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Direct Metal Transfer on Swellable Hydrogel with Dehydration-Induced Physical Adhesion

Shogo Himori,* Riku Takahashi, Aya Tanaka, and Masumi Yamaguchi

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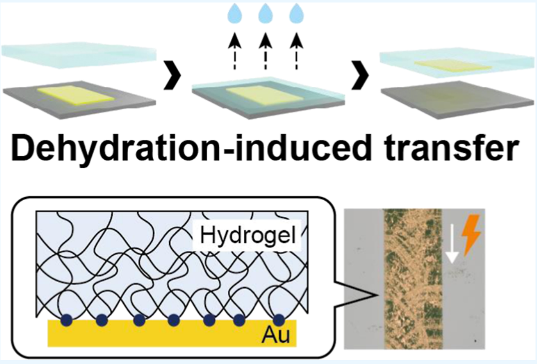
ABSTRACT: Composites of hydrogels and metals are gaining interest because of each material's unique properties. However, the stable adhesion of metals on hydrogels is challenging due to the mechanical mismatch at the soft−hard interface and the liquidity of the water components in hydrogels. We propose a facile physical-adhesion method that involves the dehydration process of hydrogels to transfer metals from a glass substrate. This method is based on the hydrophobic interaction between polymer chains and metals and is stable, even in water. Continuous metal wiring was achieved on a swollen hydrogel, and electrical conduction was effective for a soft electronic device. Therefore, our method could be a versatile method for integrating hydrogels and metals.



1. INTRODUCTION

Hydrogels are a type of soft, wet material containing large amounts of water in a three-dimensional network of polymer chains.[1] Due to their flexibility, good biocompatibility, and mass-permeability, hydrogels are attracting interest from a wide range of research fields, including sensing,[2−4] robotics,[5,6] energy harvesting,[7,8] and biomedical science.[9−13] Metals, which are dry and hard materials, exhibit excellent properties different from those of hydrogels, such as high electrical conductivity and high catalytic activity.[14−16] Therefore, if these different materials can be integrated, unique composites can be produced by taking advantage of their individual properties. However, there is a mechanical mismatch at the interface between hydrogels and metals, which have Young's moduli of $<10^6$ and $>10^{10}$ Pa, respectively,[17,18] and works against the adhesion of both materials.[19] Hydrogels also have adhesion challenges caused by their abundance of water, which easily changes neighboring molecules and provides little force transfer.[20] The weak interaction of hydrogels with metals is easily canceled by the large deformation due to hydrogel swelling.[21]

To achieve strong adhesion on a hydrogel surface with dry and hard materials such as metals, methods have been proposed of introducing an adhesive layer at the soft−hard interface with a chemical binding site[22] or physical entanglement of polymer networks.[23,24] However, there are still limitations in terms of time constraints on adhesion opportunities, either during gelation or to the ready-made hydrogels, in addition to the complicated fabrication process. Direct adhesion can reduce a step in the fabrication processes for introducing the adhesive layer, but it is limited to specific hydrogels with adhesive properties.[25−27] While a facile and versatile method for directly adhering wet hydrogel materials has not been established, polymer films without water components have recently been used for direct metal transfer due to their tackiness in soft elastomer-based electronics,[28] organic transistors,[29] and two-dimensional transistors.[30,31] Metals retain their highly ordered structure on a rigid substrate even after transfer through flexible polymer films, meeting the delicate requirements of precise electronics.[32]

We propose a method of transferring metals to hydrogels by dehydrating the hydrogel surface to make it behave as a dried polymer film. Gold, a model metal, was successfully transferred to a hydrogel surface in a patterned shape on a supporting substrate. The transferred Au on the swollen hydrogel exhibited high electrical conductivity, 3.24×10^6 S/m, which is effective for soft electronic devices. Because of the promising versatility of this transfer mechanism, our method is expected to be further improved for directly adhering hydrogels to metal layers.

2. RESULTS AND DISCUSSION

2.1. Fabrication of Gold-Transferred Hydrogels. To demonstrate that robust hydrogel-metal adhesion can be obtained, we attempted two types of dehydration-induced

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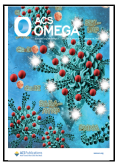

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transfer, one using a hydrogel immediately after polymerization (preswelling) and the other using a hydrogel swollen after polymerization (postswelling). We used polyacrylamide gels (swelling ratio α = 1.47) as model swellable hydrogels and transferred a thin Au layer (thickness = 20 nm) onto the hydrogels from a glass-supporting substrate. In the preswelling transfer, the hydrogel film was directly fabricated on the Au layer (Figure 1a). The as-prepared hydrogel was then dehydrated, followed by exfoliation of the hydrogel from the supporting substrate. During postswelling transfer, the hydrogel film was fully swollen with water, then excess surface water was removed and placed on the Au layer (Figure 1b). After dehydration under this condition, the hydrogel was reswollen with water and then exfoliated from the supporting substrate.

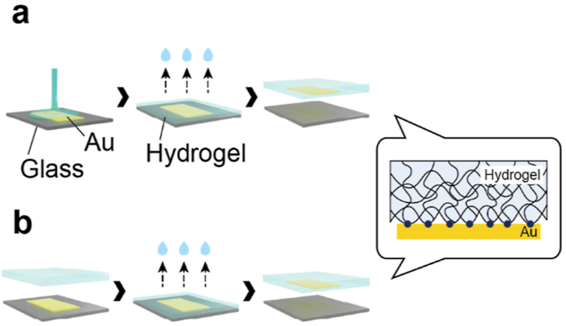

Figure 1. Schematic illustration of the dehydration-induced transfer method. (a,b) Fabrication procedure of pre- (a) and post- (b) swelling transfer.

As a result of preswelling transfer, the Au layer was successfully transferred onto the hydrogel surface (Figure 2a). Metal adhesion was also maintained after a large deformation of the hydrogel due to swelling (Figure 2b). This indicates that the adhesion is sufficiently strong to tolerate the increase in the volume and moisture content. Since the interfacial strength between the hydrogel and Au was larger than the strength within the bulk Au, the Au was finely divided into smaller pieces after the hydrogel swelled, as shown in Figure 2c. Similarly, the Au adhesion on the swollen hydrogel was successfully achieved by postswelling transfer (Figure 2d). 25% portion of water was evaporated from the hydrogel during the dehydration process, and hydrogel cracking was not observed because the horizontal deformation of the hydrogel during dehydration was suppressed by sandwiching it with coverslips. Some wrinkles were produced after the transfer due to the roughness of the hydrogel surface but did not result in breakage (Figure S1). The transferred Au was stably adhered without any subdivision after at least 1 h of immersion in water (Figure 2e) because the hydrogel was fully swollen before exfoliation from the supporting substrate. Since the continuity of Au seemed to be maintained in the enlarged image shown in Figure 2f, we discuss its applicability as electrical wiring later. The minimum transferable size of the Au square was 0.2 × 0.2 mm, and less than 0.1 × 0.1 mm was not successfully transferred (Figure S2).

The proposed method was examined for transferring metals to both sides of the hydrogel surface (front and back) by repeating the fabrication process twice. In this experiment, different types of metals (Au and Pt) were transferred to each side of the hydrogel surface. The results of this dual-sided transfer (Figure S3) indicate that transfer to both sides is possible, and the transferable metal is not limited to Au but can be extended to Pt. The versatility of the dehydration-induced transfer was also examined with other materials. Figure S4 shows the Au-transferred hydrogels with different hydrophilicity, which are made from *N*-(2-hydroxyethyl)acrylamide (HEAAm), acrylamide (AAm), and *N*,*N*-dimethylacrylamide hydrogel (DMAAm). All hydrogels were transferred by Au using the same dehydration process in the preswelling transfer. Since the poly-AAm (PAAm) hydrogel indicated higher yield compared with the other two hydrogels, the dehydration condition should be optimized for each material. As shown in Figure S5, Ag and Cu layers can be transferred on PAAm hydrogels with the postswelling transfer. These results indicate that dehydration-induced transfer can be applied to diverse hydrogels and metals. In the following discussion, we used Au and PAAm hydrogels as model materials.

2.2. Adhesion Mechanism of Dehydration-Induced Transfer.

To explore the effectiveness of the dehydration process, the successfully transferred area of Au was observed at each dehydration ratio (Figure S6). The Au was transferred onto fully swollen hydrogels by postswelling transfer. The yield of the transfer increased as dehydration increased. This indicates that the dehydration process improves the adhesion between the hydrogels and Au. The increase in yield is obvious, while the dehydration ratio is not so obvious (less than 10%). The transferable Au is in contact with the surface of the hydrogel, and water at the hydrogel surface is easily removed compared to that inside bulk hydrogel. The surface evaporation should be further investigated to understand more detailed phenomena of the dehydration-induced transfer. When the hydrogel was exfoliated immediately without the

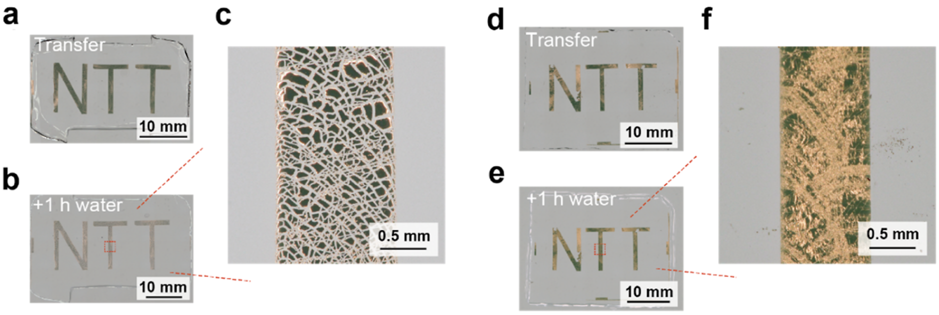

Figure 2. Optical images of Au-transferred hydrogels. (a,b) Hydrogel fabricated by preswelling transfer taken immediately after transfer (a) and after swelling in water for 1 h (b). (c) Expansion of red-dashed square in (b). (d,e) Hydrogel fabricated by postswelling transfer taken immediately after transfer (d) and after immersion in water for another 1 h (e). (f) Expansion of red-dashed square in (e).

dehydration process, however, Au was not transferred to the hydrogel. In addition, Au was not transferred when the hydrogel was placed on Au that had already been immersed in water, incubated for another 1 h, and then peeled off. These results indicate that the hydrogel should be placed on Au in the air for transfer, and physical adhesion enhances in air and even in water.

The adhered interface was observed by SEM (Figure S7). The image contains a cross-section of the hydrogel and the surface of the transferred Au, and the cross-section of the Au is not obvious due to its thinness (several tens of nm). The porous hydrogel and solid Au show different structures, but the adhered interface appears smooth. Fine wrinkles on the Au surface were induced by the flexibility of the hydrogel, but the minor deformation was not enough to cause a fracture. Adhesion strength was evaluated by conducting a 90° peeling test (Figure S8). Gold substrates were fabricated with a Cr adhesive interlayer to suppress Au exfoliation from the glass substrate, and hydrogels adhered to the Au substrate by dehydration process in the pre- and postswelling transfer. Adhesive strength was evaluated from the peeling force at constant, which means that the sample peeled from the substrate.[23] However, the hydrogels ruptured before the peeling force reached constant, indicating that the adhesion strength induced by hydrogel dehydration is greater than the strength of the hydrogel itself. We assumed that the adhesion strength induced by pre- and postswelling transfer is greater than 35.2 and 4.5 N/m, respectively. The value difference is the difference in the physical properties of the hydrogels due to the swelling state.

On the basis of the experimental results, we introduce a dehydration-induced transfer mechanism, as shown in Figure S9. Since hydrogels contain a large amount of water, there is little exposure of polymer chains to the surface. Therefore, it is difficult for hydrogels to contact with the substrate. The dehydration process decreases the moisture content in hydrogels and increases the amount of the exposed polymer chain. Hydrophobic interactions are made at the contact points between polymer chains and Au and enhanced even in water.[33] Gold is transferred to the hydrogel by exfoliation when the interaction between them is greater than that between Au and the glass substrate. The proposed method addresses the two adhesion challenges between hydrogels and metals, as mentioned in the introduction. One is the liquidity of hydrogels, and the other is mechanical mismatch, which is mitigated by stiffening the hydrogel due to dehydration.[34] Since our method is based on a hydrophobic interaction, various metals can be transferred onto various types of hydrogels. This versatility should be explored in a future study.

2.3. Electrical Properties of the Transferred Gold Layer on Hydrogels.

The adhered Au by postswelling transfer was a continuous on the swollen hydrogels; thus, application to electrical wiring was examined. When the transferred Au was used as a component of a light-emitting diode (LED) circuit, the LED was successfully lit (Figure 3a, b) and turned off when the composite was removed. The transferred Au showed conductivity as an electrical path, and the composite can be used as electrical wiring in soft electronics. Since the Au transferred with our method is exposed to the external environment without being covered by adhesive layers, Au can be further studied as a sensing electrode.

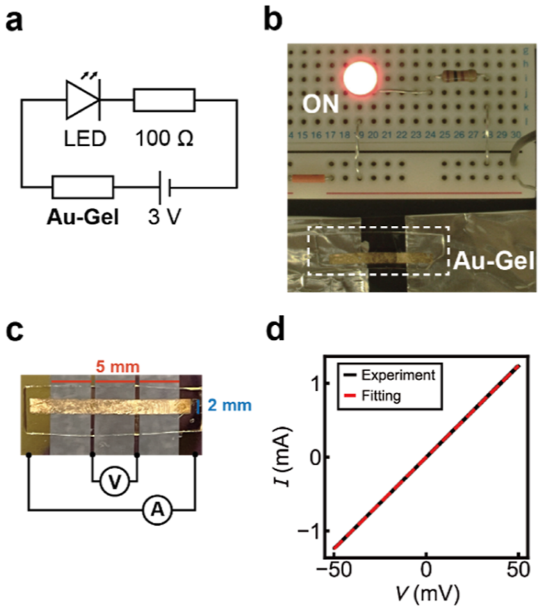

Figure 3. Fundamental electrical properties of Au fabricated by postswelling transfer. (a) Circuit diagram for demonstration of LED lamp. (b) Circuitry partially made of Au-transferred hydrogel to power LED lamp. (c) Photograph of Au-transferred hydrogel on electrodes for four-point probe measurement. (d) Current−voltage curve obtained from (c).

To understand the electrical conductivity of transferred Au on swollen hydrogels, we conducted a four-point probe measurement (Figure 3c). The obtained current was linear over the scanned potential range (−50−50 mV), and conductivity was calculated as $3.24 \pm 0.22 \times 10^6$ S/m (n = 3), as shown in Figure 3d. This value is greater than those of previous hydrogel-based conductive materials and comparable to those of highly conductive elastomer-based materials.[35,36] The proposed method transfers Au directly from the substrate, thus preserving the connectivity within Au almost as if it was sputtered onto the rigid and flat surface. While Au transferred on hydrogels is not suitable as a conductor with large deformation, we expect to apply this material as a conductor with little deformation due to its facile fabrication process and effective electrical transmission.

2.4. Water-Responsive Electrical Wiring.

While Au adhered on hydrogels by preswelling transfer is divided into small pieces during hydrogel swelling, the geometry of Au returns to a continuous piece by dehydration due to a deformation principle of hydrogels. Therefore, we examined the recovery of conductivity by rearranging the Au pieces induced by the deformation of the hydrogel (Figure 4). A piece of Au was transferred onto a hydrogel film with by preswelling transfer, and the current through both edges of the Au piece was obtained. The current flowed at the beginning of the electrical recording since the hydrogel was dehydrated as it was transferred. However, the Au-hydrogel exhibited an insulative property immediately after the addition of water due to the Au segmentation by hydrogel swelling. After removing the excess water from the hydrogel surface, the current recovered after 100 s and reached saturation after 200 s. The current ON/OFF cycle was repeated three times, and the recovered current was similar for all cycles. This indicates that Au-hydrogel composite integrates the conductivity of Au and swellability of hydrogel and recovers the conductivity by rearranging the

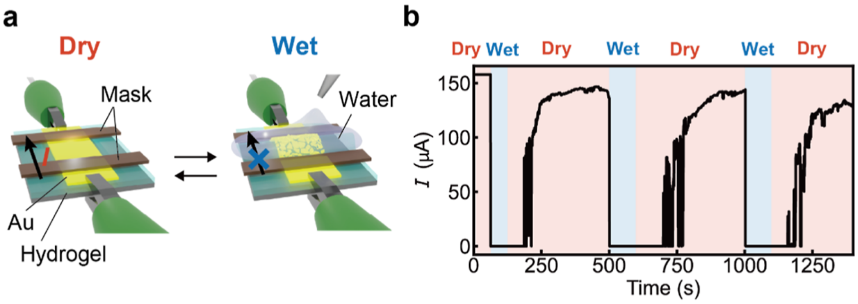

Figure 4. Electrical-switching device using preswelling transfer. (a) Schematic of device in air (dry) and water (wet). (b) Time-series plot of current through device with desiccation (dry) and moistening (wet).

divided Au depending on the water content. To understand the geometric reproducibility of Au, microscopic images were obtained after each dry/wet cycle (Figure S10). The images show that the Au geometry was almost similar but some cracks were produced after each cycle. The slight degradation in the recovered current could be based on crack subdivision, and we should study the device design to stabilize the crack geometry and current recovery.

3. CONCLUSIONS

We proposed a facile physical-adhesion method for transferring metal to a swellable hydrogel surface that involves a dehydration process without any adhesive layers. The transferred Au exhibited high electrical conductivity and functioned as an electric wire for an LED circuit. The hydrogel-based Au wire was divided by deformation due to swelling and recovered to a conductive mode by returning to the geometry at the transfer. To improve the transfer yield, we should investigate increasing the interfacial adhesion between metals and hydrogels by moderate dehydration as well as reducing the adhesion between metals and the supporting substrate prior to the transfer. Since the adhesion between polymer chains and metals is based on the hydrophobic interaction, the proposed method will be further improved for versatile patterning of any metal on any hydrogel surface.

4. MATERIALS AND METHODS

4.1. Materials. The acrylamide (AAm), *N*-(2-hydroxyethyl)acrylamide (HEAAm), *N*,*N*′-methylenebis[acrylamide] (MBAA), and lithium phenyl(2,4,6-trimethylbenzoyl)phosphinate (LAP) were purchased from Tokyo Chemical Industry Co., Ltd. The 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) and *N*,*N*-dimethylacrylamide hydrogel (DMAAm) were purchased from Sigma-Aldrich. Acetic acid, ethanol (EtOH), and sodium hydroxide (NaOH) were purchased from Kanto Chemical Co., Inc. The thin glass substrates (no.1, 18 × 18 and 24 × 32 mm coverslip) were purchased from Matsunami Glass Ind., Ltd. Deionized water (18 MΩ·cm) was used in all experiments. All of the reagents were directly used without further purification.

4.2. Gold Patterning on Hydrogel Films. The Au layer to be transferred was first fabricated onto coverslips under an Ar atmosphere using an ion sputter coater (E-1030, Hitachi High-Tech Corporation). The thickness of Au was controlled to 20 nm using a quartz crystal unit in the coater. The unsputtered area was masked with a dicing tape (T-80MB-23A, Denka). After sputtering, the dicing tape was removed, and the sputtered substrate surface was cleaned with an oxygen plasma etcher (CV-e300, Plasmec). The same procedure was used for the Pt transfer. A pregel solution was prepared containing 4 M AAm as a monomer, 12 mM MBAA as a cross-linker, and 0.4 mM LAP as an initiator in deionized water.

During preswelling transfer, Au was transferred soon after the dehydration process (Figure 1a). The pregel solution was sandwiched with bottom Au-sputtered and top cleaned coverslips (24 × 32 mm) with a 500 μm-thick silicone sheet as a spacer. After 3 min UV irradiation (10 mW cm^{-2}) under a nitrogen atmosphere (O2 < 0.1%) at room temperature, a hydrogel film was obtained. The spacer was then removed, and a glass substrate (S9213, Matsunami) was put on the sandwiched hydrogel film with coverslips to suppress deformation during dehydration. The dehydration was executed in an oven heated to 70 °C for 30 min. The Au transfer was completed by removing the coverslips from the hydrogel film. We observed the morphology of the Au surface immediately after transfer and 1 h after swelling in water with a digital microscope (VHX-7000, KEYENCE).

During postswelling transfer, Au was finally transferred after reswelling of the hydrogel following the dehydration process (Figure 1b). The 500 μm thick hydrogel film was premade using a similar process as per the gelation method during preswelling transfer using two cleaned glass substrates followed by immersion in deionized water to be completely swollen. The swollen hydrogel film was cut to the same size of the coverslips and dehydrated with the same process as the preswelling transfer (70 °C for 30 min). The dehydrated hydrogel and coverslips were immersed in deionized water for 1 h for reswelling. The coverslips were then removed, and Au-transferred hydrogel film was obtained. We repeated the postswelling transfer on each surface side (front and back) for the dual-sided transfer.

The versatility of the dehydration-induced transfer was investigated with several hydrogels and metals. Hydrogels were prepared from pregel solution containing 3 M HEAAm, AAm, or DMAAm as a monomer, 90 mM MBAA as a cross-linker, and 3 mM LAP as an initiator in deionized water. Gold was evaporated using a vacuum vapor deposition system (SVC-700TMSG/7PS80, Sanyu Electron) and transferred using the preswelling transfer as described above. Silver and Cu were deposited on coverslips and transferred onto PAAm hydrogels using postswelling transfer.

To examine the transfer yield in relation to dehydration time, the dehydration process was carried out at room temperature without the use of the oven. The yield is the ratio of the Au area on a hydrogel after transfer to the Au area on a glass before transfer. The Au for the yield measurement was sputtered in a 5 × 5 grid, with one square having an area of 2 × 2 mm with a 1 mm gap between each. The dehydration ratio is calculated as 1-W_d/W_0, where W_d and W_0 refer to the weight of the contained water of the hydrogel after and before dehydration, respectively, and the weight of the contained water is calculated from the difference in the weight of the hydrogel and that of the fully dehydrated hydrogel (weight of the polymer part).

4.3. Characterization of Au-Transferred Hydrogels. The swelling ratio of the hydrogels α was calculated as $\alpha = D_s/D_0$, where D_s and D_0 refer to the diameter of the disc gel in the equilibrated swollen state in water at room temperature and the as-prepared state (3 mm), respectively.

SEM observations were carried out to understand the microstructure of the Au/hydrogel interface. The Au-hydrogel composite was fabricated with postswelling transfer. The completely swollen sample was immersed in liquid nitrogen to instantly freeze and dry in a freeze-dryer (FDU-1200, Tokyo Rikakikai Co., Ltd.) overnight to remove ice. The freeze-dried sample was physically cracked to expose the cross-section and coated with a 10 nm gold layer using ion sputter (E-1030, Hitachi High-Tech Science Corporation). The coated cross-section was imaged with a focused ion beam scanning electron microscope (Auriga 60 Cross Beam Workstation, Carl zeiss).

The adhesion strength was evaluated by conducting a 90° peeling test with a tensile testing machine (STB-1225S, A&D Corporation). Hydrogels were adhered onto the Cr/Au substrate with the process described in the pre/post-swelling transfer. Half the substrate was masked with dicing tape to create a nonadhesive surface, and the nonadhesive part of the hydrogels was pinched using the testing machine. The samples were vertically pulled with a constant peeling velocity of 1 mm/min. The peeling strength was determined by dividing the peeling force with the width of the sample.

4.4. Electrical Analysis. To investigate the function of transferred Au as an electric wire, we prepared a set of electronic components (SBS-202, Sunhayato). Two 1.5 V batteries were connected in series to obtain 3 V. One end of the battery was connected to a 100 Ω resistor, which in turn was connected to an LED lamp (Figure 3a). The other end of the lamp and battery were connected via the transferred Au on a hydrogel.

Electrical measurements were conducted by using an electrochemical analyzer (ALS660E, CH Instruments). The conductivity of the transferred Au on the hydrogel film was determined from four-point probe measurements in the ambient atmosphere (Figure 3c). The Au was 2 mm wide, 20 mm long, and 20 nm thick. The Au probes for the measurement were each 5 mm apart. The potential between the two inner probes shifted between −50 and 50 mV (scan speed = 100 mV s^{-1}), and the applied current between two outer probes was monitored.

4.5. Electrical Switching by Hydrogel Moistening. The reversible change in conductivity due to hydrogel moistening was demonstrated with the Au-transferred hydrogel partially immobilized on a coverslip. For hydrogel immobilization, the coverslip was chemically modified with TMSPMA, as described previously.[21] The substrate was covered with a dicing tape except for a straight line that was 0.5 mm wide and treated with oxygen plasma for 1 min to remove the TMSPMA in the line area (Figure S11). The immobilized hydrogel film was obtained with a similar process as per the gelation method in the preswelling transfer with partially silanized and cleaned coverslips and 60 μm thick dicing tape as a spacer. After removing the cleaned coverslip and spacer, the hydrogel was mounted under a coverslip sputtered with 3 mm wide linear Au, which was orthogonal to the removed TMSPMA line. Two pieces of the dicing tape were placed on the hydrogel film across the removed TMSPMA line as a mask to limit the moistening area. After complete dehydration in the ambient atmosphere, both ends of the Au line were connected to the electrochemical analyzer, and 0.1 V was applied to record the current. The hydrogel between dicing tapes was moistened with 10 μL of deionized water at 60, 500, and 1000 s, and the water was wiped off at 120, 600, and 1100 s.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c04774.

> Optical image of Au surface before and after transfer; optical image of the fine Au square transferred to hydrogel; optical images of dual-sided transferred hydrogel; Au-transferred hydrogels made from different monomers; metal-transferred hydrogels; yield in relation to the dehydration ratio during postswelling transfer including 1 h of reswelling; cross-sectional SEM image of Au-transferred hydrogel; 90° peeling test; schematic of dehydration-induced transfer mechanism; optical images of transferred Au on swollen hydrogel; and schematic of fabrication process for the electrical-switching device (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Shogo Himori − *NTT Basic Research Laboratories and Bio-Medical Informatics Research Center, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan;* orcid.org/0009-0000-0416-7965; Email: shogo.himori@ntt.com

Authors

Riku Takahashi − *NTT Basic Research Laboratories and Bio-Medical Informatics Research Center, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan;* orcid.org/0000-0002-8220-5581

Aya Tanaka − *NTT Basic Research Laboratories and Bio-Medical Informatics Research Center, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan*

Masumi Yamaguchi − *NTT Basic Research Laboratories and Bio-Medical Informatics Research Center, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan*

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

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