Flexible Nanoporous WO_{3-x} Nonvolatile Memory Device—Supporting Information

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1. The oxygen ratio of NP WO_{3-x}.

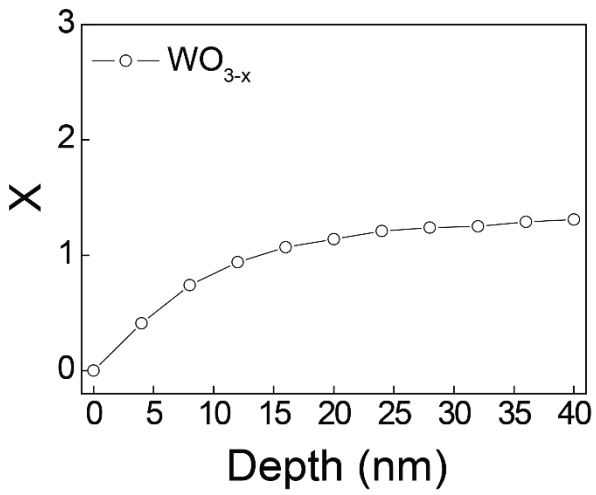

Figure S1. The plot of the 'x' of the NP WO_{3-x} as a function of its depth, which can be estimated from W and O atomic ratios by XPS.

2. Bending method for the flexible Cu/NP WO_{3-x}/ITO memory device.

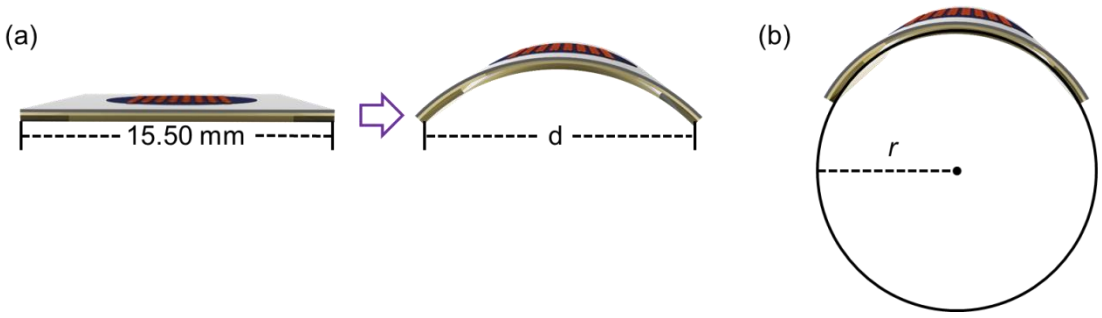

Figure S2. (a) Bending method. (b) Estimation of radius of curvature of the flexible Cu/NP WO_{3-x}/ITO memory device. The strain (%) was calculated from the equation below.

$$\text{Strain (\%)} = \frac{\text{Total thickness of device}}{2 \times \text{radius of curvature}} \times 100$$

3. XPS spectra for the flexible Cu/NP WO_{3-x}/ITO memory device.

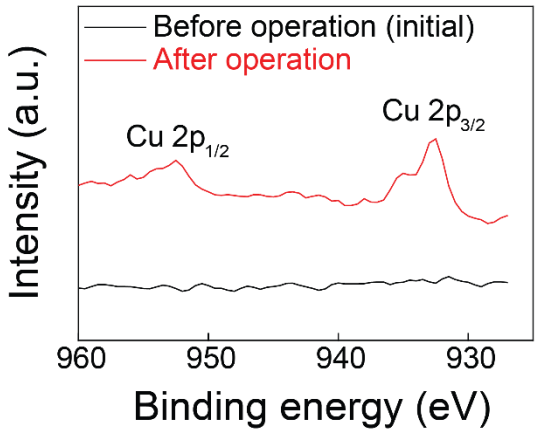

Figure S3. Cu 2p core-level XPS spectra before and after operation.

As shown in the XPS spectra of the flexible Cu/NP WO_{3-x}/ITO memory device before operation (initial state), no Cu 2p core-level signal was detected. However, the Cu 2p core-level signals, which are Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks, were observed after memory operation. These Cu 2p core-level signals imply that the oxidized Cu^{z+} (where *z* is 1 or 2) cations migrated into the switching active layer (NP WO_{3-x}) during memory operation due to the electric field.

4. Fabrication of NP WO_{3-x} memory device on a flexible substrate.

To electrochemically form a NP WO_{3-x} layer from the W layer, the sample was treated by an anodization in an ammonium fluoride (NH_4F)/ethylene glycol solution. The NH_4F/ethylene glycol solution was prepared by dissolving 0.2 M of NH_4F (98% Sigma-Aldrich, USA) in 2 M deionized water in ethylene glycol (Fisher scientific, USA). A two-electrode system was used in the anodic treatments with the W as anode and Pt foil as cathode as shown in Figures S4a,b. For anodic

treatment, the W/ITO/PET substrate was wrapped with Al foil in order to make conductive contact with the Cu plate (anode) as shown in Figure S4b. Note that the area reacting with NH_4F/ethylene glycol solution should not be wrapped with Al foil. Then, the sample and NH_4F/ethylene glycol solution was prepared as shown in Figures S4a,b for the anodization. To form NP WO_{3-x} from W, 20 V was applied for 20 s. After this anodic treatment the sample was rinsed with deionized (DI) water and dried under a nitrogen flow.

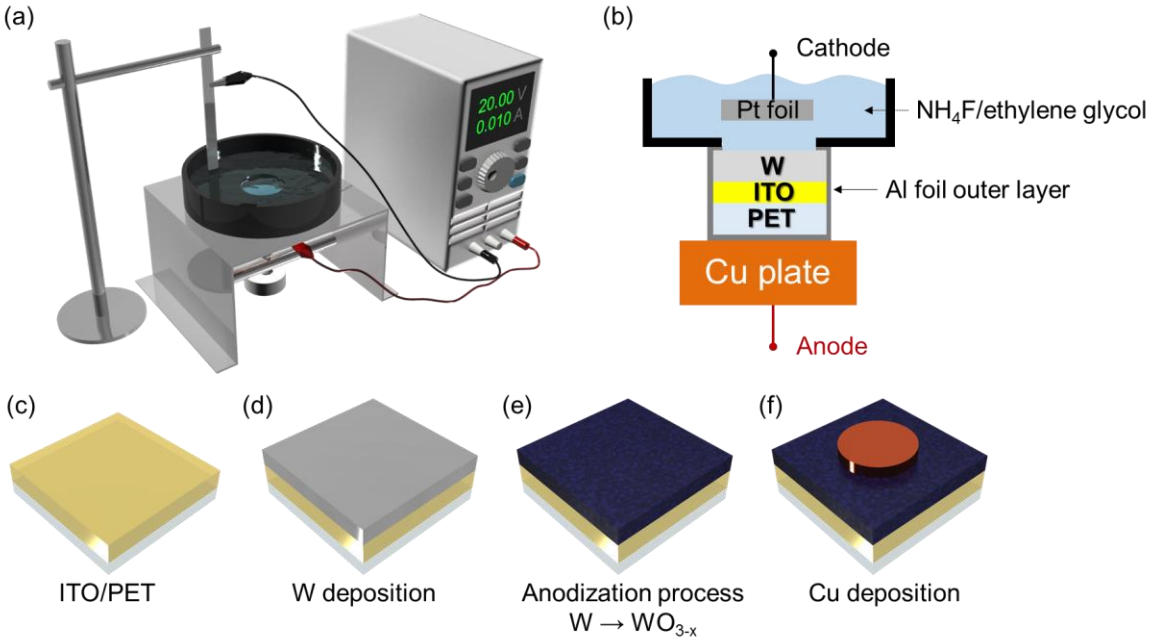

Figure S4. (a) Schematic of electrochemical cell used for anodic treatment and (b) sample preparation for anodic treatment. (c) A ~50 nm thick ITO coated film on PET substrate. (d) A 40 nm thick layer of W deposited on the ITO/PET substrate. (e) The W/ITO/PET sample after anodic treatment. (f) A 50 nm thick Cu top electrode deposited through patterned shadow mask on anodic treated sample.

In order to fabricate a flexible memory device, a 50 nm thick ITO coated PET substrate (175-μm-thick, 15.5 × 15.5 mm^2, MTI Corporation, ITO-PF-14K-300300) was cleaned by a typical ultrasonic cleaning process (Crest, CP1100HT) using acetone and isopropyl alcohol as shown in Figure S4c. As next step, a 40-nm-thick W layer was deposited on the ITO coated PET substrate using a DC sputter (Desk V, Denton Vacuum) as shown in Figure S4d. In order to synthesize the NP WO_{3-x} layer for use as a memory switching layer from the W/ITO/PET sample, the sample was prepared as in Figure S4b and anodically treated as shown in Figure S4a. The color of the area treated with NH_4F/ethylene glycol turned blue as shown in Figure S4e.

As the top electrode of the memory device, a 50-nm-thick Cu was deposited through square patterned shadow mask (200 × 200 μm^2) on the prepared sample as shown in Figure S4f.

5. Optical and electrical characteristics of films after oxygen plasma treatment.

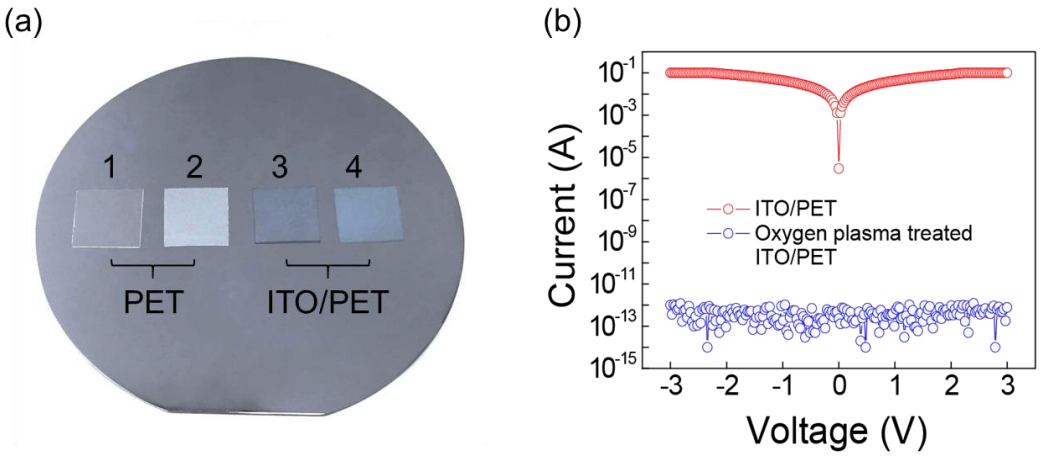

Figure S5. (a) Optical image of (1) PET, (2) oxygen plasma treated PET, (3) ITO/PET and (4) oxygen plasma treated ITO/PET films. (b) Current-voltage (*I-V*) characteristics of untreated and oxygen plasma treated ITO/PET films.

In order to determine the surface change of PET and ITO-coated PET (ITO/PET) films after oxygen plasma treatment, we carried out oxygen plasma treatment on PET and ITO/PET films using a reactive ion etching (RIE) system (Oxford plasma system 100/ICP 180). The set points for gas flow, pressure and power of the RIE were 40 sccm, 100 mTorr and 150 W, respectively, for 10 min. Figure S5a shows the untreated (1) PET and (3) ITO/PET films, which are clear, and the oxygen plasma treated (2) PET and (4) ITO/PET films, respectively, which have turned white due to oxidation.

We tested the electrical conductance of the untreated and oxygen plasma treated ITO/PET films. In order to reduce contact resistance between the probe tip and the ITO/PET films, small pieces of indium were attached to the ITO/PET films where the probe tip was placed. As shown in Figure S5b, the conductance of the oxygen plasma treated ITO/PET film was considerably degraded when compared to the untreated ITO/PET film.

6. I_{ON} and I_{OFF} current with respect to top Cu electrode diameter.

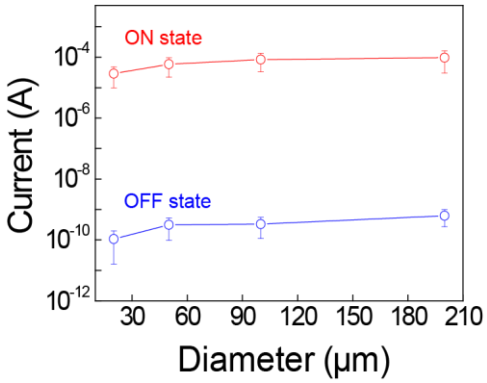

Figure S6. I_{ON} and I_{OFF} current with respect to the diameter of the top Cu electrode. The error bars represent the standard deviation of 10 working cells.

7. The estimated radius of curvature and strain of the flexible Cu/NP WO_{3-x}/ITO memory device.

Distance (mm)	2 × Radius (mm)	strain (%)
15.50	∞	0.00
15.00	29.86	0.59
14.50	22.21	0.79
14.00	18.47	0.95
13.50	14.39	1.22
13.00	12.32	1.42
12.50	11.06	1.58
12.00 Device is broken	8.97	1.95

Table S1. The estimated radius of curvature and strain of the flexible Cu/NP WO_{3-x}/ITO memory device under gradual bending conditions.