All-Transparent Stretchable Electrochromic Supercapacitor Wearable Patch Device

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ABSTRACT: Flexible and stretchable electrochromic supercapacitor systems are widely considered as promising multifunctional energy storage devices that eliminate the need for an external power source. Nevertheless, the performance of conventional designs deteriorates significantly as a result of electrode/electrolyte exposure to atmosphere as well as mechanical deformations for the case of flexible systems. In this study, we suggest an all-transparent stretchable electrochromic supercapacitor device with ultra-stable performance, which consists of Au/Ag core–shell nanowire-embedded polydimethylsiloxane (PDMS), bistacked WO3 nanotube/PEDOT:PSS, and polyacrylamide (PAAm)-based hydrogel electrolyte. Au/Ag core–shell nanowire-embedded PDMS integrated with PAAm-based hydrogel electrolyte prevents Ag oxidation and dehydration while maintaining ionic and electrical conductivity at high voltage even after 16 days of exposure to ambient conditions and under application of mechanical strains in both tensile and bending conditions. WO3 nanotube/PEDOT:PSS bistacked active materials maintain high electrochemical–electrochromic performance even under mechanical deformations. Maximum specific capacitance of 471.0 F g⁻¹ was obtained with a 92.9% capacity retention even after 50 000 charge–discharge cycles. In addition, high coloration efficiency of 83.9 cm² C⁻¹ was shown to be due to the dual coloration and pseudocapacitor characteristics of the WO3 nanotube and PEDOT:PSS thin layer.

KEYWORDS: electrochromic supercapacitor, transparent stretchable, hydrogel electrolyte, dual coloration, wearable patch device
wearable applications due to their brittle characteristics. In addition, Ag nanowire networks have the benefit of being highly reliable under cyclic bendings, where the electric conductance is maintained over a large number of cycles. However, the operation lifetime is short for Ag nanowire networks due to the delamination of the Ag nanowire/wrapping layer from the surface of the substrate and loss of electric conductivity by Ag nanowire oxidation. These reasons led to deterioration of electrochemical—electrochromic properties, thus such an electrochromic supercapacitor system cannot be applied for wearable applications. Therefore, a stretchable transparent current collector with high resistance against oxidation and mechanical deformation must be developed to realize a wearable multifunctional electrochemical device.

Another key issue that needs to be addressed is electrolyte evaporation and leakage as a result of mechanical deformations. The supercapacitor lifetime is significantly affected in the case of electrolyte evaporation, especially under ambient conditions where the electrolyte leakage can occur, which then leads to a significant decrease in the electrochemical performances. Incorporating liquid electrolytes into a polymer matrix to make gel electrolytes has been attempted; gel electrolytes, however, still possess ionic conductivity (1–50 mS cm$^{-1}$) inferior to that of aqueous electrolytes. In addition, application as wearable supercapacitors further emphasized the problematic leakage issue as a result of increased frequency of mechanical deformation. Furthermore, the loss of electrolyte due to the evaporation of solvent upon exposure to ambient conditions and the narrow operating voltage range due to constraints imposed by electrolyte dissociation are the issues of current electrolyte systems. Under the circumstances, a new electrolyte is needed to solve the poor ionic conductivity, evaporation, leakage, and narrow operation voltage range problems.

In this study, we have demonstrated ultrastable operation of a wearable patch device by devising an all-transparent stretchable electrochromic supercapacitor (hereafter, all-TSES) composed of a PEDOT:PSS thin wrapping layer and polyacrylamide (PAAm) electrolytes. WO$_3$ nanotubes on a low-density Au/Ag core–shell nanowire-embedded PDMS substrate were coated with a thin PEDOT:PSS layer. The PAAm electrolyte shows high ionic conductivity as well as stretchability of up to 80%. Thus, the incorporation of PAAm electrolyte into the device allows significant stretchability and flexibility, unlike conventional devices that use liquid and/or gel polymer electrolyte. In addition, the PEDOT:PSS/WO$_3$ nanotube composite enhances electrochromic—electrochemical performances. The all-TSES wearable patch device shows excellent electrochromic supercapacitor performance and reliability even under repeated stretching—bending motions, which substantiates its suitability for wearable applications.

RESULTS AND DISCUSSION

Designs of an All-Transparent Stretchable Electrochromic Supercapacitor Device. The designs and components of all-TSES devices are schematically shown in Figure 1. To overcome the problems of conventional Ag nanowire-coated PDMS current collector, especially the conductivity loss due to oxidation (0.15 V vs Pt counter electrode and Ag/AgCl reference electrode) and poor adhesion, the Au/Ag core–shell nanowire with high oxidation resistance and Ag nanowire network were embedded into PDMS by a molding process. The detailed fabrication process of the Au/Ag core–shell and Ag nanowire-embedded PDMS is described in the Experimental Section and is also shown in Figure S1. The Au/Ag core–shell and Ag nanowire-embedded PDMS were fixed to a highly reliable transparent stretchable counter/working current collector that maintains the electrical conductivity even with repeated deformations under tensile/bending conditions and applied positive voltage (0.9 V vs Pt counter electrode/Ag/AgCl reference electrode), as shown in Figures S2 and S3. Transparent stretchable hydrogel electrolyte was integrated with a current collector to solve the leakage, evaporation, electrode contact, ionic conductivity, and dehydration issues that arise when adopting liquid electrolytes in a flexible stretchable device. When PAAm polymer matrix, which can dissolve transparently in water, becomes a hydrogel after UV curing, it has a high resistance toward dehydration and high voltage as it contains water molecules inside the polymer chain.

The structure of the ultrastable WO$_3$ nanotube and PEDOT:PSS thin layer composite demonstrates high electrochromic—electrochemical performance. WO$_3$ was used as the cathodic electrochromic material as it simultaneously undergoes electrochemical energy storage and cathodic coloration upon Li$^+$ ion intercalation. The WO$_3$ nanotube structure is composed of densely packed nanoparticles, which enhances the electrochemical energy and power density by enhancing the contact efficiency with the Ag nanowires. To address the delamination issue, conductive polymer PEDOT:PSS was adopted as the wrapping layer. The PEDOT:PSS layer enhances the cyclic lifetime by prevention of WO$_3$ nanotube delamination. In addition, PEDOT:PSS undergoes cathodic coloration, as it is a pseudocapacitor material with high capacity and can participate in the electrochromic coloration—electrochemical energy storage in tandem with the WO$_3$ nanotubes. Both PEDOT:PSS and WO$_3$ nanotubes undergo cathodic coloration from transparent to blue, and the synergistic electrochromic reaction stemming from dual composite layers further enhances the coloration efficiency of the PEDOT:PSS-WO$_3$ nanotube electrode.

Fabrication of Electrospun WO$_3$ Nanotube and PEDOT:PSS Composite Layer. The fabrication process is shown schematically in Figure 2a, where the electrospun WO$_3$ nanotube is coated with a PEDOT:PSS thin layer and drop-coated onto the Ag nanowire-embedded PDMS substrate. To

![Figure 1. Schematic illustration of all transparent stretchable electrochromic supercapacitor device. High oxidation resistance of Au/Ag core–shell and Ag nanowire-embedded PDMS, PAAm-based transparent stretchable hydrogel electrolyte, and WO$_3$ nanotube and PEDOT:PSS wrapping layer.](acsnano.8b08560)

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fabricate the WO₃ nanotube, a cellulose nanocrystal (CNC) with the length of 100 nm and width of 20 nm was used as a sacrificial template and was incorporated in electrospinning solution containing W precursor [(NH₄)₆H₂W₁₂O₄0·xH₂O] polyvinylpyrrolidone (PVP) dissolved in DI water. During electrospinning, CNC agglomerates due to the abundance of hydroxyl groups, which results in the phase separation of the as-spun nanofiber scaffold, resulting in a CNC-rich core and W precursor/PVP-rich shell. After calcination at 600 °C, the agglomerated CNC core is completely decomposed, whereas the W precursor is oxidized to form the WO₃ nanotube. Detailed fabrication conditions are described in the Experimental Section.

The synthesized WO₃ nanotubes were then dispersed in isopropyl alcohol (IPA) to make a 0.5 wt % solution and drop-casted onto the Ag nanowire-embedded PDMS. A 1.0 wt % solution of PEDOT:PSS was diluted to 0.1 wt % and drop-casted to form a thin capping layer on the WO₃ nanotube-coated Ag nanowire-embedded PDMS. Surface scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the Ag nanowire-embedded PDMS and WO₃ nanotube—PEDOT:PSS thin layer are shown in Figure 2b—f. The SEM image of the Ag nanowire-embedded PDMS shows that the Ag nanowire network is embedded well in the PDMS and partially exposed on the surface. This partially exposed, low-density Ag nanowire network is beneficial for enhanced adhesion between the Ag nanowire and PDMS, while maintaining the electric conductivity and making it suitable for use as a transparent stretchable current collector.

SEM images of the drop-casted WO₃ nanotube with an average diameter of 300−400 nm and a length of 5 μm are in good contact with the Ag nanowire network, as shown in Figure 2c. The surface morphology of the 5 μm long WO₃ nanotube can be seen in Figure 2d, which reveals that the WO₃ nanotube has a polycrystalline structure composed of nanoparticles of around 30−50 nm in a nanotube structure. The PEDOT:PSS thin film uniformly covers the WO₃ nanotubes via a simple drop-coating (Figure 2e). Cross sectional TEM image in Figure 2f shows that the average thickness of the PEDOT:PSS is about 20 nm. Energy-dispersive spectroscopy and Raman spectroscopy analyses confirmed that the thin overlayer coated on the WO₃ nanotubes is PEDOT:PSS, as shown in Figures S4 and S5. X-ray diffraction pattern analysis revealed that WO₃ nanotubes with a monoclinic crystal structure were synthesized after calcination (Figure 2g). As CNC is prepared by chemical modification with sodium hydroxide and sulfuric acid, CNC includes partial sulfate functional molecule groups as well as traces of sodium impurity. Therefore, a negligible amount of triclinic crystal
structure was found, which originates from Na2W4O13 by the use of the CNC with Na+. CNC residue of Na2W4O13 has a layered structure and can also contribute to the electrochemical reaction with the Li+ ion33 but was concluded to have a negligible impact on the electrochromic performance.

**Electrochromic Performance of a Transparent Stretchable Electrode.** To accurately measure the transmittance variance due to dual electrochromic coloration effect, the change in transmittance was measured in a three-electrode system including the electrolyte composed of 1 M LiClO4 salt in propylene carbonate (PC) (Figure 3). As the aqueous electrolyte can undergo dehydration at a voltage higher than 1.2 V, organic electrolyte was chosen, which could maintain ionic conductivity at a voltage higher than 2 V. The electrochromic properties were characterized by applying pulse-type charge−discharge voltages over 20,000 cycles from −1.5 V (vs Pt counter electrode (Ag/AgCl)) colored state when the Li⁺ ions are intercalated into the crystal structure to −0.1 V (vs Pt counter electrode (Ag/AgCl)) bleached state when the Li⁺ ions are deintercalated. The change in transmittance was measured in real time and calculated via the light power change detected by the 635 nm laser module. Four cycles of in situ transmittance change measurements of the WO3 particles, WO3 nanotube, and PEDOT:PSS-coated electrodes are shown in Figure 3a. The coloration contrast ($ΔT = T_b - T_c$), which is the difference between the bleached state ($T_b$) and colored state ($T_c$), of the WO3 nanoparticle and the WO3 nanotube is 35.3 and 37.7%, respectively. In addition, the switch from the colored state to the bleached state occurred much faster in the WO3 NT electrode. The enhancement was also seen in the PEDOT:PSS thin layer coated WO3 NT electrode where the WO3 NT electrode showed coloration contrast 3.2% higher than that on the WO3 NP electrode. These results are attributed to the improved contact efficiency of the WO3 NT with the transparent current collector. The coloration contrast of the WO3 nanotubes was higher than that of WO3 nanoparticles (~100 nm) because 1D WO3 nanotubes offer enhanced contact with the low-density Ag nanowire compared with 0D WO3 nanoparticles.34,35 However, the overall transmittance of the electrode decreases after coating the PEDOT:PSS overlayer on the WO3 nanotubes, and the dual coloration results in the improvement of the coloration contrast by 12.0% in comparison with the electrode without PEDOT:PSS coating. The enhancement is attributed to the effect of the dual electrochromic coloration of PEDOT:PSS and WO3. Ex situ transmittance measurements over the visual light range (400−800 nm) was conducted to compare the bleached state and colored state of the electrodes with and without PEDOT:PSS coating layer (Figure 3b). For wavelengths in the range of 340−500 nm, there is a rapid increase in the transmittance due to the coloration of WO3 and PEDOT:PSS (Figure S6), and thus it is more appropriate to use wavelength of 635 nm for reliable transmittance analysis.

The cyclic life enhancement of the PEDOT:PSS-coated all-TSES was confirmed by in situ transmittance measurement over 20,000 charge−discharge cycles. The normalized coloration contrast ($ΔT/ΔT_0$) decreased to 30.8% after 20,000 cycles for the case of the WO3 nanotube only electrode. By contrast, the WO3 nanotube electrode with the

![Figure 3. Electrochromic properties of WO3 nanoparticle and nanotube coated on Ag nanowire-embedded PDMS and PEDOT:PSS layer (PL) added WO3 nanoparticle and nanotube-coated Ag nanowire-embedded PDMS. (a) In situ transmittance measurement of bleached ($T_b$) and colored state ($T_c$) electrodes at 635 nm wavelength. (b) Transmittance measurement of bleached ($T_b$) and colored state ($T_c$) electrodes at visible light wavelength range (400−800 nm). (c) Electrochromic cycle reliability testing up to 20,000 cycles in LiClO4−PC liquid electrolyte. (d) Evaluation of coloration efficiency by optical density change measurement with charge density. (e) Coloration contrast change measurement of all-TSES integrated with hydrogel electrolyte.](https://doi.org/10.1021/acsnano.8b08560)
PEDOT:PSS overlayer maintained 60.8% of its original coloration contrast (Figure 3c). Therefore, the adoption of the PEDOT:PSS thin layer enhanced the electrochromic cyclic reliability of the all-TSES wearable patch device. To quantify the enhancement of the coloration efficiency contributed by the PEDOT:PSS overlayer, the change in optical density in log scale with respect to charge density was plotted for electrodes with and without a PEDOT:PSS thin layer (Figure 3d). Coloration efficiency was obtained from the slope of the linear plots, which for the case of PEDOT:PSS layer coated all-TSES patch electrode was 83.9 cm² C⁻¹, a 20.4% improvement compared with the 66.8 cm² C⁻¹ of the pristine WO₃ nanotube electrode without the PEDOT:PSS layer. The coloration efficiency of the WO₃ nanotube and PEDOT:PSS thin layer electrode increased as both WO₃ and PEDOT:PSS have the same cathodic electrochromic coloration mechanism that changes to a blue color. Therefore, the contrast change is compounded that leads to the increase in coloration efficiency and is referred to as the dual coloration mechanism. Therefore, use of the WO₃ nanotube and PEDOT:PSS thin layer that have the dual coloration mechanism is beneficial for enhanced coloration efficiency as quantitatively compared in Figure 3d.

**Electrochemical Performance of Transparent Stretchable Electrodes.** Electrochemical properties were measured to confirm the effect of the WO₃ nanotube/PEDOT:PSS thin layer composite on the electrochemical properties. Electrochemical properties were measured in the three-electrode system based on the −2.4 to −0 V (ensures the stability of the PC) with respect to the Pt counter electrode (Ag/AgCl) using the identical electrolyte. Charge–discharge tests were conducted between current densities of 1−16 A g⁻¹, and CV tests were conducted at scan rate conditions of 0.1 and 1 V s⁻¹ as shown in Figures S7 and S8. Figure 4a plots charge–discharge tests of different electrodes at a current density of 4 A g⁻¹. Less steep discharge slope indicates a higher capacity, which is attributed to the addition of the WO₃ nanotube and
The cyclic reliability test, which indicates that the WO$_3$ nano-
particle and nanotube electrodes without the PEDOT:PSS
layer of PEDOT:PSS, charge capacitance retention. Figure 4e is a schematic illustration explaining the mechanism
behind the increase in specific capacitance. A low-density Ag
nanowire network was embedded to maximize transmittance,
which leaves the majority of WO$_3$ nanoparticles disconnected
from the Ag nanowire network. The disconnected WO$_3$
nanoparticles do not participate in the electrochromic and
electrochemical energy storage reaction, thereby resulting in
reduced specific capacitance. By contrast, the WO$_3$
nanotubes offer good contact with the Ag nanowire network and therefore result in superior electrochromic supercapacitor performance.

To examine the cyclic lifetime of the electrode using thin
layer of PEDOT:PSS, charge–discharge tests up to 50 000 cycles were conducted to characterize the change in capacitance retention. Figure 4d shows the electrochemical cyclic reliability test, which indicates that the WO$_3$ nanoparticle and nanotube electrodes without the PEDOT:PSS wrapping layer retained 71.6 and 72.4% of its original capacity. On the other hand, the PEDOT:PSS-coated WO$_3$ nanotube electrode retained 79.5% of its original capacity. The PEDOT:PSS wrapping layer improved the cyclic reliability by 7.1% due to the effective prevention for delamination of the WO$_3$ nanotubes. The energy and power densities of the all-TSES wearable patch device are compared with other transparent energy storage systems in Figure 4f. Flexible transparent device using MoO$_3$ as the active material exhibited power and energy densities of 0.7 kW kg$^{-1}$ and 22.89 Wh kg$^{-1}$, respectively. Another flexible electrochromic supercapacitor using poly[4,7-bis(3,6-dihexyloxythieno[3,2-b]-thiophen-2-yl)]-benzo[c][1,2,5]thiadazole (PBOTT-BTD) demonstrated energy and power densities of 0.8–8.8 kW kg$^{-1}$ and 3.5–6.3 Wh kg$^{-1}$. In addition, a device using the PEDOT analogue as the active material reported a power density of 0.8–3.3 kW kg$^{-1}$ and energy density of 4.0–18.0 Wh kg$^{-1}$. The fabricated all-TSES wearable patch device exhibits superior power density of 7.7–19.1 kW kg$^{-1}$ and energy density of 44.67–52.6 Wh kg$^{-1}$ due to the use of WO$_3$ nanotube–PEDOT:PSS thin film composite. It is important to note that the CNT/MnO$_2$ macrofilm stretchable energy storage systems, which is not transparent, still demonstrates lower power and energy densities compared with our all-transparent stretchable device. These results highlight that the Ag nanowire-embedded PDMS-WO$_3$ nanotube–PEDOT:PSS thin layer based all-TSES wearable patch device offer high suitability for wearable applications requiring high electrochemical performance.

Dehydration Properties of Transparent Stretchable Hydrogel Electrolytes. To confirm the enhancement and retention of ionic conductivity of transparent stretchable hydrogel electrolyte in exposure to ambient conditions, hydrogel electrolyte was exposed to the environment with a

PEDOT:PSS thin layer. IR drop does not occur in the charge–discharge curve for the electrode with the PEDOT:PSS thin layer based on this result. The result confirms that the PEDOT:PSS thin layer improves the Coulombic efficiency by enhancing the conductivity of WO$_3$ active materials.

In addition, the CV test conducted at a scan rate of 1 V s$^{-1}$ in Figure 4b shows that the enclosed area of the CV curve, which indicates the capacity, increases with the addition of the WO$_3$ nanotube and PEDOT:PSS overlay. Therefore, the charge–discharge and CV tests qualitatively confirm that the capacity increases with the use of WO$_3$ nanotubes and PEDOT:PSS. Normalized capacitance with respect to changes in current density is plotted in Figure 4c. The maximum specific capacitances of the WO$_3$ nanoparticle, WO$_3$ nanotube, and WO$_3$ nanotube–PEDOT:PSS thin layer were 298.0, 375.4, and 471.0 F g$^{-1}$, respectively. Specific capacitance increased by 20.6% with the use of WO$_3$ nanotubes and a further 20.3% increase for the WO$_3$ nanotube–PEDOT:PSS thin layer.

![Figure 5](Image 137x489 to 488x749)

Figure 5. (a) Impedance test results of PAAm-based hydrogel electrolyte after exposure to ambient conditions of relative humidity of 30% for 16 days. (b) Water contents and ionic conductivity change of hydrogel electrolyte after exposure in ambient conditions of relative humidity of 30% for 16 days. (c) Charge–discharge test of stainless steel electrodes using PAAm-based hydrogel electrolyte. (d) Cyclic voltammetry test result of Au/Ag core–shell nanowire-embedded PDMS symmetric electrode and PAAm hydrogel electrolyte.
low relative humidity of 30% for 16 days, and the changes in ionic conductivity and water content (%) were measured. In order to evaluate the change in ionic conductivity, an impedance test was conducted by a two-electrode system inserting the hydrogel electrolyte between stainless steel discs electrodes, as shown in Figure 5a and Figure S9. The ionic conductivity of the hydrogel electrolyte is 265 mS cm$^{-1}$ (Figure 5b) and thus has superior ionic conductivity in comparison to that of the conventional gel electrolytes used in supercapacitors such as zwitterionic poly(propylsulfonate dimethylammonium propylmethacrylamide) (PPDP) gel electrolyte$^{26}$ (17 mS cm$^{-1}$), PVDF-co-HFP gel polymer$^{27}$ (9 mS cm$^{-1}$), and polyacrylamide cross-linked by vinyl hybrid silica nanoparticles hydrogel electrolyte$^{28}$ (17 mS cm$^{-1}$). In addition, 94% of ionic conductivity (mS cm$^{-1}$) was maintained (from 265 to 249 mS cm$^{-1}$) and 93% of water content was maintained, minimizing the performance loss (Figure 5b) even after exposure to ambient conditions of relative humidity of 30% for 16 days. As a result, PAAm-based hydrogel electrolyte can solve evaporation and leakage problems in mechanical deformations and the high performance of the electrochromic supercapacitor can be maintained by integration with the PAAm-based hydrogel electrolyte in ambient conditions even after repeated stretching–bending deformations.

To demonstrate the high resistance to dehydration of the PAAm-based transparent stretchable hydrogel electrolyte when a bias is applied, charge–discharge test was conducted by a two-electrode system inserting the hydrogel electrolyte between symmetric electrodes using stainless steel discs. As shown in Figure 5c, dehydration did not occur at 5 V, and the performance was maintained in the hydrogel electrolyte, which confirmed that the device would be stable under 2 V, which is the operating voltage for a wearable electrochemical–electrochromic reaction. Furthermore, a cyclic voltammetry test was conducted in order to demonstrate the wider operation potential range of Au/Ag core–shell nanowire-embedded PDMS integrated high dehydration resistance hydrogel electrolyte. A hydrogel electrolyte integrated Au/Ag core–shell nanowire-embedded sandwich electrode was used in a two-electrode system. Unlike the conventional Ag nanowire
current collector, the developed Au/Ag core-shell nanowire PDMS current collector operated stably in the range of −0.9 to 0.9 V and also −1.5 to 1.5 V, which confirmed the resistance to oxidation, as confirmed in Figures S3 and 5d. Therefore, the PAAm-based hydrogel electrolyte demonstrates high resistance to dehydration that enables long cyclic lifetime in ambient condition even after repeated stretching—bending deformations and applied external voltage.

**Demonstration of All-Transparent Stretchable Electrochromic Supercapacitor Wearable Patch Device.** The fabricated all-TSES was further integrated into a wearable patch device that performs as an electrochromic coloration device and an electrochemical energy storage device. The arrangement of the current collectors in the all-TSES device consisted of Ag nanowire-embedded PDMS working electrode and Au/Ag core—shell nanowire-embedded PDMS counter electrode, as shown in Figure 6a. Ag nanowire-embedded PDMS current collector which could operate at relatively negative voltage with respect to Pt counter electrode was used as the working electrode. The Ag nanowire in the counter electrode, which is susceptible to oxidation under relative positive voltage, was also replaced with a Au/Ag core—shell nanowire-embedded in PDMS. Two electrodes, one loaded with active materials and another embedded only with Au/Ag core—shell nanowire network, were sandwiched with the hydrogel electrolyte in the middle. The hydrogel electrolyte, which physically separates the two electrodes provides high conduction path for Li⁺ ion diffusion and good adhesion with the Cu foil. Both the electrode and electrolyte are transparent and solid, hence eliminating issues associated with electrolyte evaporation/leakage as well as electrode shorting during stretching—bending deformation.

The performance of the fabricated all-TSES wearable patch device was tested while fixed onto the wrist, as organized in Figure 6b,c. The image in Figure 6b confirms reversible colored (−1.5 V) into bleached state (−0.1 V) of the all-TSES wearable device. In addition, the all-TSES wearable device was fixed onto the wrist, placed under constant stretching—bending state and put through electrochromic and electrochemical reactions. Stable operation on the wrist means that the patch device will be stable when applied to other areas of the body as a wearable device. Figure 6c shows reversible coloration at −1.5 V and transparent state by returning to −0.1 V of the patch device. Application on the wrist imposes 15% tensile strain followed by bending of the device with bending radius of 4 cm for 0.2 cm substrate thickness. As a result, the total strain imposed in the device on the surface of the substrate is summation of 15% tensile and 5% bending strains. The patch device demonstrated stable electrochromic and electrochemical properties when subjected to prolonged stretching—bending condition. Figure 6d shows that the patch device retains 95.0 and 97.6% of its normalized transmittance change and normalized specific capacitance even after being exposed to the ambient conditions for 2 weeks. Furthermore, to evaluate the suitability of a fabricated all-TSES device for wearable application, the change in capacitance was measured in Figure 6e,f while applying 20% total strain that showed 98.6% retention of capacitance under 20% total strain. Therefore, the all-TSES wearable device suitable for wearable applications was fabricated, which demonstrates high transmittance and stable operation even under stretching—bending deformations.

**CONCLUSION**

In this study, the all-TSES system that demonstrates enhanced performance and reliability even under tensile and bending strains. The improved electrochromic supercapacitor performance is attributed to the dual coloration and pseudocapacitive characteristics of theWO₃ nanotube and PEDOT:PSS active material. The coloration efficiency improved by 20.4% to 83.9 cm²·C⁻¹ and specific capacity improved by 38.6% to 471.0 F g⁻¹ with the introduction of PEDOT:PSS wrapping layer on theWO₃ nanotube electrode. The improved electrochemical capacity also had an effect on enhanced energy and power densities with the fabricated device, exhibiting maximum power density of 19.1 kW kg⁻¹ and maximum energy density of 52.6 Wh kg⁻¹. In addition, the electrochromic supercapacitor cycle reliability also improved due to the PEDOT:PSS wrapping layer, resulting in 30.0 and 7.1% enhancements in electrochromic reliability and electrochemical energy storage reliability compared to pristine WO₃ nanotube electrode, respectively. The fabricated system demonstrated stable performance and reversible coloration from transparent to colored state even under mechanical bending—stretching deformation and in atmospheric conditions. A rationally designed an all-TSES system consisted of 1D oxide material combined with conductive polymeric overlayer is highly suitable for wearable applications.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Monoclinic WO₃ nanoparticles purchased from Sigma-Aldrich (<100 nm) and WO₃ nanotubes synthesized using electrospinning method were used as electrochromic supercapacitor coupling materials. Electrospinning solution was prepared with 0.2 g of ammonium metatungstate hydrate [(NH₄)₆H₂(W₁₀O₃₀)xH₂O], 0.25 g of polyvinylpyrrolidone (PVP, Mₙ = 130000 g mol⁻¹), and 2 g of 5.0 wt % cellulose nanocrystal dispersed DI water. The solution was vigorously stirred at 500 rpm at room temperature for 8 h. Then, electrospinning was carried out at a constant voltage of 17 kV between the stainless steel, which served as the collector, and the syringe needle (25 gauge) with a feeding rate of 0.1 mL min⁻¹. The as-spun W precursor/PVP composite nanofibers were calcined at 600 °C for 1 h with a ramping rate of 5 °C min⁻¹ in air to obtain a WO₃ nanotube. As sodium naturally doped CNC was utilized in this work, a minor Na₃W₁₀O₃₃ phase was partially formed during high-temperature calcination, forming a composite nanotube with heterojunctions between Na₃W₁₀O₃₃ and WO₃. In addition, a 1.0 wt % PEDOT:PSS solution (Clevios PH 1000) was diluted to 0.1 wt % and drop-casted onto the WO₃ nanotube-coated Ag nanowire-embedded PDMS to coat a thin layer of PEDOT:PSS.

**Fabrication of a Au/Ag Core—Shell Nanowire.** PVP (1.1 g, Mₙ = 50000 g mol⁻¹, Sigma-Aldrich), 88 mg of i-ascorbic acid (AA, Sigma-Aldrich), and 40 mg of NaOH (Sigma-Aldrich) were dissolved in 30 mL of DI water. Then, 100 μL of a 0.5 wt % Ag nanowire aqueous solution (Nanopxys, Korea) was dispersed in PVP solution. Six milliliters of aqueous solution of HAuCl₄ (0.15 Mm, Sigma-Aldrich) was slowly stirred and injected to AgNW-dispersed solution for 6 h. After the injection process, the Au/Ag core—shell NWs were washed by DI water twice and collected in ethanol.

**Fabrication of Au/Ag Core—Shell and Ag Nanowire-Embedded PDMS.** Hydrophobic treatment was performed to Si wafer by (perfluoroctyltrichlorosilane) vapor deposition. Au/Ag core—shell and Ag nanowire were uniformly coated on hydrophobic Si wafer by air-spray. After the air-spray process, PDMS (Sylgard 184, Sigma-Aldrich), with a ratio of cross-linking agent to monomer of 1:10 wt %, was poured onto the Si wafer with the air-sprayed Au/Ag core—shell and Ag nanowire network. Then, the nanowire-embedded PDMS was achieved by detachment of cured PDMS.

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Synthesis of PAAm-Based Stretchable Transparent Hydrogel Electrolyte. The stretchable transparent hydrogel electrolyte was synthesized using a polyacrylamide polymer matrix. Acrylamide (Sigma-Aldrich), N,N-methylenebisacrylamide (Sigma-Aldrich), ammonium persulfate (Sigma-Aldrich), and (N,N,N′,N′-tetramethylylenediamine) were used as polymer matrix monomer, cross-linker, photoinitiator, and cross-linking accelerator, respectively. A high concentration of LiCl salt (Sigma-Aldrich) 8 M was dissolved in DI water, and 2.2 M of acrylamide monomer (Sigma-Aldrich) was added to the Li-dissolved solution. To N,N-methylenebisacrylamide and ammonium persulfate were added 0.0006 and 0.0017 the weight of acrylamide monomer. The cross-linking accelerator N,N,N′,N′-tetramethylylenediamine (0.0025 the weight of acrylamide monomer) was dropped into the solution and cured using ultraviolet light treatment for 30 min. Lastly, the stretchable transparent hydrogel electrolyte was achieved.

Electrochromic Property Measurements. Electrochromic properties were measured by using a three-electrode system. The three-electrode system was used with an Ag/AgCl reference electrode (Fisher Scientific), a platinum wire counter electrode (Fisher Scientific), and transparent stretchable electrode working electrode. LiClO4 salt (1 M, Sigma-Aldrich) in propylene carbonate (Sigma-Aldrich) electrolyte was used for electrochromic characterization. Pulse-type voltage was applied between approximate 0.1 V (vs Pt counter electrode (Ag/AgCl)) and change in transmittance was measured in real time (WONWOO Co.). Coloration efficiency was calculated using the following equation:

\[
\log(T_0(\lambda)/T_\text{sat}(\lambda)) = \Delta\text{o density} \quad (1)
\]

\[
\text{coloration efficiency} = \Delta(\text{o density})/(\text{charge density}) \quad (2)
\]

Electrochemical Properties Measurements. The 1 M of LiClO4 salt (Sigma-Aldrich) in propylene carbonate (Sigma-Aldrich) electrolyte was used for electrochemical characterization. The three-electrode system was used with a voltage window of −2.4 to 0 V (vs Pt counter electrode (Ag/AgCl)). Specific capacitance (Cₚ) was calculated with reference to the discharge time, and the equations below were used to calculate energy density and power density.

\[
C_p = I_m/(AV/\Delta t) \quad (3)
\]

\[
E = \frac{1}{2}CT(\Delta V)^2 \quad (4)
\]

\[
P = (\Delta V)^2/(4mESR) \quad (5)
\]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b08560. Experimental details of sample preparation, fabrication of Au/Ag core–shell nanowire, fabrication of Au/Ag core–shell and Ag nanowire-embedded PDMS, synthesis of PAAm-based stretchable transparent hydrogel electrolyte, electrochromic property measurements, and electrochemical property measurements of transparent stretchable electrode (PDF)

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The authors declare no competing financial interest.

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