Supporting Information

MoS_2 nanosheets chemically modified with metal phthalocyanine via mussel-inspired chemistry for multifunctional memristive devices

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Experimental section

Measurements and Instrument

All of the chemicals used in this study were of reagent grade, were purchased from Aldrich and were used without further purification. Organic solvents were purified, dried, and distilled under dry argon (Ar).

The ultraviolet visible (UV-Vis) absorption spectra were recorded using a Shimadzu UV-2600 spectrophotometer (Shimadzu, Japan). A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer (HORIBA Scientific, France) was used to record the steady-state fluorescence spectra. Fourier transform infrared (FTIR) spectra were performed wtih a Nicolet Nagma-IR 550 spectrophotometer (Nicolet, UK) using KBr pellets. Raman spectra were recorded using a LabRAM HR Evolution Raman spectrometer (HORIBA Scientific, France) with an excitation laser at a wavelength of

532 nm. The thermal properties of the samples were measured using a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) in flowing nitrogen (60 mL/min). Transmission electron microscopy (TEM) images were recorded using a JEOL-2100 (JEOL Ltd., Japan) TEM system operated at 200 kV. Atomic force microscopy (AFM) images were recorded using a Dimension Icon & FastScan Bio, Nanonavi E-Sweep instrument (SII). Conductive Atomic Force Microscopy (C-AFM) images were recorded using a Solver P47 PRO microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. Field emission scanning electron microscope (FESEM) images and Energy dispersive X-ray spectra were recorded using a GeminiSEM 500 instrument. The electrical characterics of the materials were investigated using a Keithley 4200 apparatus.

Synthesis of few-layer MoS_2 NSs

The MoS_2 NSs were obtained by the lithium intercalation and exfoliation method according to the previous report in the literature[1]. In a typical experiment, anhydrous n-hexane (10 mL) was added as solvent to MoS_2 powder (1.5 g, 9.4 mmol) in a Schlenk tube under Ar protection. After the addition of n-butyllithium (2 mL, 2.5 M) to the system, the mixture was stirred at room temperature for 72 h. Subsequently, distilled water (100 mL) was added to the reaction mixture and ultrasonicated for 2 h to complete the exfoliation. Then, the reaction mixture was extracted with hexane (twice) to remove organic impurities, and the aqueous phase was collected. The above aqueous phase was centrifuged at 6000 rpm for 30 min to remove the thick MoS_2. Then, the supernatant was collected and centrifuged at 12000 rpm for 90 min to obtain MoS_2 NSs.

Synthesis of polydopamine modified MoS_2 NSs (MoS_2-PDA)

The previously obtained MoS_2 NSs (100 mg) were dispersed in Tris-HCl buffer solution (10 mM, pH=8.5, 100 mL), and then dopamine hydrochloride (100 mg) was added into the aforementioned solution and sonicated for 5 min. The mixture was stirred at room temperature for 6 h. Then, the mixture was centrifuged at 6000 rpm

for 20 min to collect the precipitate solid. The crude product was washed several times with water and ethanol to remove the free PDA, and then was freeze-dried to obtain MoS_2-PDA (116 mg).

Synthesis of 2,(3)-(tetra-tertbutylphthalocyaninato) titanium (IV) oxide (tBu_4PcTiO)

A mixture of 4-tert butylphthalonitrile (21.8 mmol, 1.0 g), urea (12 mmol, 180 mg), and 1,8-diazabicyclo [5.4.0]undec-7-ene, DBU (0.5 mL) in freshly purified pentanol (15 mL) was heated under an argon atmosphere to 120°C. At the temperature of 120 °C, titanium(IV) butoxide (6 mmol, 0.51 mL) was added to the mixture with a syringe. Then, the reaction mixture was allowed to reflux for 7 h at 155°C. The crude product was precipitated from a methanol/water mixture with 1:1 ratio and dried in vacuum. Subsequently, the crude product was purified by column chromatography on a silica gel (toluene/$CHCl_3$ as eluent) to remove impurities. The pure *t*Bu_4PcTiO was obtained by recrystallization from a mixture of CH_2Cl_2/MeOH (v/v, 4:3), and dried under vacuum at 60°C for 24 h. Yield: 35% (380 mg); ^{1}H NMR ($CDCl_3$): δ ppm^{-1} = 1.95–1.89(s, 36H, CH_3); 8.39–8.29(m, 4H, H-1); 9.23–9.12(m, 8H, H-2,2′); FD-MS: *m*/*z* = 801.0 (M^+); UV/Vis absorbance: 699.0, 630.0, and 351.0 nm (DMF).

Synthesis of MoS_2-PDA-tBu_4PcTiO

A mixture of tBu_4PcTiO (200 mg), and MoS_2-PDA (50 mg) in nanhydrous $CHCl_3$ (50 mL) was bubbled with dry argon for 30 min, and then refluxed for 48 h. After cooling to room temperature, the reaction solution was dialyzed (molecular weight cut-off 1.0 kDa) against anhydrous $CHCl_3$ for 2 d during which the used $CHCl_3$ was replaced with the fresh $CHCl_3$ every 4 h, and then continued to be dialyzed against deionized water for additional 2 d. The used water was replaced with the fresh deionized water every 4 h. The collected solid product was freeze-dried for 24 h to give MoS_2-PDA-tBu_4PcTiO as dark powder (128 mg).

Device fabrication

The ITO glass substrate was carefully pre-cleaned sequentially with ethanol, acetone, and 2-propanol in an ultrasonic bath for 15 min, and then treated with oxygen plasma. A sample solution (100 μL, 10 mg·mL^{-1}) in DMF was spin-coated on the

pre-cleaned ITO sheet at a spinning speed of 800 rpm for 20 s and then at 2000 rpm for 60 s, followed by the removal of the solvent under vacuum at 80^{o}C overnight. Al top electrodes were deposited on the surface of active layer through a shadow mask at 10^{-7} Torr via e-beam evaporation. All electrical measurements were performed using a Keithley 4200 semiconductor parameter analyzer in ambient conditions without any device encapsulation.

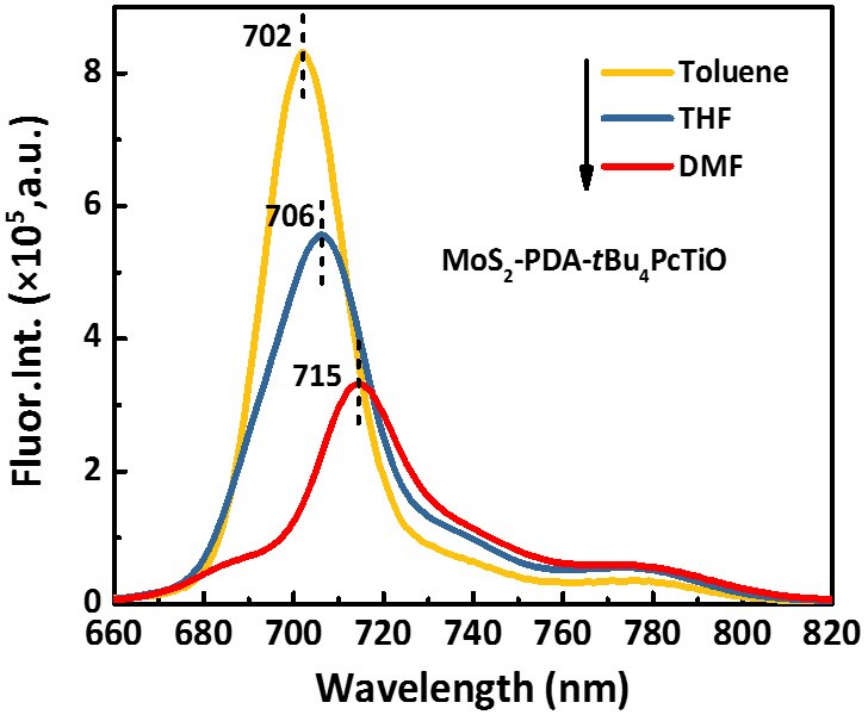

Figure S1. Photoluminescence spectra of MoS_2-PDA-tBu_4PcTiO in different organic solvents (λex = 630 nm).

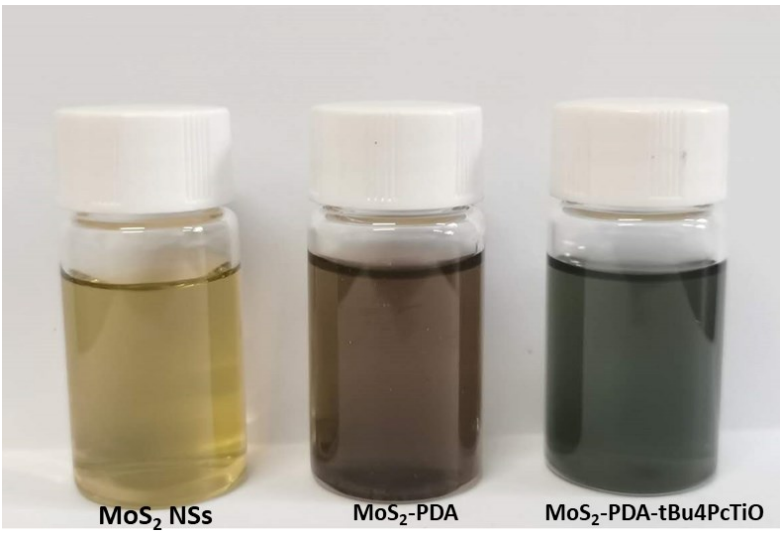

Figure S2. Digital pictures of the samples dispersed in DMF.

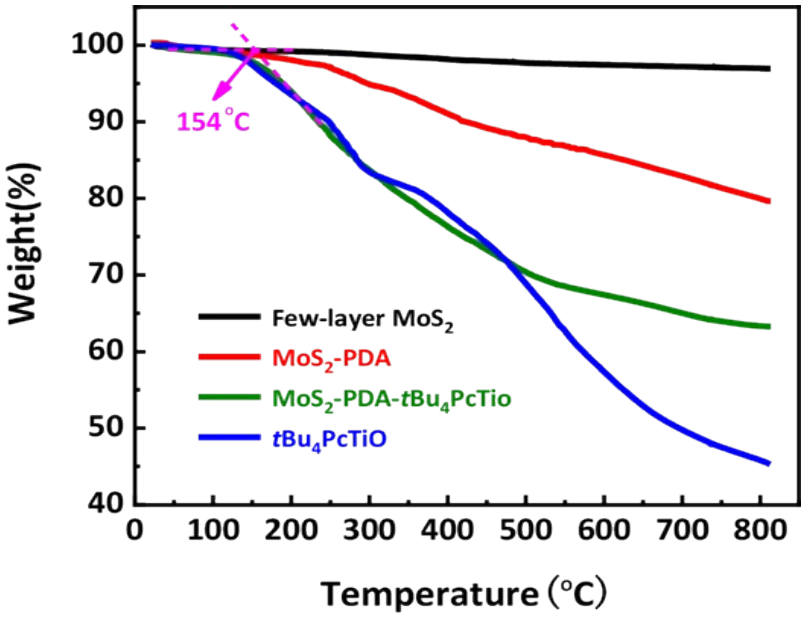

Figure S3. TGA curves of the samples.

Thermodynamic analysis (TGA) was employed to test the thermal properties of the samples and estimate the real content of individual counterpart in the MoS_2-PDA-tBu_4PcTiO composite. As shown in **Figure S3**, the decomposition temperature of the MoS_2-PDA-tBu_4PcTiO composite is above 150°C, which indicates that the composite has good thermal stability. When heated to 800 °C, the weight loss of the few-layer MoS_2, MoS_2-PDA, and tBu_4PcTiO are about 3.1 %, 20.0 %, and 54.0 %, respectively.

Thus, it can be roughly estimated that the content of PDA in MoS_2-PDA is 16.9 % (20.0 % - 3.1 % = 16.9 %), and the content of MoS_2 is 83.1 %. Noted that the weight loss of the MoS_2-PDA-tBu_4PcTiO is about 41.0 % at 800 °C, it can be roughly estimated that the content of tBu_4PcTiO in the composite is 61.7 % ((41 % - 20 %) / (54 % - 20 %) = 61.7 %).

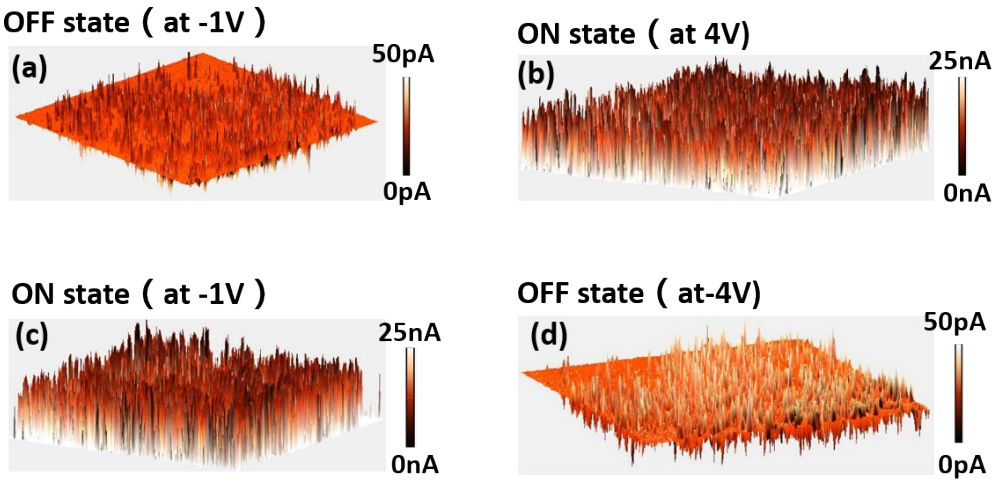

Figure S4. C-AFM current maps of the MoS_2-PDA-tBu_4PcTiO film with a scanning size of 5 × 5 μm^2 upon being subjected to voltage.

To intuitively understand the surface morphological changes of the active layer film under the electric field-induced during the operation of the device, we used conductive atomic force microscopy (C-AFM) to characterize the active layer in situ[4]. As shown in Figure S4, when a sweep voltage of +1 V or -4 V was applied to the active thin film, only a very low current (approximately 22 pA) can be observed. When a sweep voltage of 4 V or -1 V is applied, a large number of high conductive regions (approximately 12 nA) appear in the three-dimensional current map. This phenomenon is related to the electric field induced charge transfer in the MoS_2-PDA-tBu_4PcTiO material[5].

Notes and references

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