Electronic Supplementary Information

Efficient work-function engineering of solution-processed MoS_2 thin-films for novel hole and electron transport layers leading to high-performance polymer solar cells

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Experimental section

Preparation of MoS_2 nanosheets

All chemicals were purchased from Sigma-Aldrich and used without further purification. MoS_2 nanosheets were prepared by a slightly modified method published elsewhere.[1] Typically, natural MoS_2 powder (0.3 g) was immersed into 2.0 M n-buthyl lithium in a cyclohexane solution (4 mL) for 2 days under an inert atmosphere. The resultant Li_xMoS_2 was thoroughly washed with anhydrous hexane in order to remove un-intercalated n-buthyl lithium and organic residues. And then, Li_xMoS_2 powder was exfoliated by ultrasonication in distilled water for 1 h. Next, a small amount of LiCl was added into the resultant dispersion in order to precipitate MoS_2 nanosheets, which were centrifuged and washed with DI water several times to completely remove the lithium compounds. The resultant MoS_2 dispersion was stored under ambient temperature for 2 days. Finally, the produced MoS_2 was filtered and re-dispersed in DMF at a concentration of ~1 $mgml^{-1}$ and used for sample characterization and device fabrication.

Preparation of p- and n-doping solution

As a p-type dopant, gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) was dissolved into methanol at concentrations of 20, 10, and 1 mM through brief bath-sonication. For the n-type dopant, 0.1, 0.01, and 0.006 M of sodium borohydride ($NaBH_4$) solutions were prepared by addition into dimethylformamide (DMF): water mixture (9.5:0.5 v/v), and the resultant solution was briefly sonicated until the solution was clear.

Fabrication of n-PSCs

ITO-coated glass substrates were sequentially cleaned in an ultrasonic bath with detergent, acetone, deionized water, and isopropyl alcohol each for 10 min, and then dried in an oven at 100 °C for 30 min. All substrates were then treated with UV/O_3 for 30 min. To fabricate the MoS_2-based HTL, MoS_2 dispersed in DMF was spin-coated onto UV/O_3-treated ITO substrates at 3,000 rpm for 30 s in air, and subsequently annealed at 150 or 250 ^oC for 30 min in N_2-filled glove box. To dope the MoS_2 film with $HAuCl_4$, each doping solution (20, 10, and 1 mM $HAuCl_4$) was spin-casted onto 150 ^oC-annealed MoS_2 film at a rate of 3,000 rpm for 30 s in air, and subsequently dried for 15 min under an N_2 atmosphere. The *o*-dichlorobenzene (*o*-DCB) solution containing a 25 $mgml^{-1}$ of P3HT (Rieke Metals) and a 25 $mgml^{-1}$ of PCBM (Nano-C) was spin-coated onto the hole extraction layer-coated substrate at 700 rpm for 60 s, and then the resultant active-coated substrate was kept in a glass jar at room temperature to allow the *o*-DCB solvent to evaporate slowly for 2 h in an N_2-filled glove box, followed by annealing at 120 °C for 15 min inside the glove box. Finally, top electrodes composed of Ca (20 nm)/Al (100 nm) with an area of 4.64 mm^2 were deposited using a thermal evaporator in vacuum with a pressure of 10^{-6} Torr.

Fabrication of i-PSCs

MoS_2-based ETLs were prepared by doping the MoS_2 film with $NaBH_4$, each doping solution (0.1, 0.01, and 0.006 M $NaBH_4$) was spin-casted onto 150 ^{o}C-annealed MoS_2 film at a rate of 3,000 rpm for 30 s in air, and subsequently dried for 15 min under an N_2 atmosphere. To construct a HTL, the PEDOT:PSS:iso-propyl alcohol solution (1:6 v/v) was spin-casted onto the prepared photoactive layer at 3,000 rpm for 30 s in air. Next, the resultant device was annealed at 120 ^{o}C for 10 min in an N_2-filled glove box. Note that preparation and fabrication procedures of the photoactive layer were the same as those described for inverted-structure PSCs. Finally, the top electrode composed of Ag (100 nm) with an area of 4.64 mm^2 was deposited using a thermal evaporator in vacuum with a pressure of 10^{-6} Torr.

Device characterization

Photovoltaic characteristics were measured using a Keithley 1200 instrument under 100 $mWcm^{-2}$ with AM 1.5 G. A reference Si solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc) was used to calibrate an accurate measurement.

Sample characterizations

UV-vis/NIR spectra were obtained using a Jasco V-570 UV-vis/NIR spectrophotometer. XPS were measured using an AXIS-NOVA (Kratos) system with a monochromatized Al Kα under a pressure of 5×10^{-8} Torr. AFM images were obtained with a Veeco Dimension 3100 instrument with a silicon cantilever operated in tapping mode. UPS measurements were conducted using an AXIS-NOVA (Kratos) system with He I under a base pressure of 5×10^{-8} Torr. Sheet resistance of the MoS_2 thin-film was measured with a 4-point probe (FPP-RS8, Dasol Eng.).

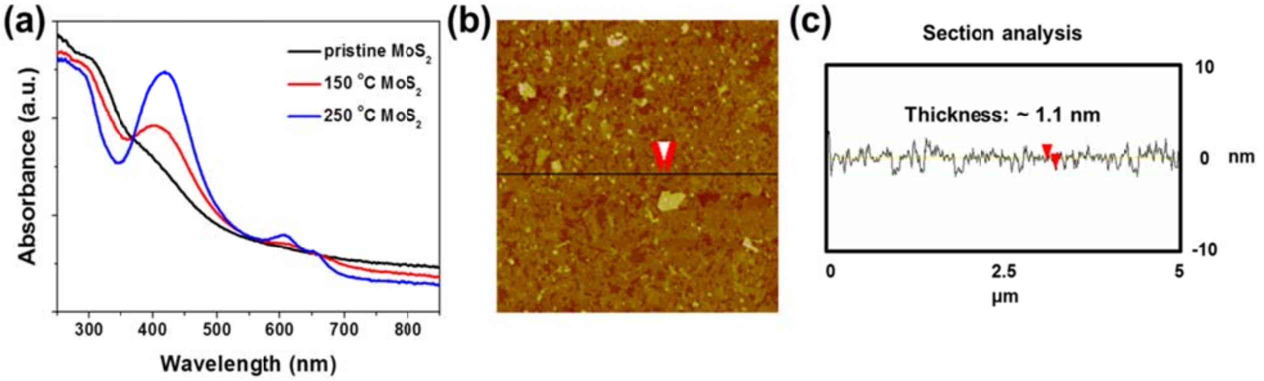

Fig. S1 (a) UV-vis spectra of pristine and annealed MoS_2 thin-films coated onto glass substrates. With increasing annealing temperature, structural transformation occurred from the metallic 1T- to the semiconducting 2H-MoS_2 phase, which is consistent with a previous report.[2] (b) The AFM image and (c) section analysis of MoS_2 sheets casted onto a glass substrate. The z-range and scan size are 20 nm and 5 μm, respectively.

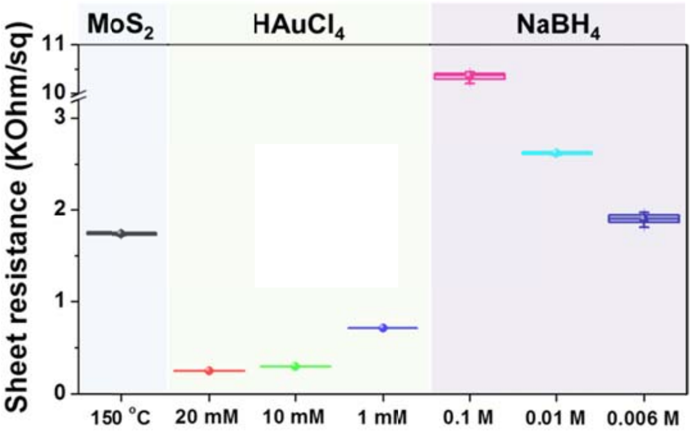

Fig. S2 (a) Sheet resistance values of MoS_2 films before and after doping treatments.

Compared with the 150 °C-annealed un-doped MoS_2 film, the sheet resistance values of the p-doped MoS_2 films were all reduced due to the following reasons: (a) Cl ions chemisorbed onto MoS_2 sheets decrease the sheet resistance due to the fact that Cl ions having the strong electronegativity extract electrons directly from the MoS_2. (b) Electrons were extracted from MoS_2 sheets due to the reduction of Au^{3+} to Au^0 so that p-type doping was occurred and the hole carriers concentration was increased. From the above two reasons, the sheet resistance of $HAuCl_4$-treated MoS_2 film was decreased.

By contrast, the sheet resistance of n-doped MoS_2 films was all higher than that of 150 °C-annealed un-doped MoS_2 film. In general, MoS_2 prepared using the Li-intercalation/exfoliation method is reported to be a p-type material. Therefore, the n-doping treatment was considered to have decreased carrier concentration, thus resulting in an increased sheet resistance of the MoS_2 film.[3]

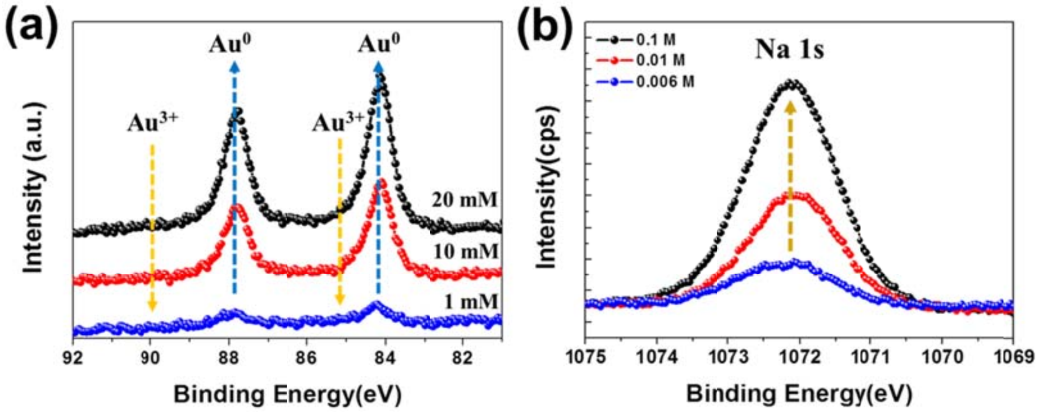

Fig. S3 XPS spectra of (a) Au 4f and (b) Na 1s peaks for MoS_2 thin-films doped with different $HAuCl_4$ and $NaBH_4$ concentrations, respectively.

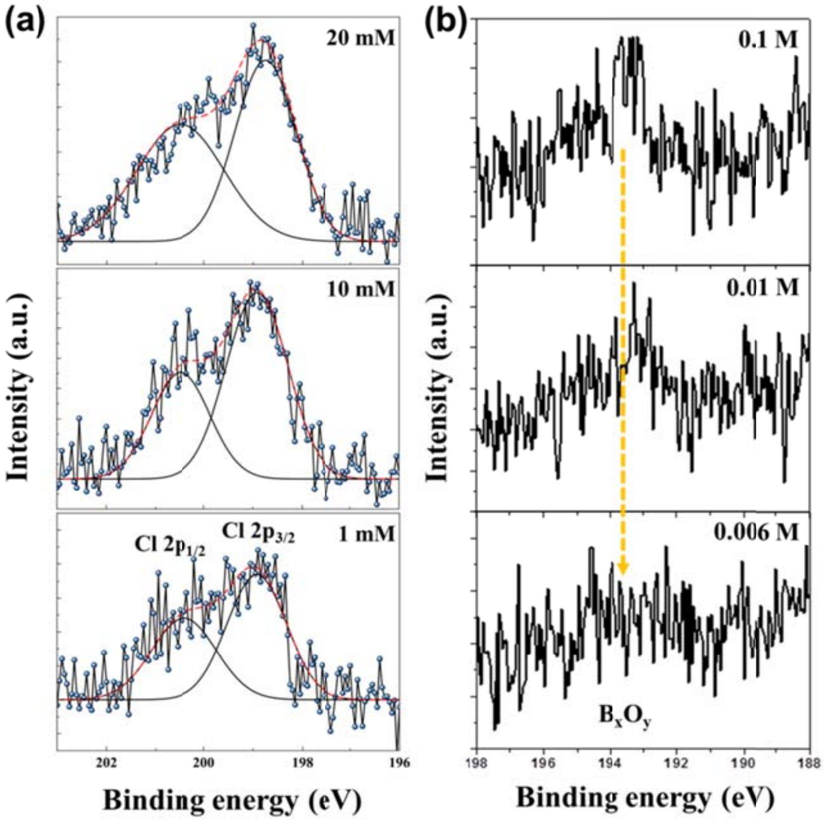

Fig. S4 XPS spectra showing (a) Cl and (b) B_xO_y peak regions for MoS_2 thin-films doped with various $HAuCl_4$ and $NaBH_4$ concentrations, respectively.

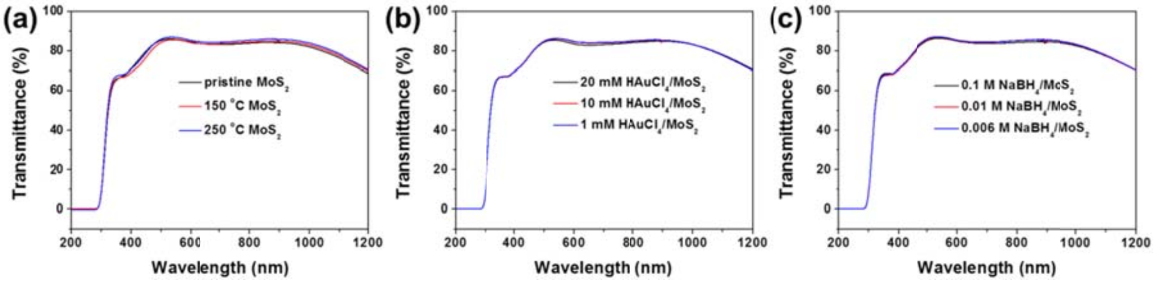

Fig. S5 Transmittance spectra of (a) un-, (b) p-, and (c) n-doped MoS_2-based interfacial layers coated onto ITO/glass substrates. The transmittance spectra of un-, p-, and n-doped MoS_2 thin-films showed similar transmittance values ranging from 85−87%, indicating that the transmittance values of MoS_2-based interfacial layers had little influence on the J_{sc} values in J-V curves.

Table S1 Work-function values of un-, p-, and n-doped MoS_2 thin-films

	Binding energy (eV)	Work-function (eV)
Pristine MoS_2	16.84	4.36
150 °C MoS_2	16.68	4.52
250 °C MoS_2	16.68	4.52
20 mM $HAuCl_4$	16.44	4.76
10 mM $HAuCl_4$	16.50	4.70
1 mM $HAuCl_4$	16.56	4.64
0.1 M $NaBH_4$	17.75	3.45
0.01 M $NaBH_4$	17.23	3.97
0.006 M $NaBH_4$	16.77	4.43

Table S2 Summary of rms roughness values for different MoS_2-based interfacial layers

sample	un-doped MoS_2			p-doped MoS_2			n-doped MoS_2		
condition	pristine	150 °C	250 °C	20 mM	10 mM	1 mM	0.1 M	0.01 M	0.006 M
rms roughness (nm)(a)	1.18	1.16	1.17	2.27	1.38	1.22	2.63	1.14	1.17

(a)The rms roughness values were calculated from the AFM data shown in Fig. 3.

Table S3 Summary of peak positions of the XPS Mo $3d_{3/2}$ and Mo $3d_{5/2}$

Sample	Mo $3d_{3/2}$ (eV)	Mo $3d_{5/2}$ (eV)
150 °C MoS_2	232.55	229.45
20 mM $HAuCl_4$	232.40	229.15
10 mM $HAuCl_4$	232.40	229.25
1 mM $HAuCl_4$	232.45	229.30
0.1 M $NaBH_4$	233.15	229.90
0.01 M $NaBH_4$	232.95	229.65
0.006 M $NaBH_4$	232.70	229.50

References

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