Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Identification of water-infiltration-induced electrical energy generation by ionovoltaic effect in porous CuO nanowire films

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Experimental Section

Synthesis of Cu nanowires (NWs)

Cu NWs were synthesized by polyol method that was introduced in the previous study. During the synthesis process, 2 mmol of CuCl (Junsei, 95%), 0.3 mmol of NH_4Cl (Daejung, 99.5%) and 30 ml ethylene glycol (Daejung, 99%) were added into a round-bottom flask. Then, 6 mmol of oleylamine (Sigma-Aldrich, 70%) was slowly added to the above solution and mixed with a magnetic stirrer. Here, the CuCl was used as a precursor, NH_4Cl and oleylamine were used as surfactants, and ethylene glycol was used as a reducing agent. The temperature was heat up to 198 ℃ in 20 min and refluxed for 15 min. With the temperature continuously rising at a constant rate, the reducing ability of the ethylene glycol gradually increased and the Cu seeds finally grew into nanowires. The Cu NWs were characterized by field emission scanning transmission electron microscope (FE-SEM) (S-4800, Hitachi), high resolution X-ray diffractomer (HR-XRD) (SmartLab, Rigaku) (Fig. S3a) and Raman spectrometer (DXR2xi, Thermo) (Fig. S4).

Preparation of porous CuO nanowires film (PCNF)

A PCNF was obtained through a drop-casting method and an oxidation process on a hot plate. First, 7 mg of Cu NWs were dispersed in 2 ml of hexane solution. Next, the Cu NWs were drop-casted on a 1.5 cm × 6 cm glass substrate to obtain a porous Cu NWs film. Finally, the Cu NWs film was placed on a hot plate and proceeded oxidation at 350 ℃ to get PCNF. The PCNF was characterized by FE-SEM (S-4800, Hitachi) and HR-XRD (SmartLab, Rigaku) (Fig. S3b). The surface potential of the PCNF was investigated by zeta potential (Malvern, ZEN3600) (Fig. S10) and scanning Kelvin probe microscopy (SKPM) measurements (Park Systems, XE-100) (Fig. S11)

Performance characterization of the PCNF

The open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) were measured with nanovoltmeter (Keithley 2182A) and picoammeter (Kethley 6485), respectively. Both electrodes of the measuring equipment and the PCNF were well connected. All measurements were performed at room temperature (25 ℃, 20 % RH).

Performance of turning on LED

An LED could be turned on by infiltrating seawater droplets and maintained about 250 s, which showed the feasibility as a power generator using ambient water including seawater, tap water and river water. This result can be determined from the actual videos (supplementary video 1 and 2).

Supplementary Analysis

Analysis 1. Characterization of the porous CuO nanowires film.

The porous CuO nanowires film (PCNF) was manufactured by drop-casting method and oxidation process. From the SEM cross section image (Fig. S1a), the thickness of the PCNF was ~123 μm. Besides, the surface contact angle of the PCNF was about 8.6º (Fig. S1b), indicating that the surface had a hydrophilic property.

Analysis 2. Adhesion test for the PCNF

Through changing the PCNF thickness, the adhesion of CuO nanowires to glass substrate was analyzed. In detail, the PCNF was completely soaked in the water, then dried it and measured the thickness. The process was repeated 5 times, and the thickness of the PCNF did not change much, which was shown in the table. The result fully showed that the PCNF maintains its form in water, which indicates the feasibility of application in the actual environment.

Analysis 3. Experimental analyzation of the contact line behavior.

To further analyze the behavior of the contact line, measurements were performed under the same environment with the PCNF surface opened and covered with a glass (Fig. S6). When the PCNF surface was covered with a glass, the movement of the contact line continued longer than that of the open condition. The maximum Voc under the two conditions were the same, and the electrical energy was generated for a longer time when the surface was covered with a glass. As water droplet infiltrated into the PCNF, meanwhile, water evaporation occurred on the surface. Here, the evaporation of water on the PCNF surface only affected the duration of the electrical energy generation but not the maximum Voc. Therefore, we proved that the electricity generated by the PCNF only depended on the water infiltration phenomenon.

Analysis 4. Experimental analyzation of the ions effect.

The effect of ions on the PCNF was further illustrated by the following experiments. 5 μl of water droplet (NaCl solution, 0.01 M) started to infiltrate into (-) electrode of the PCNF and a Voc of ~0.3 V was generated (Fig. S12a). After about 35 seconds, 5 μl of water droplet (NaCl solution, 0.1 M) infiltrated into (+) electrode of the same PCNF. At this time, the initially produced electrical energy gradually decreased, and with the inversion of the electrical signal, a Voc of ~ - 0.15 V was finally generated. It further explained that the ion concentration of the water droplet infiltrating from the (+) electrode was higher than that of the water droplet infiltrating from the (-) electrode, thereby trapping more holes and causing more carriers movement during the infiltration from the (+) electrode. In contrast, a water droplet (NaCl solution, 0.01 M) was infiltrated from the (-) electrode, and after a certain period time, the same water droplet was infiltrated again from the same location (Fig. S12b). The *V*oc did not change at this time, which showing that the electrical energy generated was certainly dependent on the ion concentration. Moreover, other anions also had similar behavior to the chloride ion. As shown in Fig. S13, the *V*oc increased as the concentration of the NaBr solution increased. The result indicated that more ionic solutions could generate electrical energy *via* infiltrating into the PCNF.

Analysis 5. Stability test for the porous CuO nanowires film.

The porous CuO nanowires film (PCNF) had good stability. When 5 μl of water droplet (NaCl solution, 0.001 M), similar to a tap water, repeatedly infiltrated into a PCNF, the *V*oc produced each time was similar (Fig. S15). The results showed that the performance of PCNF did not be degraded even after repeated use, which further proved the feasibility of usage in actual applications.

Table. Change of PCNF thickness after soaking in the water.

The number of soaking time	**1st**	**2nd**	**3rd**	**4th**	**5th**
Thickness of the PCNF	130 μm	129 μm	129 μm	127 μm	126 μm

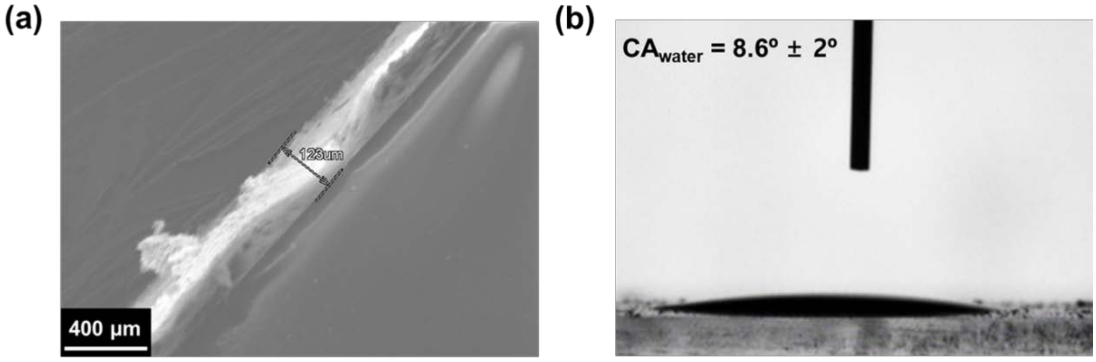

Fig. S1 (a) Cross section SEM image of the PCNF. The thickness of the PCNF was ~123 μm. (b) Contact angle of the PCNF shows that the surface was hydrophilic.

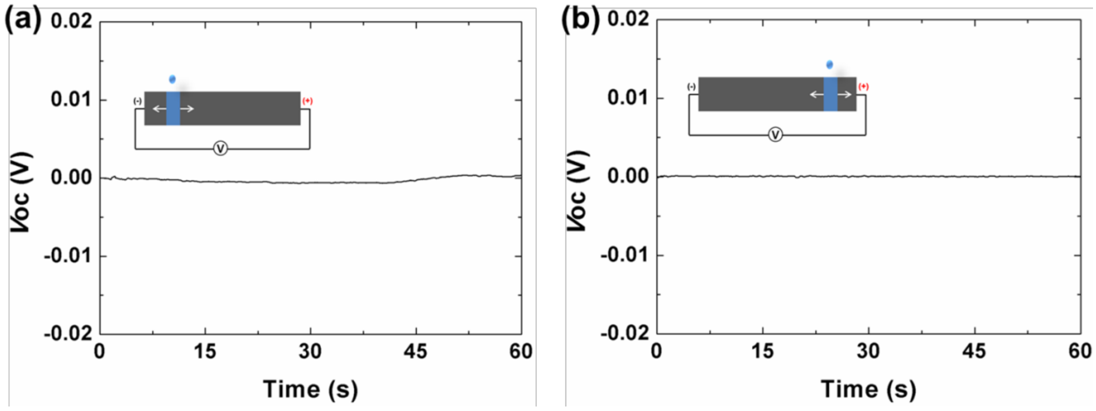

Fig. S2 No electrical energy was generated when water droplets (NaCl solution, 0.01 M) infiltrated slightly to the (a) left or to the (b) right position of the PCNF.

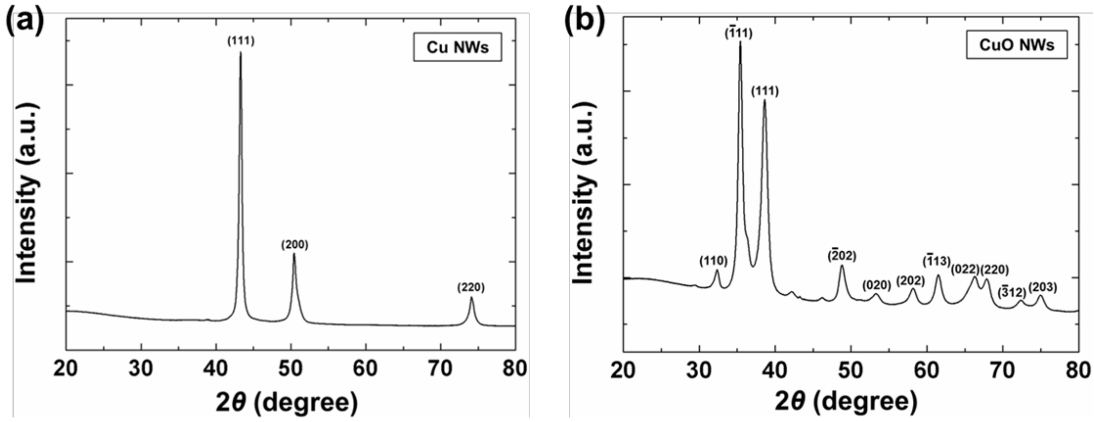

Fig. S3 XRD pattern of (a) Cu nanowires and (b) CuO nanowires.

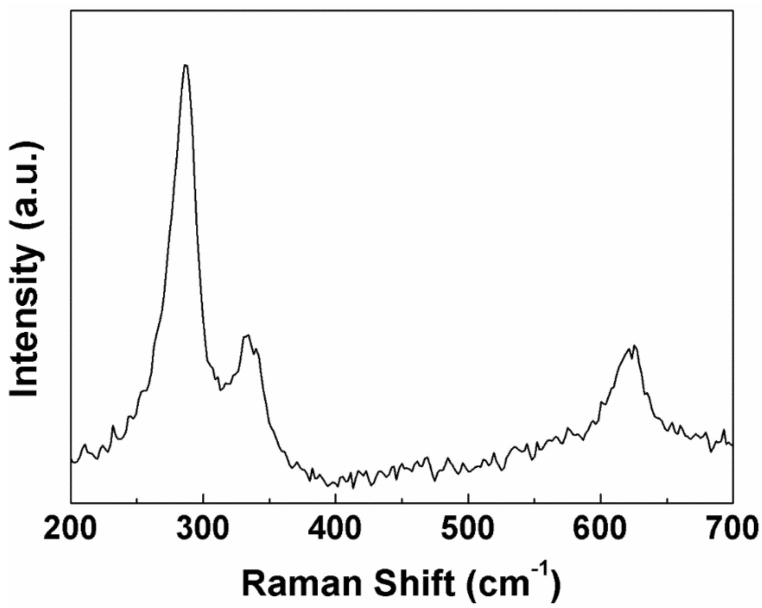

Fig. S4 Experimental Raman spectra of CuO nanowires.

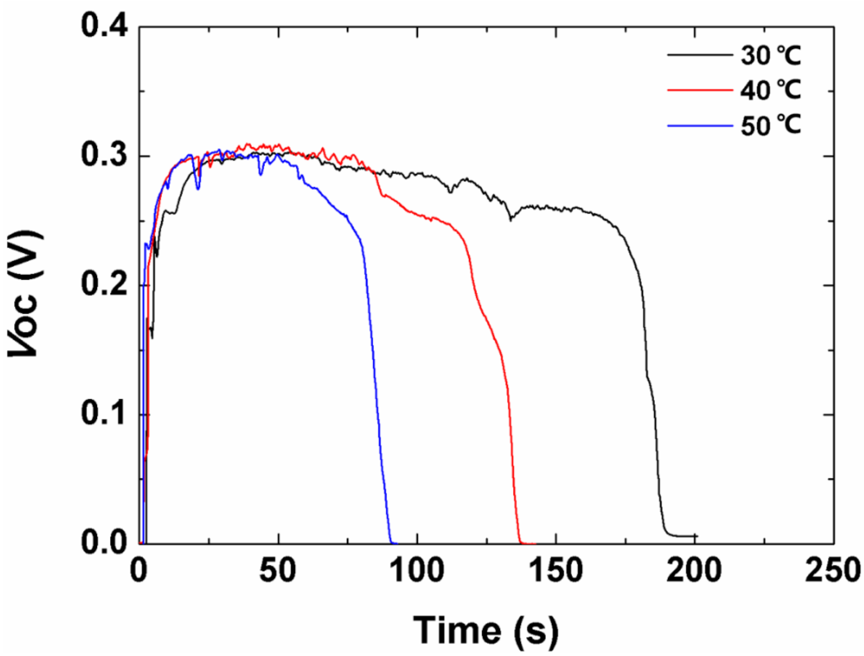

Fig. S5 *V*oc according to the environmental temperature.

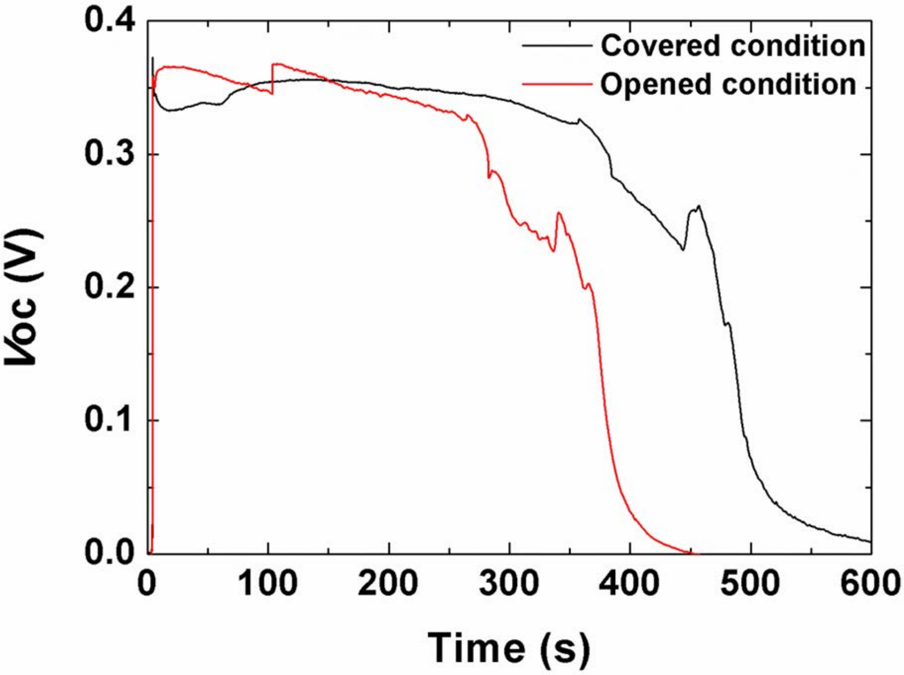

Fig. S6 *V*oc at covered and opened surface conditions.

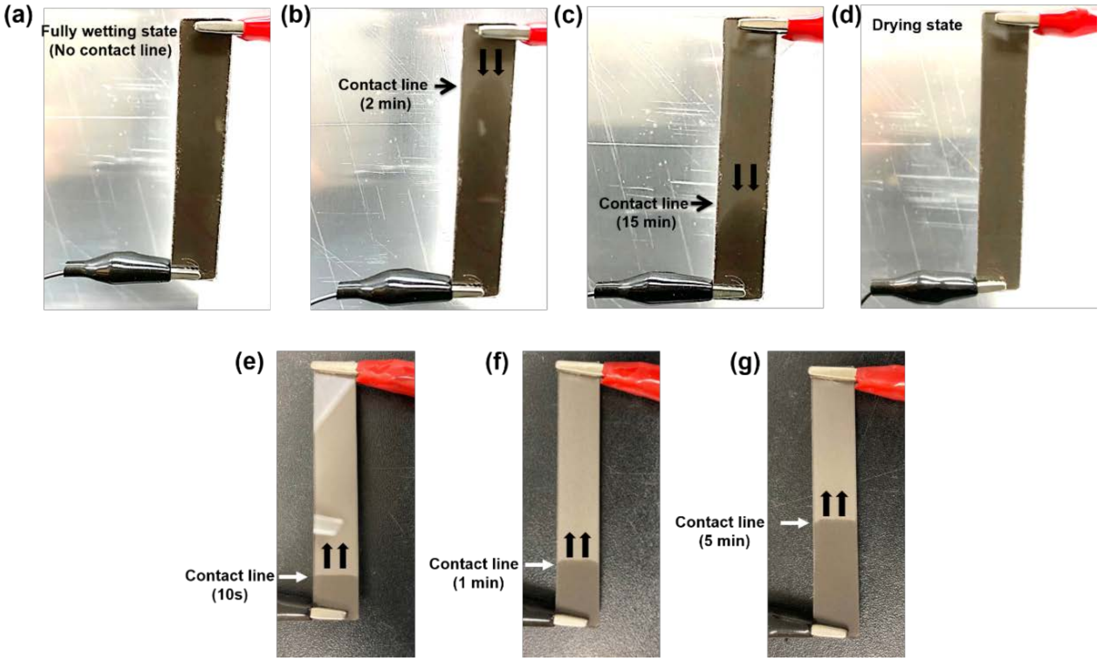

Fig. S7 Actual images of (a-d) drying process and (e-g) infiltrating process.

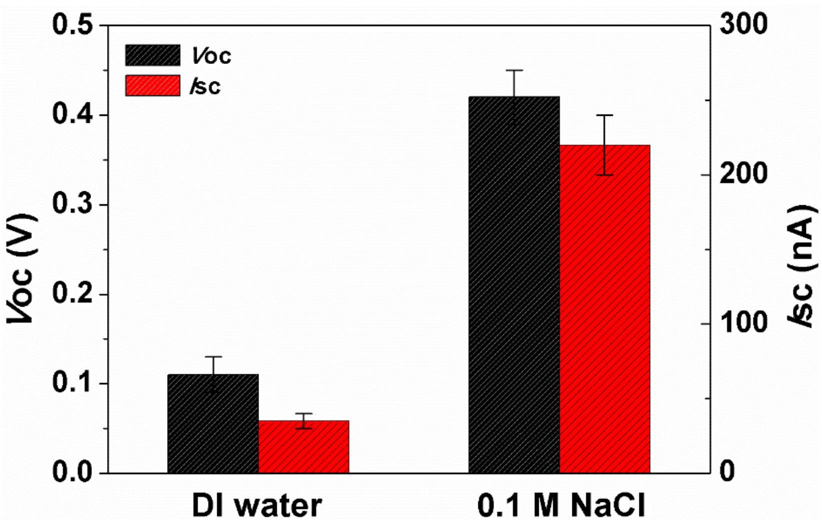

Fig. S8 Measured *V*oc and *I*sc using DI water and 0.1 M NaCl solution.

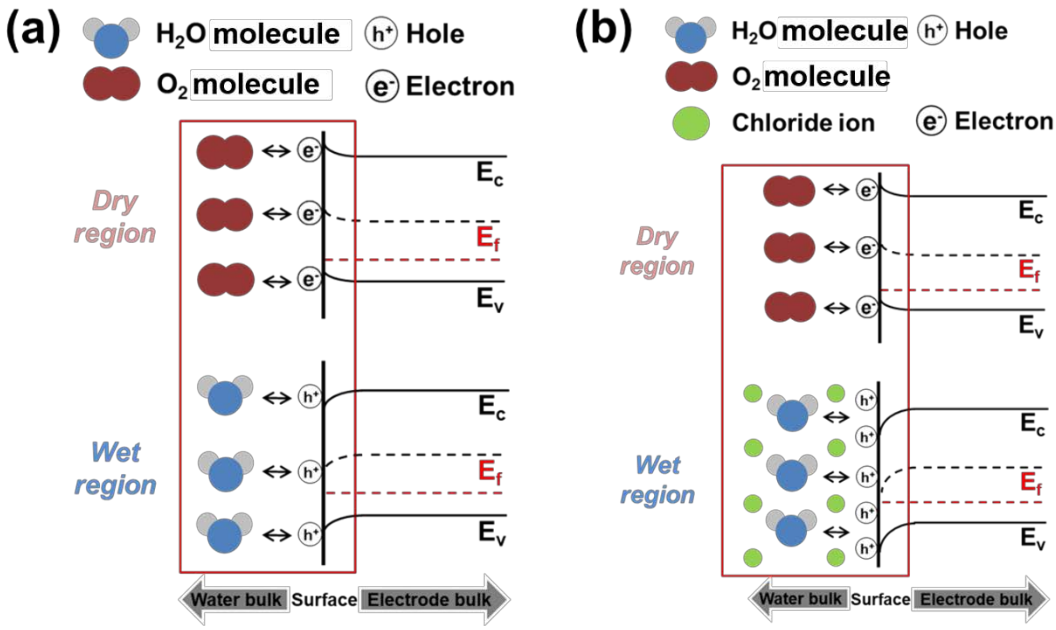

Fig. S9 Surface energy band structure of dry and wet regions. (a) At the dry region, the electrons were trapped by the oxygen molecules, which caused an upward band bending (conduction band (E_c) and valence band (E_v)). At wet region, when DI water infiltrated into the PCNF, the holes were trapped by the water molecules, which caused a downward band bending. (b) When NaCl solution infiltrated into the PCNF, more holes were trapped by the chloride ions, which also caused a downward band bending with a higher magnitude of the band bending than that of when DI water was in contact.

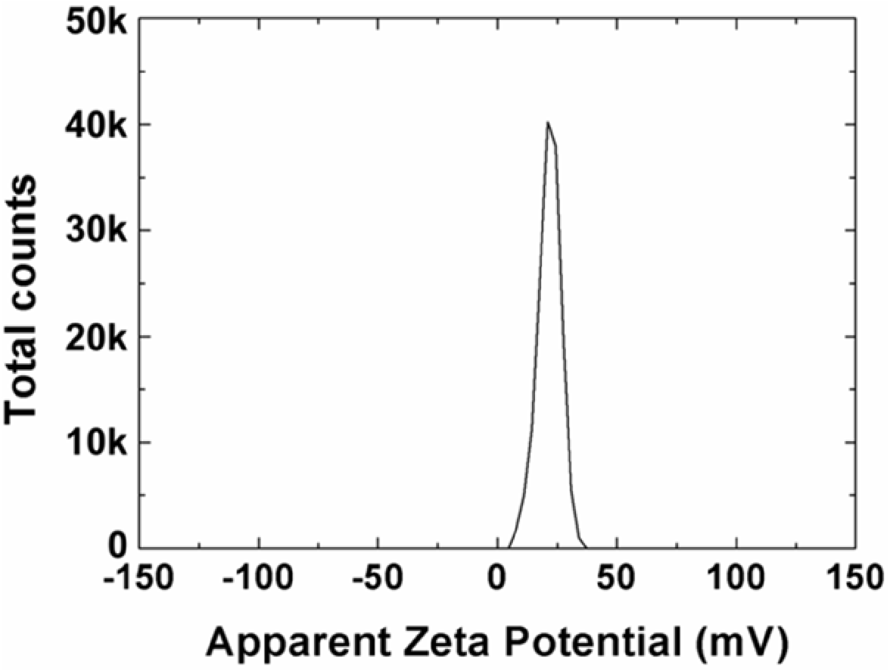

Fig. S10 Measured zeta potential of PCNF.

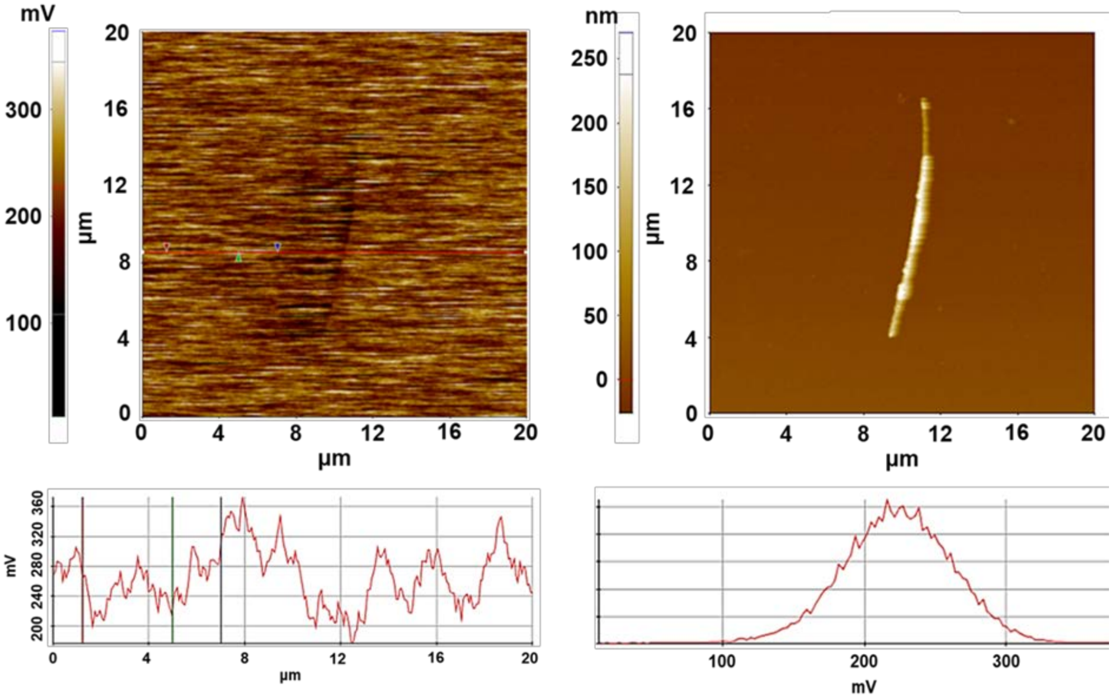

Fig. S11 Measured surface potential of the PCNF by scanning Kelvin probe microscopy.

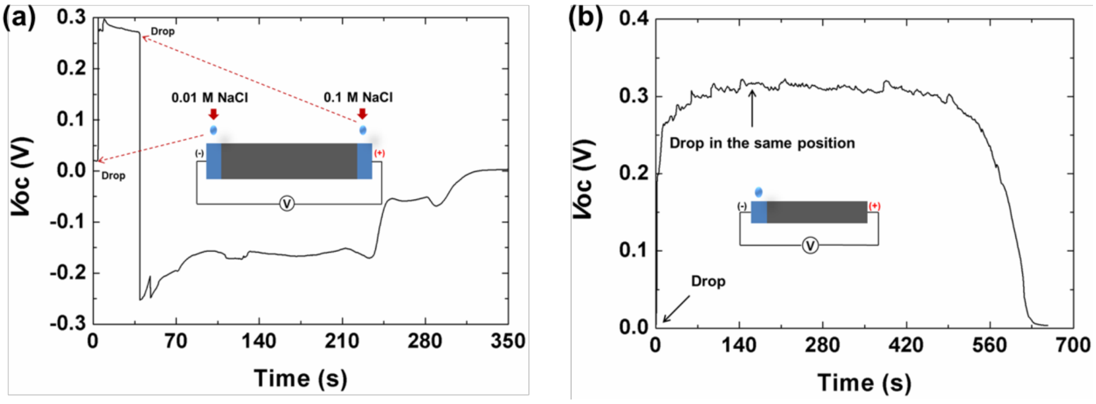

Fig. S12 (a) *V*oc by using different concentration of NaCl solution. First, a water droplet (NaCl solution, 0.01 M) was infiltrated into the (-) electrode of PCNF, ~0.3 V was generated. At this time, a water droplet (NaCl solution, 0.1 M) was infiltrated at (+) electrode of PCNF. The electrical signal was inverted, producing a *V*oc of ~ - 0.15 V. (b) The *V*oc did not change when the same water droplet infiltrated into the same position in the process of generating electrical energy.

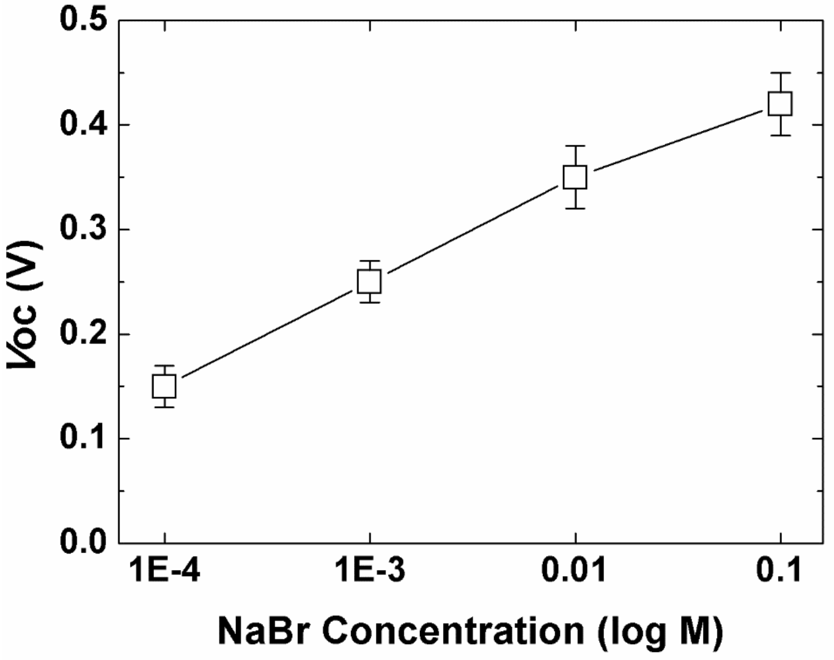

Fig. S13 The influence of Br^- ion on electricity generation. The *V*oc was enhanced as the Br^- concentration increased.

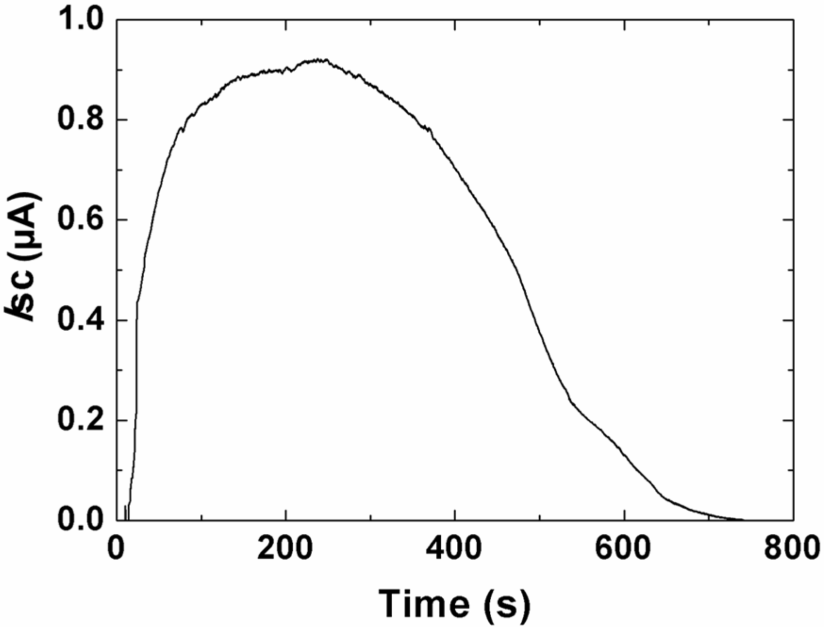

Fig. S14 *I*sc generated when seawater (Jeju Island) was infiltrated into eight PCNFs connected in series.

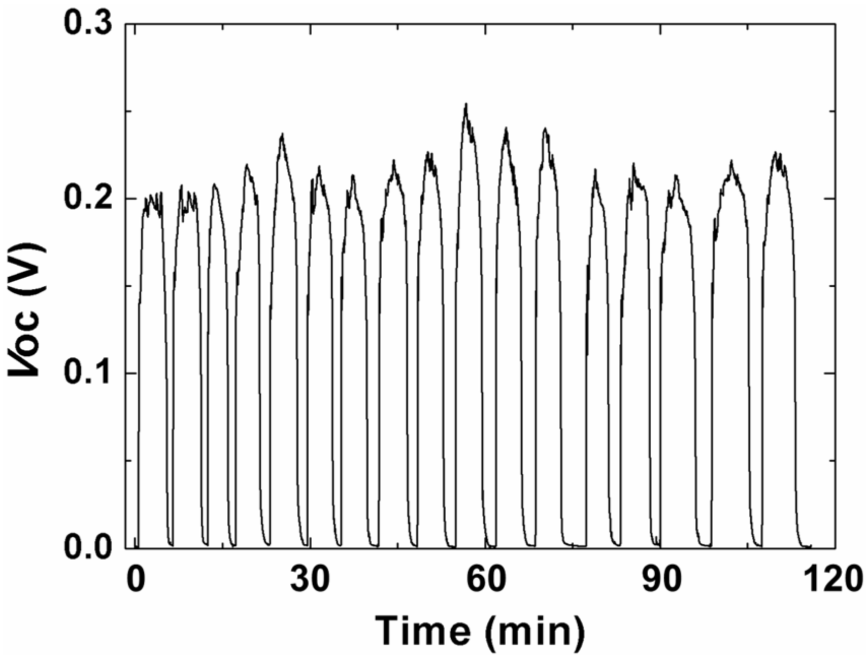

Fig. S15 Stability test for the PCNF. When a water droplet (NaCl solution, 0.001 M), similar to a tap water, repeatedly infiltrated into the PCNF, a constant *V*oc was generated.