution was determined by a pH meter (Mettler Toledo). After testing with one pH solution, the same paper device was immersed in deionized water for 5 min and then dried in air for more than 30 min before testing a different pH solution. The sweeping of V_{eg} is also fixed to the same direction and same speed (full sweep within 1 min) for each pH solution test. Figure 6a shows I_{sd} ($V_{sd} = 0.1$ V) plotted as a function of V_{eg} for a graphene paper device (5 nm thick) absorbed with various solutions with pH values ranging from 1.7 to 9.3. The Dirac points of the graphene paper device shifted in a positive direction with increasing pH values (the total shift depends on the size of the graphene sheet and aspect ratio of the junction). Such a positive shift with increasing pH value can be interpreted as the attachment of hydroxide ions, which act as electron scavengers and make graphene more p-doped.^{40,41} This clear pH-dependent electrical characteristics indicate that graphene paper

devices can be used as pH testers, and potentially other chemical or biological applications such as DNA, heavy-metal, glucose, or urine detection or in the detection of cancer biomarker.⁴²

CONCLUSION

We demonstrate high-performance liquid-gated transistors on a bilayer mesoporous nanopaper where the smooth surface is used to deposit 2D materials and the source, drain, and gate contacts and the mesoporous size is used to absorb electrolyte. Transistors with both MoS_2 and graphene are demonstrated, and MoS_2 transistors show an on/off ratio of $>10^5$. We further demonstrate the feasibility of using liquid-gated transistors for pH sensing. These devices are impossible to fabricate on traditional substrates such as plastic, regular paper, or glass and thus can enable a range of low-cost applications, especially for microfluidic based systems.

EXPERIMENTAL METHOD

Preparation of Bilayer Nanopaper. The porous side is made of micro-sized cellulose fibers with a highly porous configuration

and a porosity of 50–80% that guarantees the rapid liquid absorption capability by capillary force. Hardwood fibers have a length of about 1 mm and a width of approximately 20 μm ,

making it suitable for producing paper with more uniform formation, smoother surface, and higher bulking ability compared to softwood pulp.

Liquid Absorbency Test. To evaluate the capacity of water absorbency by capillary force, the capillary suction height of paper is measured with a Klemm method (ISO 8787:1986 paper and board – determination of capillary rise), and an OCA20 contact angle measuring instrument was used to evaluate the water intake capacity on both sides of the bilayer nanopaper.

Fabrication of Transistors on Paper. Various layered materials (graphene, MoS₂, WSe₂, and h-BN are tested in this work) can be successfully mechanically exfoliated on the smooth NFC side using the Scotch tape method; however the size of exfoliated sheets is usually smaller than the ones on the regular SiO₂ substrates, probably due to larger surface roughness, which indicates future efforts to improve the smoothness of the NFC surface are still required. The exfoliated sheets were then aligned to a silicon shadow mask with an electrode pattern under the optical microscope, followed by a direct deposition of 30–50 nm thick gold through the mask in the electron-beam evaporator.

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

Supporting Information Available: Details of pH-sensing measurement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgment. L.H. thanks the Air Force Office of Scientific Research (AFOSR) Investigator Program for their funding. Z.F. thanks the China Scholarship Council (CSC) for their financial support.

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