

## Electronic Supplementary Information (ESI)

### Photo-switchable Two-Dimensional Nanofluidic Ionic Diodes

Lili Wang,<sup>†</sup> Yaping Feng,<sup>‡</sup> Yi Zhou,<sup>§</sup> Meijuan Jia,<sup>‡</sup> Guojie Wang,<sup>†,\*</sup> Wei Guo,<sup>‡,\*</sup> and Lei Jiang<sup>‡</sup>

<sup>†</sup> School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China.

<sup>‡</sup> CAS Key Laboratory of Bio-inspired Materials and Interfacial Science, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

<sup>§</sup> School of Geoscience and Surveying Engineering, China University of Mining and Technology, Beijing 100083, P. R. China.

\* To whom correspondence should be addressed: wguo@iccas.ac.cn (Wei Guo), guojie.wang@mater.ustb.edu.cn (Guojie Wang).

#### Table of contents:

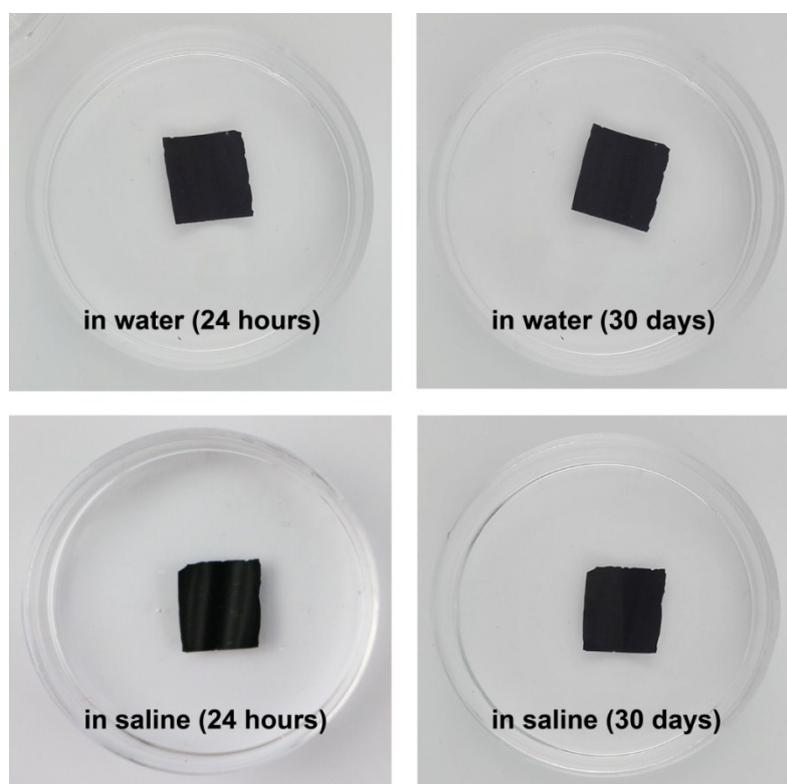
1. Chemicals
2. Stability of SP-GOM
3. Characterization of SP-GOM
4. Experimental setup
5. Transmembrane ionic conductance
6. Photochromic reaction in bulk SP solution
7. Zeta potential measurement
8. Current-voltage responses for different UV time
9. References

## 1. Chemicals

Graphene oxide (GO) powder was purchased from XFNANO, China (product number, XF002-1). 1-(2-Hydroxyethyl)-3, 3-dimethylindolino-6'-nitrobenzopyrrolospiran (SP) was purchased from TCI. Hydrochloric acid (HCl), potassium hydroxide (KOH), potassium chloride (KCl), and ethanol were purchased from Sinopharm Chemical Reagent (Beijing, China). All of the chemical reagents were used as received without further purification. Electrolyte solutions were prepared with MilliQ water (18.2 M $\Omega$ •cm).

## 2. Stability of SP-GOM

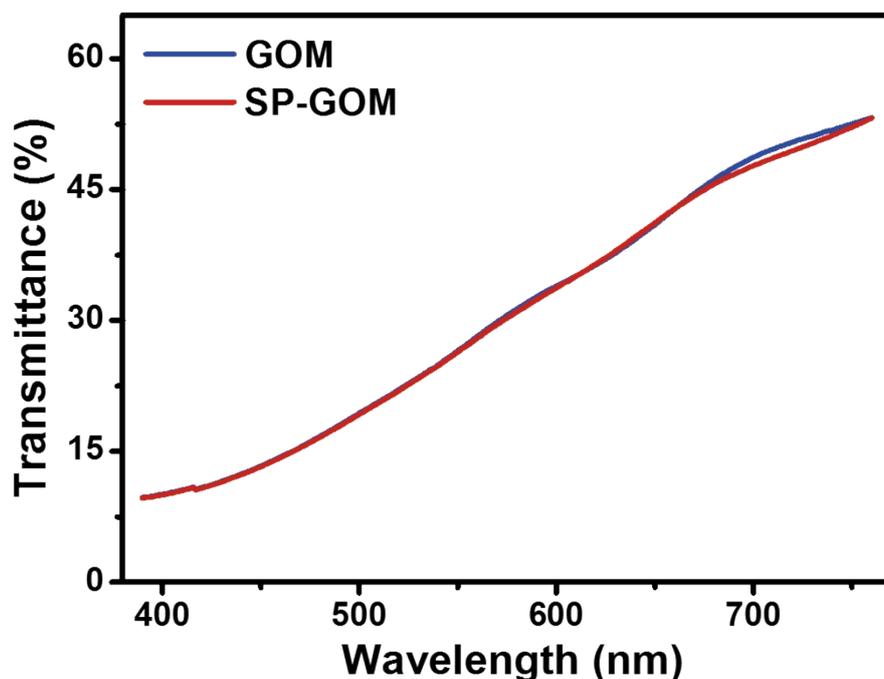
Before modification with SP, the GOMs were heated at 80 °C for 24 hours in an oven to improve the stability. After the drop-casting of SP, the unbonded SP was washed away with water. The SP-GOMs are also hydrophilic (Figure 1a). They can be stable in water or in saline for over 30 days (Figure S1). Neither GO nor SP moieties are found to be re-dispersed in water.



**Figure S1.** A photograph of SP-GOMs stably stored in water or in saline for days.

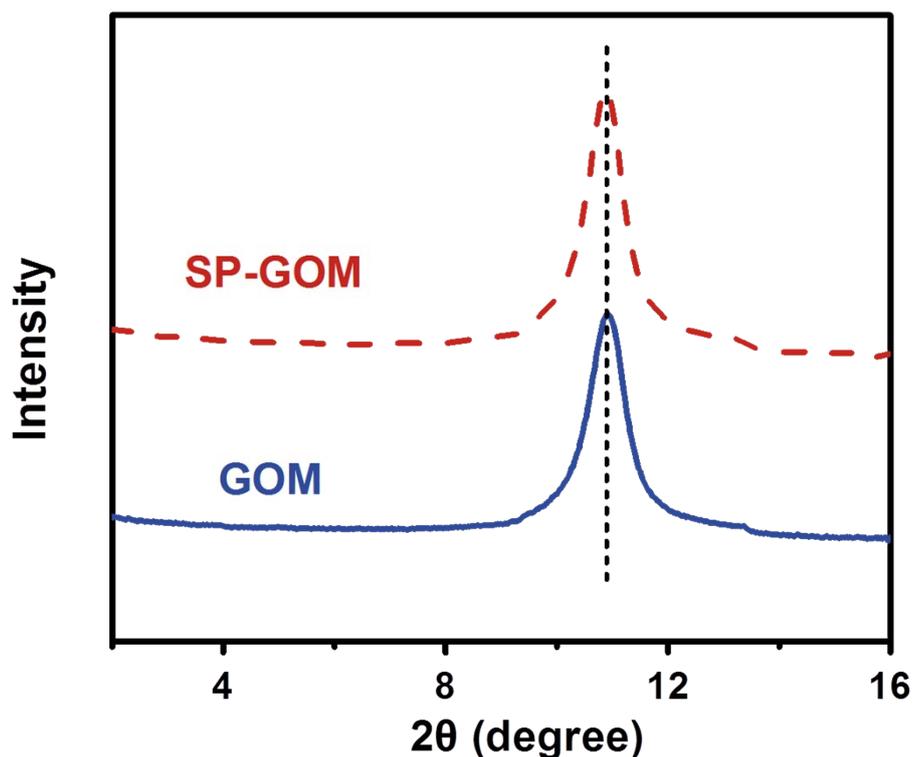
### 3. Characterization of SP-GOM

UV-vis spectrophotometer was employed to verify the transparency of the GOM and SP-GOM. The light transmittance of the membrane samples does not show obvious difference before and after modification with SP (Figure S2).



**Figure S2.** Light transmission spectra of GOM and SP-GOM. The modification of SP does not obviously influence the optical transparency of the GOM.

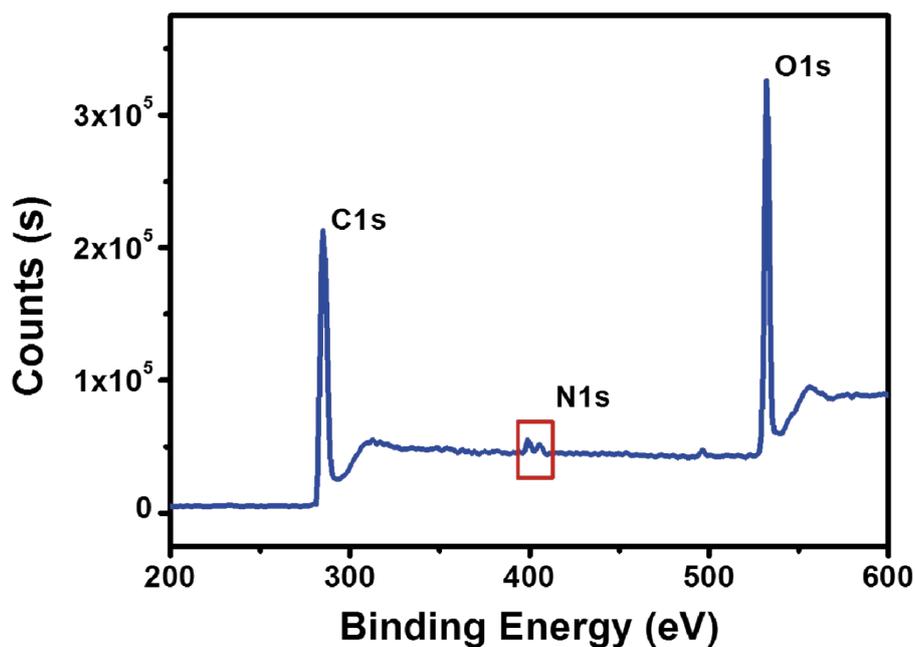
The near-surface microstructure and the interlayer distance of the SP-GOM and GOM is investigated via grazing incidence X-ray diffraction (GI-XRD) with  $0.1^\circ$  fixed incidence angle, in the range of  $0-16^\circ$ . The scan velocity was  $0.3^\circ/\text{min}$  (Figure S3). Very similar diffraction peaks centered at  $2\theta \sim 10.9^\circ$  are discovered for both SP-GOM and GOM in dry state, indicating identical interlayer distance of about 0.81 nm. Since the GI-XRD was tested in vacuum, both the modified and unmodified GOMs were dried prior to the test. The diffraction peaks measured here are different from that obtained with wet membranes in Figure 1d. This evidence confirms that the single-sided addition of trace amount of SP does not impair the layered structure and the interlayer distance of the GOM, even in the near-surface layers.



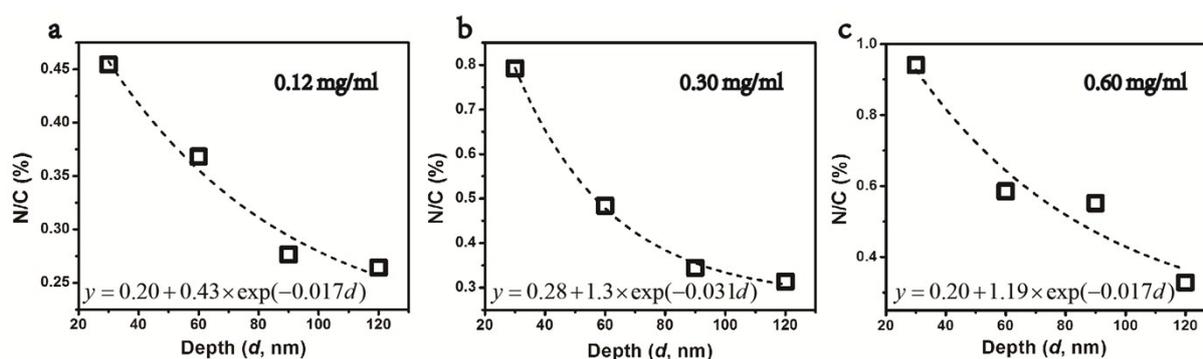
**Figure S3.** Grazing incidence X-ray diffractograms of the SP-GOM and GOM. Very similar diffraction peaks centered at  $2\theta \sim 10.9^\circ$  is discovered. No evident change is found in XRD patterns before and after the asymmetric modification of trace amount of SP molecules.

X-ray photoelectron spectroscopy (XPS) is further employed to verify the chemical composition of the SP-GOMs. XPS measurements were carried out on an ESCALab220i-XL electron spectrometer from TF Scientific using 300W Al K $\alpha$  radiation. The binding energy of 284.8 eV corresponds to the C1s line.<sup>[1]</sup> Figure S4 shows the XPS spectrum of SP-GOM. An N1s peak near 400 eV is observed. The N/C atomic ratio approaches 1.15% on the top surface, much higher than the background level of  $\sim 0.29\%$ , obtained on unmodified GOMs. This evidence confirms that SP was attached onto the surface layers of GOM.

XPS depth profiling is further employed to verify the penetration of SP moieties into GOM. The N/C ratio were collected during depth profiling up to 120 nm of a nominal etching into the film from the top side. The measured N/C ratio with respect to the depth beneath the top surface can be numerically fitted with a set of natural exponential function (Figure S5). With the fitting curves, the penetration depth of the SP molecules can be estimated, at which the N/C ratio drops into the range of unmodified GOMs.

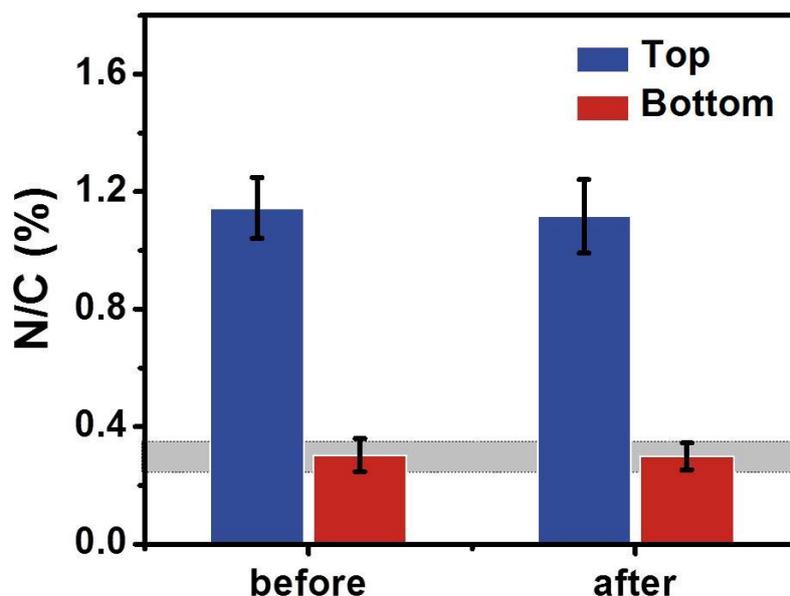


**Figure S4.** XPS spectrum of SP-GOM.



**Figure S5.** Depth profiling of SP-GOM from the top surface, modified at various SP concentrations of 0.12 (a), 0.30 (b), and 0.60 mg/ml (c). The decay of the N/C ratio can be well fitted by a set of natural exponential functions (the down insert in each figure).

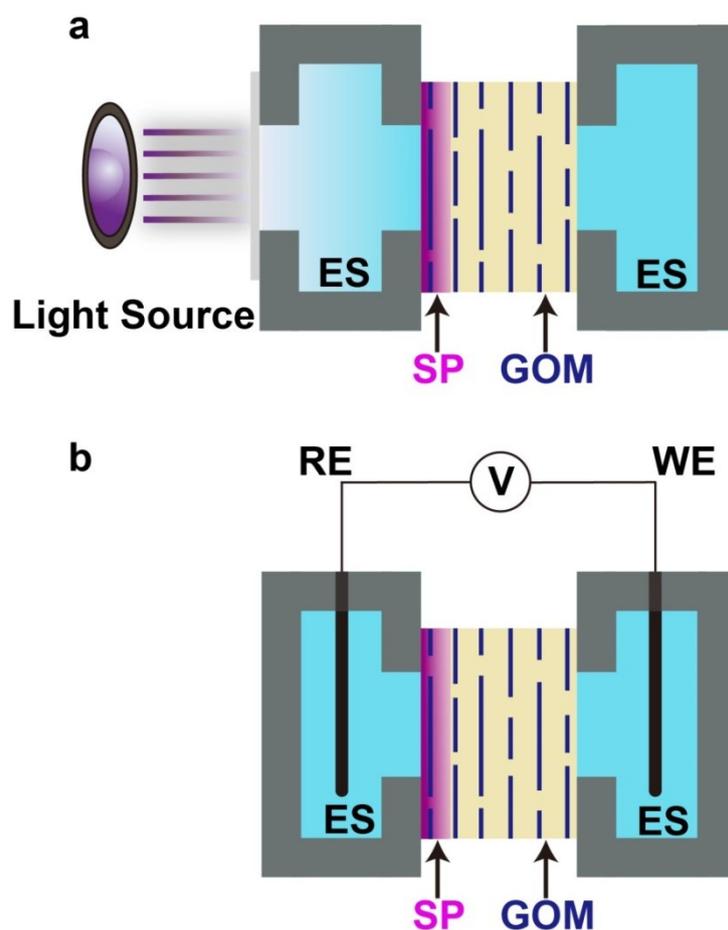
Even after being soaked in water for hours, no evident change in the nitrogen content is found compared to the as-prepared SP-GOM (Figure S6). The nitrogen content from the bottom surface still falls into the range of background level. This evidence suggests that the attached SP molecules do not further penetrate into the membrane after being soaked in water.



**Figure S6.** N/C ratio measured on the top and bottom surface of the SP-GOM before and after being soaked in water for three hours. The shadow indicates the background N/C ratio of  $0.29 \pm 0.05$  % measured on unmodified GOMs.

#### 4. Experimental setup

To investigate the ion transport properties through the GOM or SP-GOM, the tested membrane was mounted in between a two-compartment photoelectrochemical cell, as described in detail in our previous publications.<sup>[2-4]</sup> 1 ml of 10 mM KCl solution was injected in each half-cells. To perform light irradiation, a glass-sealed window was opened in the half-cell facing the SP side (Figure S7a). During light irradiation, no electrode was placed in the photoelectrochemical cell to avoid light pollution. After light irradiation, a pair of Ag/AgCl electrode was used as current collector to measure the current-voltage response of the tested membrane (Figure S7b). The current-voltage properties were recorded by a source meter (Keithley 2636B). Sweeping voltage from -2 to +2 V was applied with a step voltage of 100 mV. The effective membrane area for current recording is about 1.6 mm<sup>2</sup>.

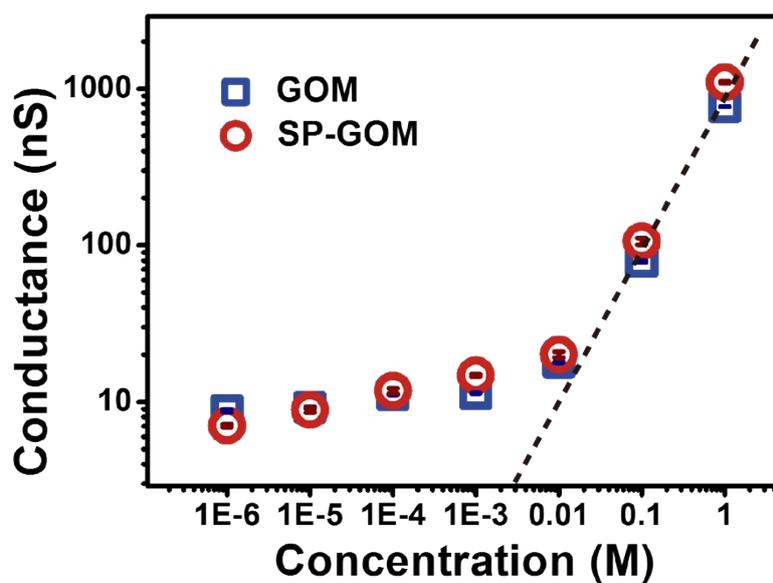


**Figure S7.** The photoelectrochemical cell used for measuring the ion transport through the tested membranes. (a) For light irradiation, a transparent window was opened in one half-cell facing the SP side and no electrode was placed in the cells. (b) For ionic current recording, a pair of Ag/AgCl electrode was placed in the two half-cells. RE stands for the reference electrode, WE stands for the working electrode, and ES stands for electrolyte solution. The electrical potential applied on WE is referenced to that on the RE.

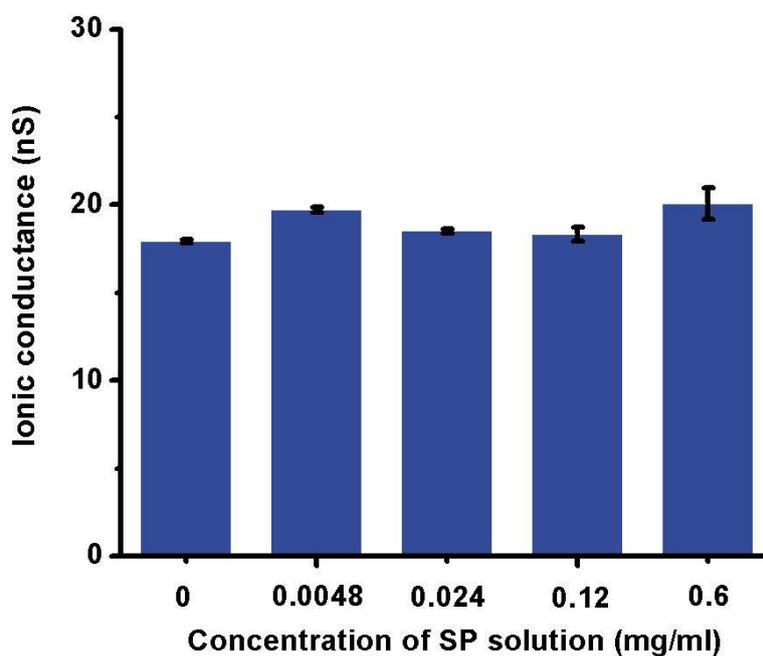
## 5. Transmembrane ionic conductance

The transmembrane ionic conductance of the SP-GOM and GOM were measured in various KCl electrolyte solutions with concentration ranging from 1  $\mu$ M to 1 M. The attachment of SP shows very limited change to the total ionic conductance (Figure S8). This result verifies the fact that merely a very thin layer of GO lamina is modified by SP moieties.

For the unmodified and modified GOMs with different concentration of SP solution (0.0048 to 0.60 mg/ml), the total ionic conductance remains in the same level (Figure S9), suggesting that the attachment of SP molecules do not form effective blockade to the transmembrane ion transport.



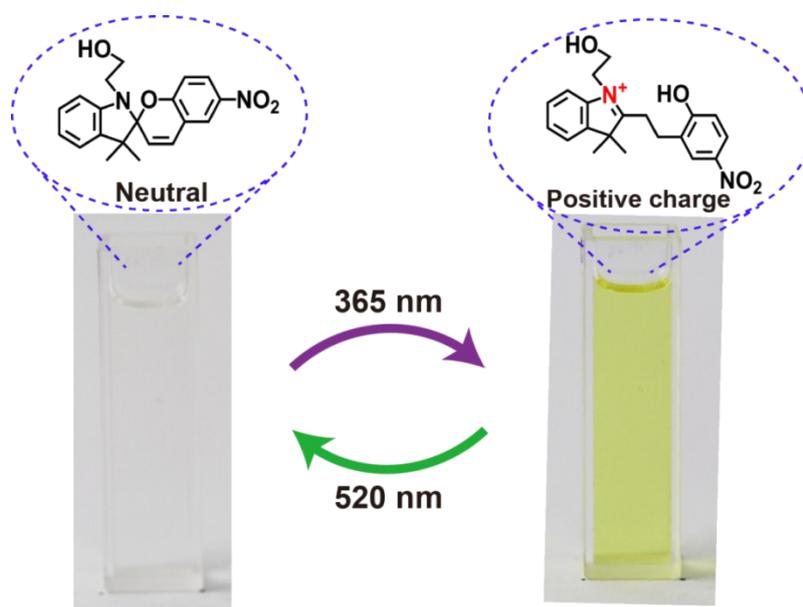
**Figure S8.** Transmembrane ionic conductance through the SP-GOM and GOM in KCl electrolyte solutions from 1  $\mu$ M to 1 M.



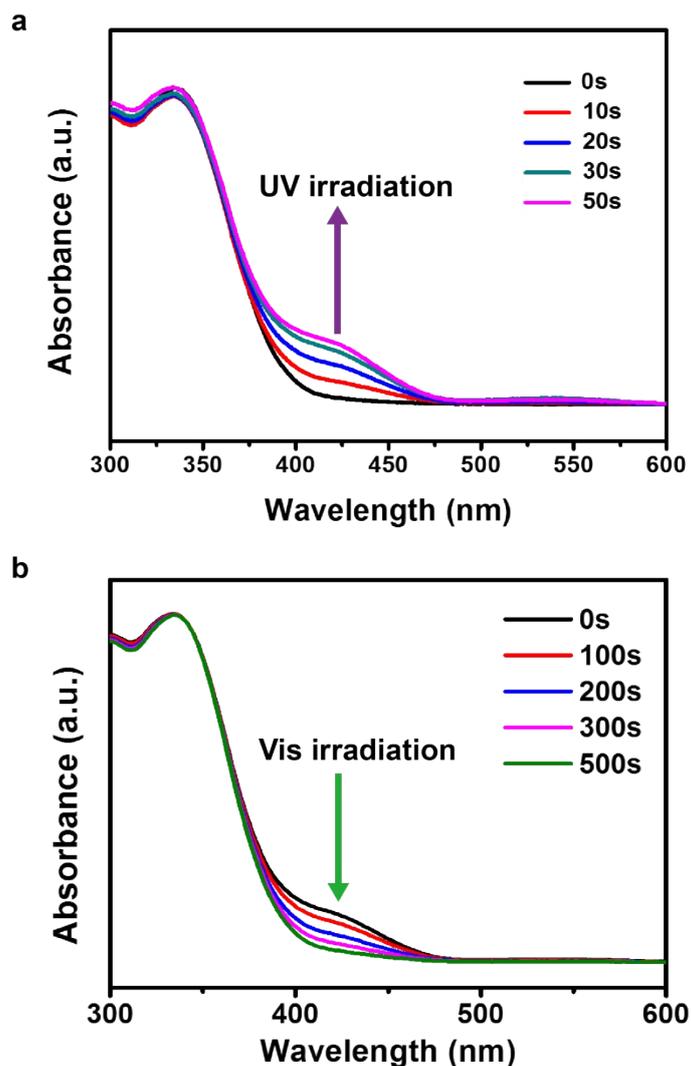
**Figure S9.** No evident change in transmembrane ionic conductance is observed after the modification of SP.

## 6. Photochromic reaction in bulk SP solution

It is known that spiropyran can be photoisomerized when exposed to UV light.<sup>[5]</sup> The color of the SP solution changes to yellow upon UV irradiation, and it returns to colorless upon visible light irradiation (Figure S10). This process is fully reversible. UV-vis absorbance spectra provide evidence to the photoisomerization of SP molecules in solution (Figure S11). The characteristic absorption band of MCH<sup>+</sup> near 430 nm gradually increases with prolonged UV irradiation time. Reversibly, it gradually decreases when irradiated with visible light.



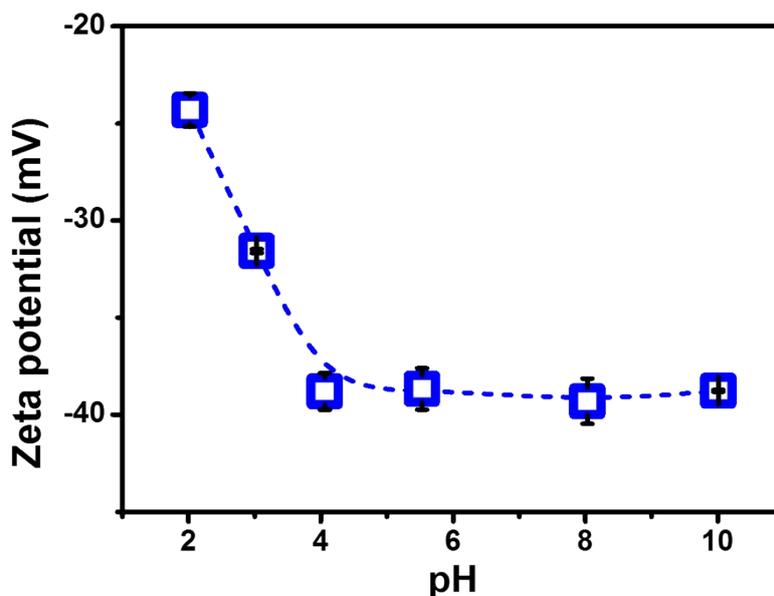
**Figure S10.** A photograph of the photochromic reaction in acidic SP ethanol solution.



**Figure S11.** UV-vis absorbance spectra of the SP ethanol solution at pH 3. (a) UV irradiation ( $365\text{ nm}$ ,  $1\text{ mW/cm}^2$ ) was conducted for different time from 0 to 50 seconds. (b) Visible light irradiation ( $520\text{ nm}$ ,  $15\text{ mW/cm}^2$ ) was conducted for different time from 0 to 500 seconds.

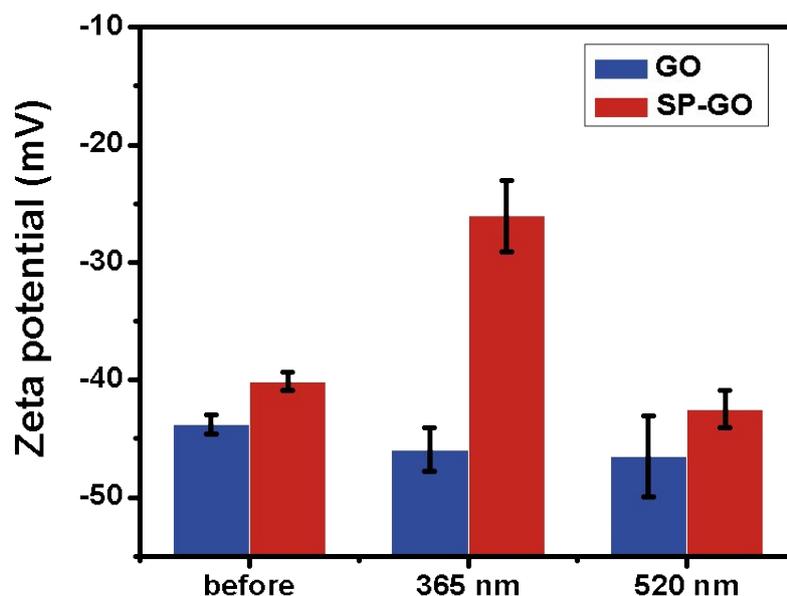
## 7. Zeta potential measurement

Zeta potential is employed to evaluate the surface charge properties of GO colloids ( $1.0\text{ mg/ml}$ ) at varied pH (Figure S12). Over the tested pH range from 2 to 10, the measured zeta potentials are negative and below  $-20\text{ mV}$ .



**Figure S12.** Zeta potential of GO colloids at different pH.

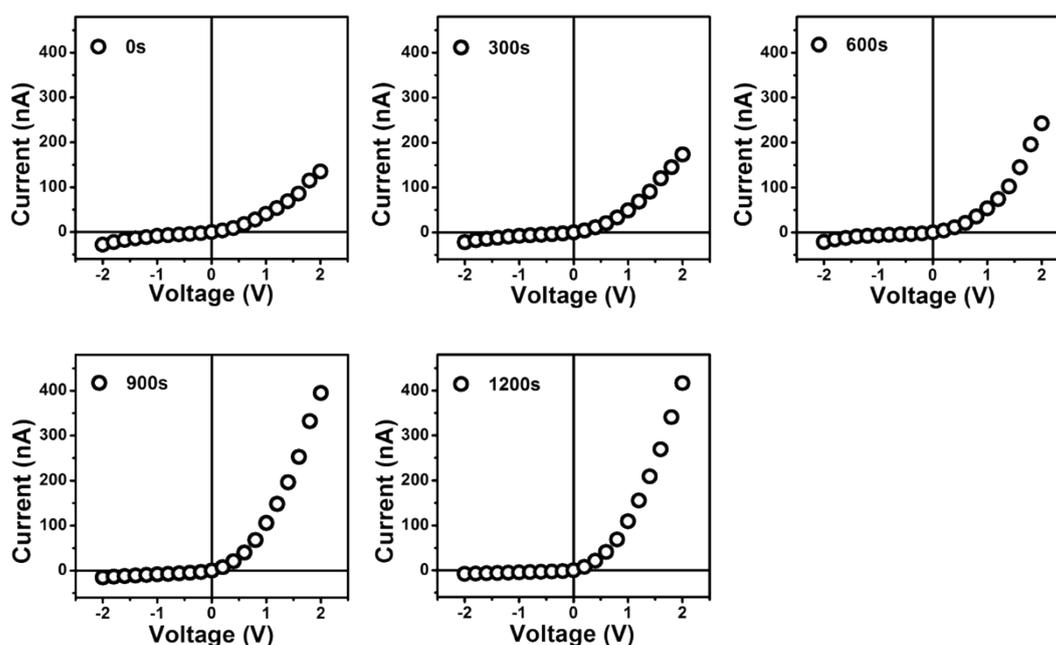
The formation of charge heterostructures in SP-GOM cannot be characterized in-situ. Instead, we perform zeta potential measurement on the SP attached GO nanosheets (SP-GO) in solution in response to light irradiation. 0.25 ml GO dispersion (2.0 mg/ml) was dropped into 10 ml SP ethanol solution (0.2 mg/ml) to obtain SP-GO dispersion. Compared with pure GO, a slight positive shift in zeta potential is found after the attachment of SP (Figure S13). Upon UV irradiation (wavelength of 365 nm, for 300 seconds), a remarkable positive shift in zeta potential is found in SP-GO. This positive shift can be retrieved upon the irradiation with visible light (wavelength of 520 nm, for 300 seconds). In contrast, GO nanosheets do not show such photo-responsive change in zeta potential. These results support the change in surface charge properties upon the irradiation with light of different wavelengths due to the photochemical isomerization of SP moieties.



**Figure S13.** Zeta potential measurement on GO and SP-GO dispersion before and after irradiation with UV (wavelength of 365 nm) and visible light (wavelength of 520 nm).

### 8. Current-voltage responses for different UV time

The current-voltage responses of SP-GOM are collected under different UV irradiation time (Figure S14). The ICR ratio is summarized in Figure 4a. It gradually increases with prolonged illumination time.



**Figure S14.** Current-voltage curves of the SP-GOM under UV irradiation for 0 s (a), 300 s (b), 600 s (c), 900 s (d), and 1200 s (e), respectively. 10 mM KCl was used as electrolyte solution.

## 9. References.

- [1] L. Huang, Y. Li, Q. Zhou, W. Yuan, G. Shi, *Adv. Mater.* **2015**, *27*, 3797.
- [2] Y. Jiang, N. Liu, W. Guo, F. Xia, L. Jiang, *J. Am. Chem. Soc.* **2012**, *134*, 15395.
- [3] N. Liu, Y. Jiang, Y. Zhou, F. Xia, W. Guo, L. Jiang, *Angew. Chem. Int. Ed.* **2013**, *52*, 2007.
- [4] J. Gao, W. Guo, D. Feng, H. Wang, D. Zhao, L. Jiang, *J. Am. Chem. Soc.* **2014**, *136*, 12265.
- [5] R. Klajn, *Chem. Soc. Rev.* **2014**, *43*, 148.