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Electronic Supplementary Information

Reversible self-powered fluorescent electrochromic windows driven by perovskite solar cells

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Experimental Section

Materials and methods

$Na_2WO_4 \cdot 2H_2O$, H_3PO_4 (85%), KCl, C_2H_6O, CH_3OH, KAc, TEOS, Rhodamine 6G (Rh6G), $NH_3 \cdot H_2O$ and Lysine (LY) were purchased from Sinopharm Chemical Reagent Co., Ltd. $K_2HPO_4 \cdot 3H_2O$ and KH_2PO_4 were used to prepare the phosphate buffer. Lithium perchlorate trihydrate ($LiClO_4 \cdot 3H_2O$) was obtained from Shanghai HuShi Co., Ltd., China. Propylene carbonate (99%) was purchased from Shanghai Makclin Biochemical Co., Ltd., China. All other chemicals were of analytical grade and ultrapure water (>18 MΩ·cm) from Milli-Q Plus system (Millipore) was utilized throughout the experiments. The ITO chips (transmittance > 83%, sheet resistance < 15 Ω sq^{-1}) were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd., China.

Apparatus

Field-emission scanning electron microscope (SEM) images were performed with a FEI

Quanta200F. Luminescence measurements were taken on a Hitachi F-7000 fluorescence spectrophotometer (Hitachi High Technologies, Japan). All electrochemical experiments were carried out on a CHI 660 electrochemical work station (Chenhua Instrument Corporation, China).

Synthesis of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot15H_2O$ (POMs)

POMs were prepared according to our previous report.[1] 33 g $Na_2WO_4\cdot2H_2O$ was dissolved in 26.5 mL H_3PO_4 (85%) and 30 mL water, and heated at 120 °C for 9 hours. After cooling to room temperature, 10 g KCl and 15 mL of water was added, respectively. The precipitate was filtered off and washed with 2 M potassium acetate and methanol, and then dissolved in hot water. After cooling to room temperature, white crystals were formed, and a second recrystallization was needed for the pure product. Finally, the POMs IR absorption spectrum is conducted. As shown in Fig. S1, the typical peaks of P–Oa, W–Od, W–Ob–W and W–Oc–W were observed, and further confirmed the formation of POMs.

Synthesis of Rh6G-doped silica nanoparticals (Rh6G@SiO_2 NPs)

In order to minimize the photobleaching and photodegradation phenomena from the surrounding environment, dye-doped silica NPs were adopted by encapsulating the dye molecules into a silica matrix. The organic dye, Rh6G, was selected as the compatible fluorescent component, mainly because the excitation and strong emission spectra of Rh6G (centered at 566 and 600 nm, respectively) overlap well with the absorption band of the POMs (500-1000 nm), which is beneficial to the efficient fluorescence quenching. The Rh6G@SiO_2 NPs were prepared as previously described.[2] 0.5 mg Rh6G was dissolved in solution mixing of 1.0 mL of TEOS, 7.5 mL of ethanol and 2.5 mL of water, then adjusted it with ammonia water to be about pH = 7, and stirred for 10 min. The mixture was placed in 35 °C water bath aging for 1 h, and adjusted with ammonia water until jelly-like substance formed. The final Rh6G@SiO_2 NPs were prepared after the calcinating at 300 °C about 20 min, and then centrifuged for the further experiments. The general morphology of the as-prepared Rh6G@SiO_2 is shown in Fig. S2, near-spherical structures were formed, and the average diameter was estimated about 50 nm.

Preparation of LY-POMs/Rh6G wet adhesives and EFCD film

Before modification, the ITO glasses with 0.80 × 5.30 cm^2 were washed by acetone, ethanol and water sequentially, then activated in ethanol/NaOH solution under ultrasonic. LY and POMs were selected to fabricate the adhesive. Because LY exhibits positive charge when $pH < 7$. The stable and reproducible electrochromic performance of POM also makes it a promising candidate for fabricating ECDs. In this work, POMs work not only as electrochromic material, but also as cathode of the battery because of the high redox potential difference between two electrodes of the battery. The non-covalent crosslinking between lysine and POMs is driven by the hydrogen bond and electrostatic interactions between positive-charged POMs and protonated $-NH_3^+$ of LY. POMs and LY with mole ration of 6:1 were dissolved in water and pH was adjusted to about 3, resulting in mixture of LY-POMs. Then Rh6G@SiO_2 was added to the above mixture, and kept still at room temperature until formation of reddish-brown LY-POMs/Rh6G@SiO_2 adhesive.

Fabrication of Mg/POMs battery

The Mg/POMs battery was composed of metallic Mg and POMs, which works as anode and cathode, respectively. The part of Mg rod exposed to the air was polished each time. The electrolyte used in this work was propylene carbonate solution containing 2 mol/L of $LiClO_4$. Through connecting POMs and Mg electrodes, the battery can discharge smoothly. The performance of the Mg/POMs battery was measured using Chronopotentiometry with Current Ramp (CPCR, CHI660) method, in which POMs served as working electrode, and Mg worked as both the counter and reference electrode.

Preparation of $CH_3NH_3PbI_3$ perovskite film

The perovskite precursor solution (45 wt%) was composed of PbI_2 and CH_3NH_3I (both 1.2 mmol) dissolved in mixture of 2 mL anhydrous N,N-dimethylformamide and 1 mL dimethyl sulfoxide (v:v=1:1). Then TiO_2 and $CH_3NH_3PbI_3$ precursor solution was successively spin-coated on ITO substrate at a speed of 5000 rpm for 10 s, and put at 110 ^oC for post-annealing to form uniform $CH_3NH_3PbI_3$ film. After that, the hole transport layer (HTL) was prepared by spin-coating 30 μL of 2,2',7,7'-tetrakis (N,Ndi-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) solution on the perovskite layer. Finally, Au layer with 80 nm was thermally evaporated as a top electrode to finish the fabrication of the device. The active areas of all devices were defined to 6.8 cm^2. All these procedures were carried out in a dry N_2 environment.

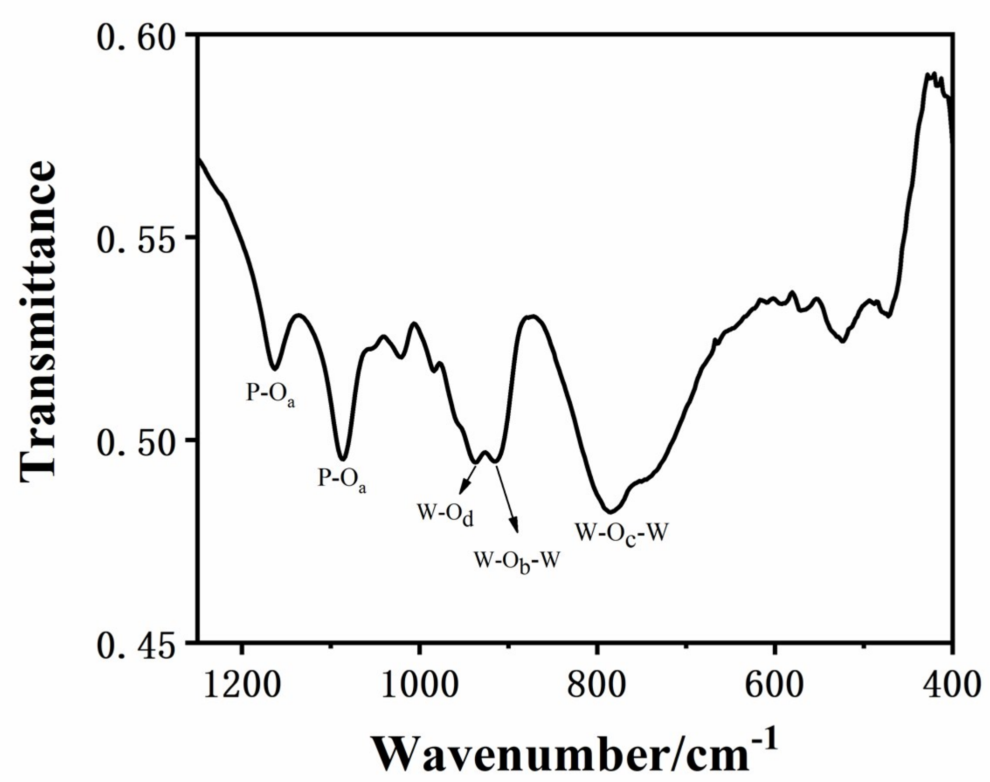

Fig. S1 FTIR absorption spectrum of POMs powder in KBr pellet.

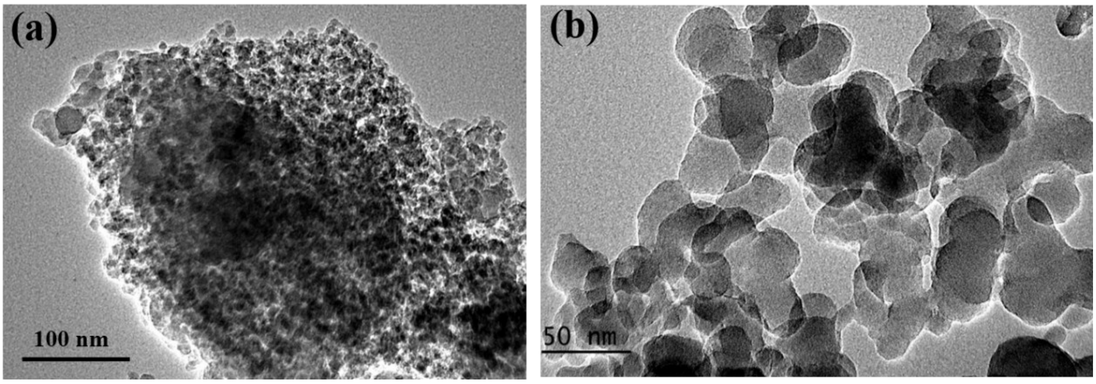

Fig. S2 TEM images of the prepared Rh6G@SiO_2 NPs.

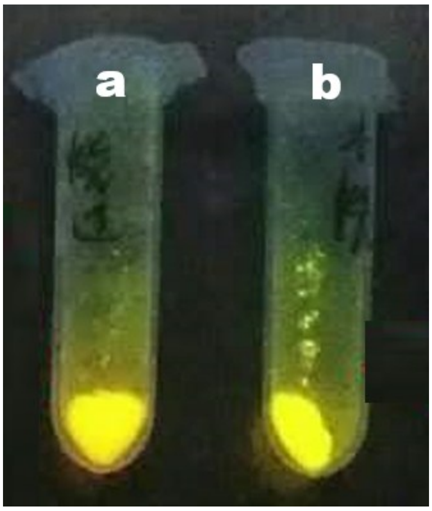

Fig. S3 Fluorescence images of Rh6G@SiO$_2$ (a) before and (b) after annealing treatment excited with a hand-held UV lamp (365 nm).

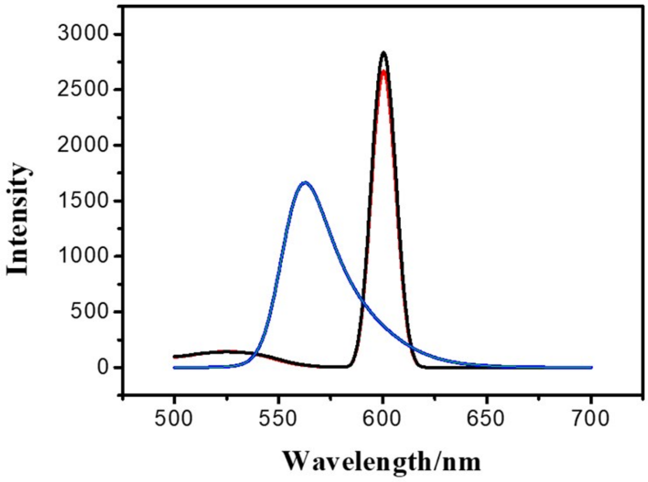

Fig. S4 Fluorescence excitation (blue line) and emission spectra of pure Rh6G (black line) and the synthesized Rh6G@SiO$_2$ NPs (red line).

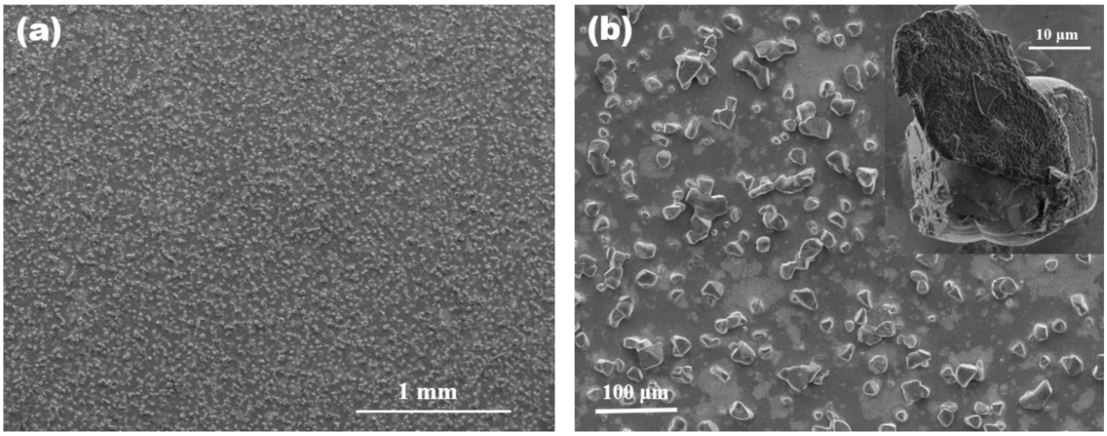

Fig. S5 SEM images of LY-POMs/Rh6G@SiO$_2$ film on ITO.

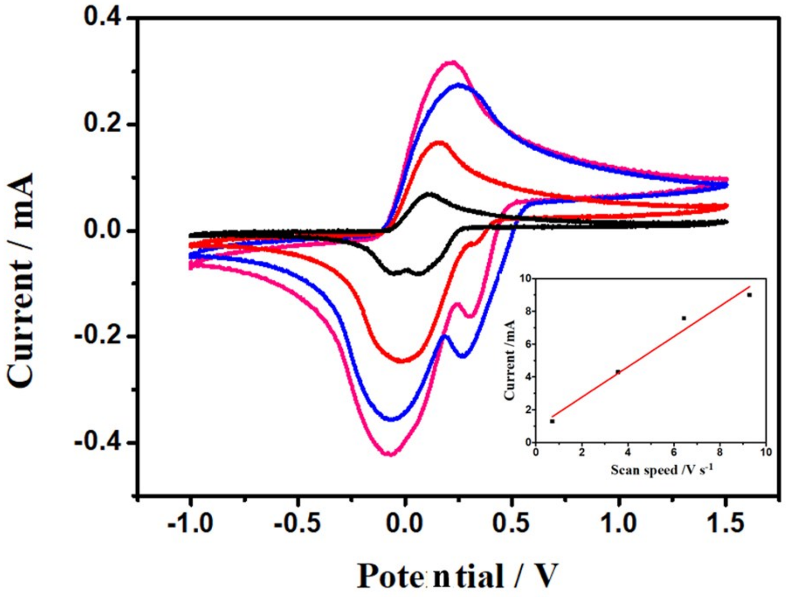

Fig. S6 CVs of ITO/LY-POMs/Rh6G@SiO$_2$ electrode at different scan rates (from inner to outer): 0.01, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 v/s. Inset: plot of peak current (Ip) vs. scan rate.

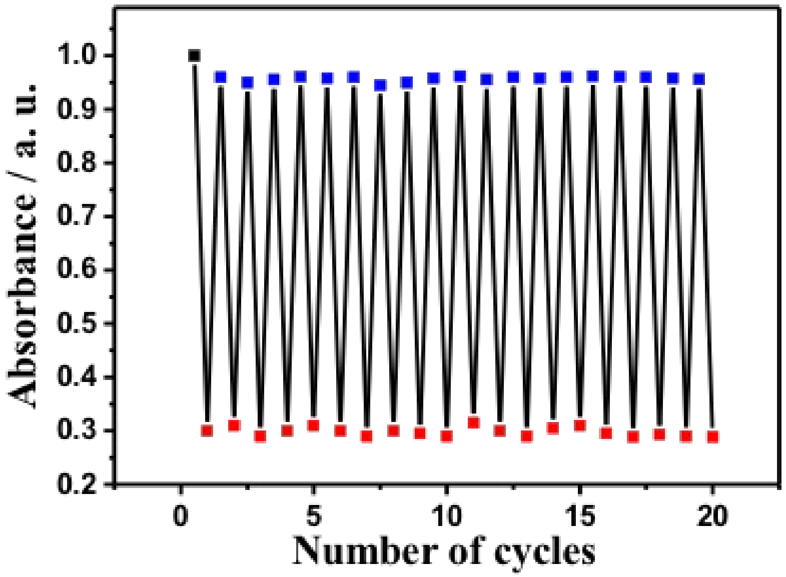

Fig. S7 The normalized UV-Vis absorption intensity of EFCD as a function of cycle numbers.

Table S1. The detailed status of the device and POMs in “ON” “OFF” and “intermediate” states.

states	ON	intermediate	OFF
color of device (under UV radiation)	yellow (coloring)	light yellow	dark (bleaching)
color of POMs (no UV radiation)	white	light blue	dark blue

Table S2 Photovoltaic parameters of the fabricated PSC.

V	**Voc**	**Jsc mA cm^{-2}**	**Fill Factor**	**Efficiency**
5.08	1.02	16.48	61.69	10.33

The designed PSCs showed typical performance with a V_{OC} of 1.02 V, a short circuit current density (J_{SC}) of 16.48 mA cm^{-2}, a fill factor (FF) of 61.7%, and a PCE of 10.3%.

Video S1. The video record of LY-POMs/Rh6G wet adhesives formation.

References

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2. Y. Zhai, L. Jin, C. Zhu, P. Hu, L. Han, E. Wang and S. Dong, *Nanoscale*, 2012, **4**, 7676-7681.