Enhancement of Photodetection Characteristics of MoS$_2$ Field Effect Transistors using Surface Treatment with Copper Phthalocyanine

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1. Ti/MoS$_2$ contact

Figure S1 shows the output characteristic (current versus drain-source voltage; $I_{DS}$–$V_{DS}$) plots for MoS$_2$ FET devices with and without the CuPc layer. These results indicate that the Ti/MoS$_2$ contacts exhibit ohmic contacts.

![Figure S1](image-url)

Figure S1. (a) The output characteristics ($I_{DS}$–$V_{DS}$) for MoS$_2$ FETs (a) without and (b) with CuPc layer.
2. Devices Fabrication

Figure S2 shows the device fabrication processes. First, MoS$_2$ flakes were mechanically exfoliated from a bulk MoS$_2$ crystal purchased from SPI Supplies. Then, the MoS$_2$ flakes were transferred on 270 nm-thick SiO$_2$ on a highly doped p++ Si Wafer (resistivity $\sim 5 \times 10^{-3} \, \Omega/\text{cm}$) that can be used as a back gate. Proper MoS$_2$ flakes were located with an optical microscope and the height of selected MoS$_2$ flakes were measured with atomic force microscope (NX 10 AFM system, Park Systems). To make electrode patterns, we spin-coated methyl methacrylate (9% concentration in ethyl lactate) and PMMA 950K (5% concentration in anisole) at 4000 rpm. After the spin-coating of each layer, the sample was baked at 180 °C for 90 s on a hot plate. We used an electron beam lithography system (JSM-6510, JEOL) to pattern electrodes. Development of patterns was performed with a MIBK/IPA (1:3) solution for 50 s. Electrodes was made by depositing 30 nm thick Ti with an e-beam evaporator (KVE-2004L, Korea Vacuum Tech). Finally, the copper phthalocyanine (CuPc) was deposited on fabricated MoS$_2$ field effect transistor (FET) devices by a thermal evaporator (GVTE1000, GV-Tech).

Figure S2. Schematic processes of fabricating MoS$_2$ FET devices.
3. Raman spectroscopy data

Figure S3a shows the Raman data of a pristine MoS$_2$ flake before CuPc layer was deposited. We observed that the MoS$_2$ flake exhibited two Raman characteristic bands at 383 and 405 cm$^{-1}$, corresponding to the out-of-plane vibration of atoms ($A_{1g}$ mode) and in-plane vibration of atoms ($E_{2g}$ mode) of MoS$_2$, respectively. Figure S3b shows the Raman data of a CuPc film on MoS$_2$. In this case, the most intense Raman bands were observed at 1144, 1345, 1454, and 1531 cm$^{-1}$ for pyrrole groups, phthalocyanine, C-N bond, and C-C bond of CuPc, respectively. The Raman peaks represented in Figure S3b suggest that CuPc layer was well deposited on MoS$_2$ surface.

Figure S3. Raman spectroscopy data of (a) pristine MoS$_2$ and (b) CuPc/MoS$_2$. 
4. X-ray photoelectron spectroscopy data

The X-ray photoelectron spectroscopy (XPS) scans on a MoS$_2$ flake confirmed the chemical bonding states of the Mo and S. The Mo 3d showed two peaks at 229.64 and 232.84 eV, attributed to the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively, in Figure S4a. The S 2p showed two peaks at 163.74 and 162.54 eV, corresponding to the S 2p$_{1/2}$ and S 2p$_{3/2}$, respectively, in Figure S4b. When the CuPc layer was deposited on MoS$_2$, the Mo 3d two peaks shifted from 229.64 to 229.04 and from 232.84 to 232.14 eV, attributed to the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively. The S 2p two peaks also shifted from 162.54 to 162.01 and from 163.74 to 163.26 eV, corresponding to the S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively. In addition, the peaks of Mo and S in the CuPc/MoS$_2$ show a shift toward lower binding energies compared to those of the pristine MoS$_2$ flake. This shift is attributed to lowering of the Fermi level upon the p-doping.$^1$

The CuPc-covered MoS$_2$ flakes showed the element peaks of only Cu, N and C in the XPS spectra. The Cu 2p spectra had two peaks at 934.8 and 954.5 eV, attributed to the Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$, respectively, in Figure S4c. For the N 1s spectrum, the main peak appeared at 398.8 and a shoulder peak emerged at 400.4 eV (C=N=C bond), shown in Figure S4d. The C 1s showed two peaks at 284.5 and 285.7 eV, corresponding to the C=C bond and C=N bond, respectively, in Figure S4e.
Figure S4. XPS data of MoS$_2$ and CuPc films.
5. CuPc layer thickness by AFM

Figure S5. AFM images of CuPc layers deposited by thermal evaporator system.
6. CuPc/MoS₂ hybrid FETs with CuPc layers of 5, 10, 20, and 30 nm thickness

Figures S6a and S6b show the transfer and output characteristics of the CuPc/MoS₂ hybrid FET devices with different CuPc thickness (5, 10, 20, and 30 nm). Consistent with the results in Figure 2 of the main manuscript, the channel current decreased at positive gate voltage and the threshold voltage shifted to the positive gate voltage direction. Figure S6c summarizes the threshold voltage and electron carrier concentration estimated at \( V_G = 20 \) V and \( V_{DS} = 0.1 \) V for these CuPc/MoS₂ hybrid FET devices.

Figure S6. (a) \( I_{DS} - V_G \) curves and (b) \( I_{DS} - V_{DS} \) curves of CuPc/MoS₂ hybrid FET devices with different CuPc thickness (5, 10, 20, and 30 nm). (c) Threshold voltage and electron carrier concentration for the CuPc/MoS₂ hybrid FET devices.
7. The electron mobility versus the CuPc thickness

Figure S7. The electron mobility as a function of the CuPc thickness.
8. Electrical and photoresponsive properties of CuPc FETs

Figure S8a illustrates the cross-sectional schematic of CuPc-alone FET (i.e., CuPc FET without MoS$_2$) under light illumination. Figure S8b shows the transfer curves of CuPc FETs with different CuPc layer thickness (3, 5, and 10 nm). The channel current of CuPc FETs increased as the increasing CuPc layer thickness. Inset plot in Figure S8b indicates the channel could not formed when we stacked CuPc layer of 1 nm thickness. This is because 1 nm-thick CuPc was not formed as a uniform film across the source and drain electrodes. Figure S8c exhibits the photoresponsive characteristics of CuPc FETs under 520 nm light illumination. This data means that the hole carrier density of CuPc increase with the thickness of CuPc.

![Figure S8. (a) The schematic of a CuPc FET under light illumination (520 nm). (b) $I_{DS}$-$V_G$ curves of CuPc FETs with different CuPc layer thickness (3, 5 and 10 nm) measured at $V_{DS}=1$ V. (c) Photoresponsive data of CuPc FETs measured at $V_G=-40$ V and $V_{DS}=0.1$ V under light on and off.](image-url)
9. Gate voltage dependence of the photocurrent and the photoresponsivity

Figure S9 shows the gate-voltage dependence of the photocurrent and the photoresponsivity. The photocurrent and photoresponsivity were enhanced with positively increasing the gate voltage. The application of positive gate voltage leads to increase electron carrier density in the MoS$_2$ channel layer, but it decrease the hole density in the CuPc layer, which results in the reduction of charge recombination at the interface between MoS$_2$ and CuPc layers. Interestingly, for the MoS$_2$ device with the 2 nm-thick CuPc layer, the photocurrent and photoresponsivity were larger than those of the MoS$_2$ device without the CuPc layer, indicating the photo-generated electrons in the CuPc layer assist enhancement of the photoresponse properties of MoS$_2$ device.

![Figure S9. Gate voltage dependence of the photocurrent and the photoresponsivity.](image-url)
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