Supplementary Information for

Tuning Analog Resistive Switching and Plasticity in Bilayer Transition Metal Oxide Based Memristive Synapses

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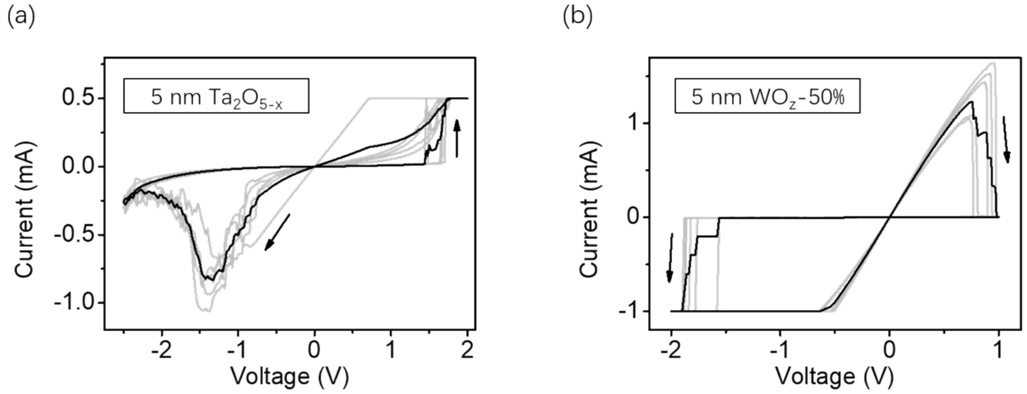

Figure S1. (a) 5 consecutive I-V sweeps (gray) and averaged I-V curve (black) of a Pt/Ti/Ta_2O_{5-x}/ Pt device. (b) 5 consecutive I-V sweeps (gray) and averaged I-V curve (black) of a Pt/Ti/WO_z-50%/ Pt device.

We have fabricated single-layer devices including Pt/Ti/Ta_2O_{5-x}/Pt and Pt/Ti/WO_z-50%/Pt. The I-V sweep of the device is illustrated in Supplementary Fig. S1. In Ta_2O_{5-x} single-layer based devices (Fig. S1a), the cells present unstable resistive switching behavior with increased switching voltages. In WO_z-50% single-layer based devices (Fig. S1b), some cells can show regular bipolar resistive behavior but the set voltage is also higher. Both types of devices have low yields, due to the absence of good oxygen vacancy reservoirs in the device structures. Therefore, the introduction of an oxygen-vacancy-rich base layer seems necessary for the optimization of the resistive switching behaviors.

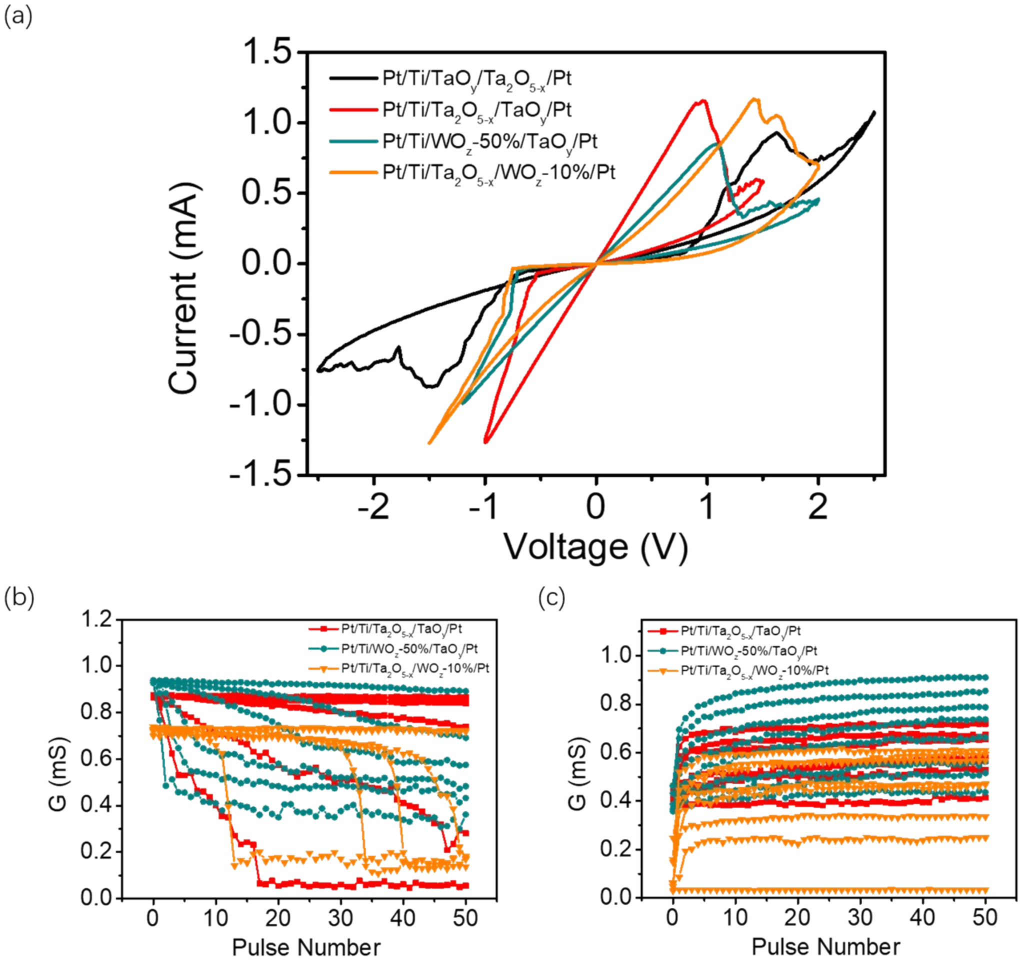

Figure S2. (a) Averaged I-V curve of four different types of devices with bilayer structure. (b-c) LTD and LTP of bipolar resistive switching devices with different stacking materials.

The DC, LTD and LTP electrical results of different devices are summarized in Supplementary Fig. S2. One can find from Fig. S2a that while Pt/Ti/TaO$_y$/Ta$_2$O$_{5-x}$/Pt devices showed CRS behavior, all the other three types of devices exhibited bipolar switching characteristics differing in switching voltages and currents. Pt/Ti/Ta$_2$O$_{5-x}$/TaO$_y$/Pt devices have the lowest set and reset voltage but highest on-state and off-state currents, probably due to the reduced thickness of Ta$_2$O$_{5-x}$ as a result of interfacial reactions.

In order to make further comparison on the three types of device showing bipolar switching, we have also plotted pulse measurement results of the three bipolar devices together, as can been seen in Fig. S2b for LTD and Fig. S2c for LTP. One can see that compared with the Pt/Ti/Ta$_2$O$_{5-x}$/TaO$_y$/Pt and Pt/Ti/Ta$_2$O$_{5-x}$/WO$_z$-10%/Pt devices with higher nonlinearity during the conductance adjustment processes, the Pt/Ti/WO$_z$-50%/TaO$_y$/Pt devices have shown more gradual conductance adjustment and therefore larger number of states.

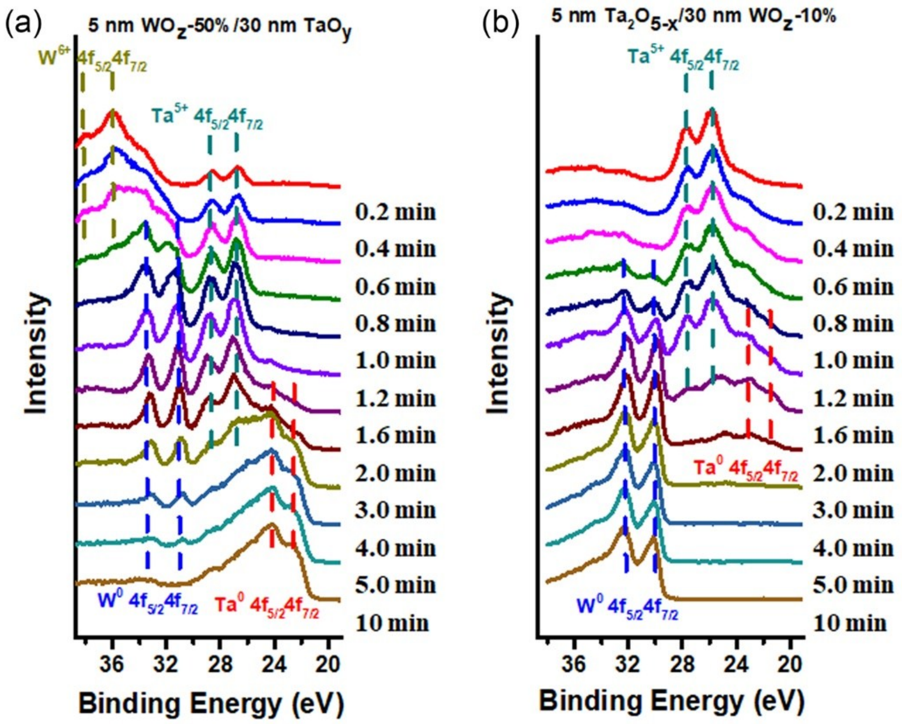

Figure S3. XPS depth profiling analysis of (a) WO$_z$-50%/TaO$_y$ and (b) Ta$_2$O$_{5-x}$/WO$_z$-10% structures.

We have performed XPS depth profiling analyses of WO$_z$-50%/TaO$_y$ and Ta$_2$O$_{5-x}$/WO$_z$-10% bilayer structures as illustrated in Supplementary Figure S3. One can clearly see the coexistence of W and Ta peaks at the interfaces for both structures, therefore suggesting that there might be some extent of intermixing between the two layers. This is an expected phenomenon due to the inevitable inter-diffusion between the switching layer and base layer materials.

Supplementary Table S1 R code of number of multilevel states

```
data_original<-read.csv('data.csv',header=TRUE,stringsAsFactors = FALSE);#read original data(with noise) from 'data.csv'
data_lowess<-lowess(data_original[,1],data_original[,2]);#use lowess function to predict actual value(without noise)
noise<-data_original[,2]-data_lowess$y;#calculate the noise
noise_var<-var(noise);#calculate the variance of the noise
range<-max(data_lowess$y)-min(data_lowess$y);#calculate the range of data
state<-range/sqrt(noise_var);#the number of multilevel states
```

We have developed a method to estimating the NOS for both linear and nonlinear conductance adjustment processes with consideration of device variations, and similar criteria were also used to analyze the data in the cited literature as shown in Fig. 6a. It should be noted that when the multilevel switching was achieved by DC sweeping in the literature, the number of distinguishable sweeping curves was directly adopted as the NOS in Fig. 6a. Below we mainly describe our approach for determining NOS from pulse measurements.

First of all, we filter the LTP and LTD data that meet the condition "maximum/minimum > 1.3" to make sure that the conductance states are recognizable and meaningful. Since in real cases, the filament growth (dissolution) dynamics of memristor usually results in nonlinear and sometimes locally non-monotonous switching, we use a smooth function to fit the experimental data and ascribe locally non-monotonous switching to the noise. Specifically, in this study we fitted the filtered LTP or LTD curves using locally weighted scatter plot smoothing function (lowess). The function calculates the value of each point by a weight average[1] of adjacent points[2]. The amplitude of noise is subsequently extracted by comparing the actual value and the fitting curve, therefore giving standard deviation of the noise. Conductance changes below the standard deviation are therefore considered inaccessible, and the NOS is estimated by dividing the overall conductance change range by the standard deviation.

We have calculated the number of multilevel states in the R Project and the code is provided in Supplementary Table 1. The Ta_2O_5 based devices Pt/Ti/Ta_2O_{5-x}/TaO_y/Pt and Pt/Ti/Ta_2O_{5-x}/WO_z-10%/Pt have the best state number of 22 and 8, respectively. In contrast, the WO_z based devices Pt/Ti/WO_z-50%/TaO_y/Pt has the best state numbers of 38, in agreement with the proposed correlation between the NOS and the number of intermediate phases.

1. the weight function is a tri-cube weight function, which means $weight=(1-|x|^3)^3$, here x is the distance.
2. "nearby" is determined by a parameter "f", which means the lowess function will take number=f*total_point_number of points nearby and use them to calculate the weighted average, the default value of "f" in The R Project is 2/3.