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Supporting Information

Novel Design for the Odd-Symmetric Memristor from Asymmetric Switches

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1. Preparation of Ag₂S film.

Ag₂S films were synthesized with a following method. 2 g sulphur and one silver foil with the thickness of 0.5 mm were loaded into a quartz tube and separated by quartz wool. Then, the tube was sealed via a Bethlehem lathe (model GL50A) after vacuum up to 1 mtorr. The sealed tube was heated to 200 °C at a rate of 2 °C/min and then remained at the temperature for 1 hour reaction between sulphur vapour and a Ag foil, followed by quenching in water at room temperature. The obtained sample was a Ag foil with Ag₂S layers on its both sides as Ag₂S/Ag/Ag₂S system. Furthermore, after one side of the Ag₂S of Ag₂S/Ag/Ag₂S was grinded off (Fig. S1), a Ag₂S/Ag structure sample was obtained.



Fig. S1 The cross sectional FE-SEM image of Ag₂S/Ag switch.

2. Characterization and I–V measurements.

X-ray diffraction data for Ag₂S film was obtained under 1 atm at room temperature by using a Scintag XDS-2000 powder diffractometer at 45 kV and 35mA for Cu K α (λ =1.54062 Å) radiation, with a scan speed of 1°/min and a step size of 0.03° in 2 θ . The morphologies of Ag₂S film and the cross section of Ag₂S/Ag interface were evaluated with a Field Emission Scanning Electron Microscope (Hitachi S-4700) at an acceleration voltage of 5 kV. Surface topographies of Ag₂S film were further analysed by an atomic force microscopy (Veeco Dimension 3000) operated at room temperature. Fourier transform near infrared spectroscopy (FT-NIR) spectra were recorded with an ABB-Bomem MB 160 **FT-NIR** spectrometer using polytetrafluoroethylene as the reference at a resolution of 16 cm⁻¹ with scan numbers of 256. Electrochemical impedance spectroscopy (EIS) was performed using a CHI660A Electrochemical workstation in the frequency of 1000 Hz and the amplitude of 5 mV. Cycle voltammetry was swept from -0.2 V to 0.2 V in 0.1 M NaNO₃ solution with three electrode system (a Platinum wire as the counter electrode, a Hg/Hg₂Cl₂ electrode as the reference electrode, and Ag₂S-based electrode as the working electrode). Hysteresis I-V curves were collected by an electrochemical workstation (Princeton Potentiostat/Galvanostat Model 273A) which allowed the measurement (the contact area was 0.064 mm²) of currents from 100 nA-1A.

3. Band gap from FT-NIR spectrum.

A FT-NIR spectrum was exploited to calculate the band gap of the quenched-Ag₂S. As shown in Fig. S2a, the spectrum of Ag₂S has a rapid decrease while that of silver remains flat. From Fig. S2b, which is $(\alpha hv)^2$ versus hv with Tauc plot, we can obtain the band gap (0.88 eV) of the quenched-Ag₂S.



Fig. S2 (a) FT-NIR spectra of Ag and the quenched-Ag₂S film and (b) $(\alpha hv)^2$ versus hv of the quenched-Ag₂S.

4. Flat-band Potential from EIS measurements.

Mott-Schottky equation can be expressed as follows (Eq. S1):

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon A^2 e N_D} (V - V_{fb} - \frac{k_B T}{e})$$
(S1)

where C is the interfacial capacitance, ε is the permittivity of the semiconductor, ε_0 is the permittivity of vacuum, A is the area, N_D is the number of donors, V is the externally applied potential, V_{fb} is the flat-band potential, k_B is Boltzmann's constant, T is the absolute temperature, and e is the electronic charge. According to this equation, a straight line can be generated by the plot of I/C^2 against V, and flat-band potential (V_{fb}) can be obtained from the intercept (on the V axis). According to this principle, we generated the Mott–Schottky plot for the quenched Ag₂S from the EIS measurement. As shown in Fig. S3, the flat-band potential is -0.25 eV. Therefore, if ignoring the slight difference between flat-band and conduction band, the valence band potential is 0.63 eV.



Fig. S3 Mott–Schottky plot for the quenched-Ag₂S.

5. The stability of Ag₂S/Ag switch and Ag₂S/Ag/Ag₂S memristor.



Fig. S4 Typical I–V characteristic of (a) Ag_2S/Ag switch and (b) $Ag_2S/Ag/Ag_2S$ memristor in the 1st (black), 500th (blue), and 1000th (red) cycles at room temperature.

6. The bias voltage and resulting current versus time for Ag₂S/Ag switch and Ag₂S/Ag/Ag₂S memristor.



Fig. S5 The bias voltage (blue) and resulting current (red) versus time for (a) Ag_2S/Ag switch and (b) $Ag_2S/Ag/Ag_2S$ memristor at room temperature.