

Supporting Information

Defect-Engineered MoS₂ with Extended Photoluminescence Lifetime for High-Performance Hydrogen Evolution

Sangmin Kang^{a,b,‡}, Ja-Jung Koo^{a,‡}, Hongmin Seo^c, Quang Trung Truong^d, Jong Bo Park^a, Seong Chae Park^e, Youngjin Jung^a, Sung-Pyo Cho^f, Ki Tae Nam^c, Zee Hwan Kim^{*a}, Byung Hee Hong^{*a,c,d}

^a *Department of Chemistry, ^c Department of Materials Science and Engineering, and ^e Graduate School of Convergence Science and Technology, ^f National Center for Inter-University Research Facilities, Seoul National University, Seoul 08826, Korea.*

^d *Graphene Square Inc. Inter-University Semiconductor Research Center at Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea.*

^b *Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA.*

‡ These authors contributed equally to this work.

Supplementary Methods

MOCVD growth and transfer of monolayer and bilayer MoS₂ films. As illustrated in Fig 1a, the synthesis of monolayer or bilayer MoS₂ was carried out in a computer controllable chemical vapor deposition system from Graphene Square Inc. (Model TCVD-100CA), where a furnace with 4-inch quartz tube were connected with high purity (99.999 %) argon, hydrogen gas and hydrogen sulphide (H₂S) gas (diluted in 5 % in argon). The system is equipped with one bubblers for liquid precursor which is carried by argon gas at controllable gas flow rate. The growth substrate (2-inch in size, 300 nm thick SiO₂ on Si wafer or sapphire) was firstly cleaned with hot piranha solution composed of 50 % H₂SO₄ and 50 % H₂O₂ in order to remove impurity. Then, it is loaded at the center of the quartz tube vertically with a quartz wafer supporting pillar. Liquid precursor was prepared by dissolving molybdenum hexacarbonyl (Sigma Aldrich, > 99.9 %) in toluene solvent (Sigma Aldrich, > 99.9 %) with a concentration of 0.07 mg/mL. After loaded into the bubbler, the bubbler was firstly pumped to 100 torrs and purged with argon gas, then repeatedly pumped and purged 2 times to remove residual air in the bubbler. Prior to growth, the system was pumped to a based vacuum of 10⁻³ torr using rotary pump. The optimum growth parameters were set up and operated using 100 sccm argon and 10 sccm hydrogen gas. The quartz tube was rapidly heated up to 600 °C for 15 min then, 30 sccm of H₂S gas was switched on and waiting for 1 min to stabilize pressure at controlled pressure of 20 torrs before starting liquid precursor supply. During growth, the temperature was maintained at 600 °C and 3 sccm argon was bubbled via liquid for the duration time. (60 min for monolayer or 120 min for bilayer MoS₂ synthesis). After growth, the quartz tube was rapidly cooled down to room temperature by fast moving furnace aside while argon and hydrogen gas flow continuously. The synthesized sample was loaded out of the chamber after venting to atmospheric pressure with argon gas.

The TEM and electrochemical samples were prepared through a PMMA-assisted transfer method. The MoS₂/SiO₂/Si substrate was first spin-coated by a PMMA thin film. Then, 1 M KOH solution at 90 °C was used as the etchant to etch away the SiO₂ layer. After that, the

MoS₂ on the PMMA was rinsed with DI water and then transferred the target substrate. Finally, the sample was baked 70 °C in 1 hour and then the PMMA was washed off with acetone and iso-propanol. In case of UV-ozone treatment samples, the UV-ozone irradiated to the samples after all transfer processes.

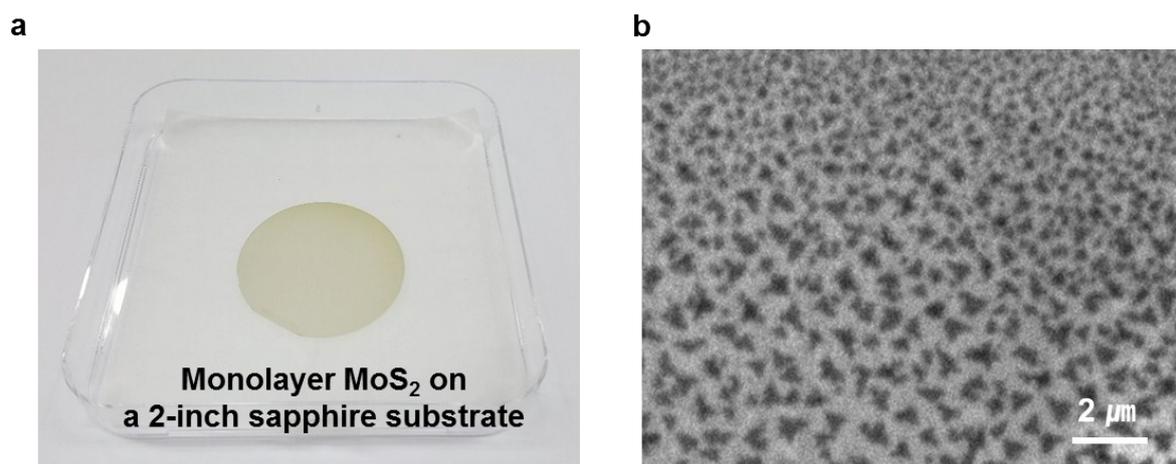


Fig. S1. A photograph and SEM image of MOCVD-grown monolayer MoS₂ on a sapphire substrate. Not only SiO₂/Si wafer but also sapphire could be also used as a growth substrate. Triangular crystal shape, which size is below 250 nm, is confirmed at 60 min growth time.

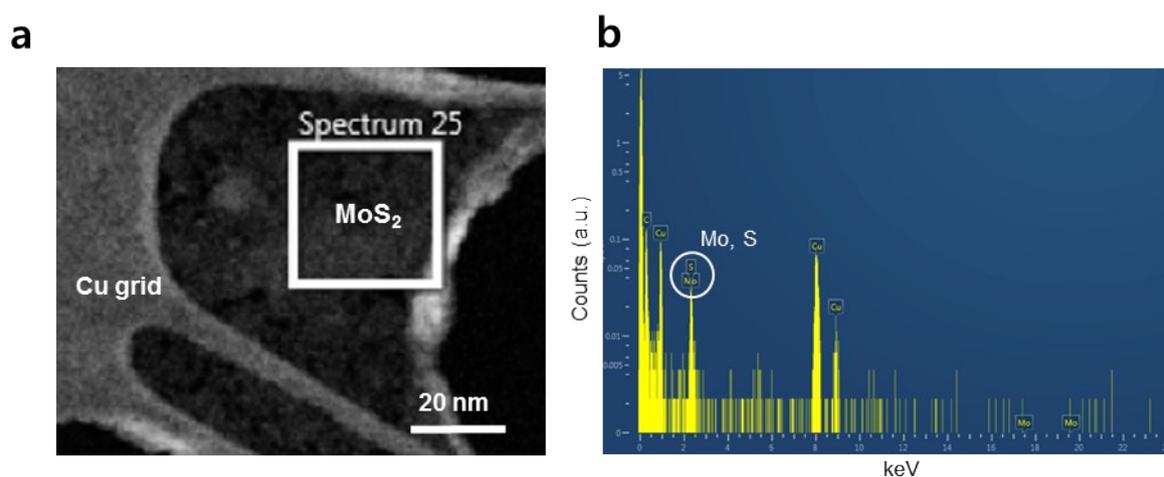


Fig. S2. TEM image and EDS spectrum of the pristine bilayer MoS₂ films. (a) TEM image of the bilayer MoS₂ on a conventional lacey copper grid. (b) EDS spectrum of the bilayer MoS₂ films at white square in (a).

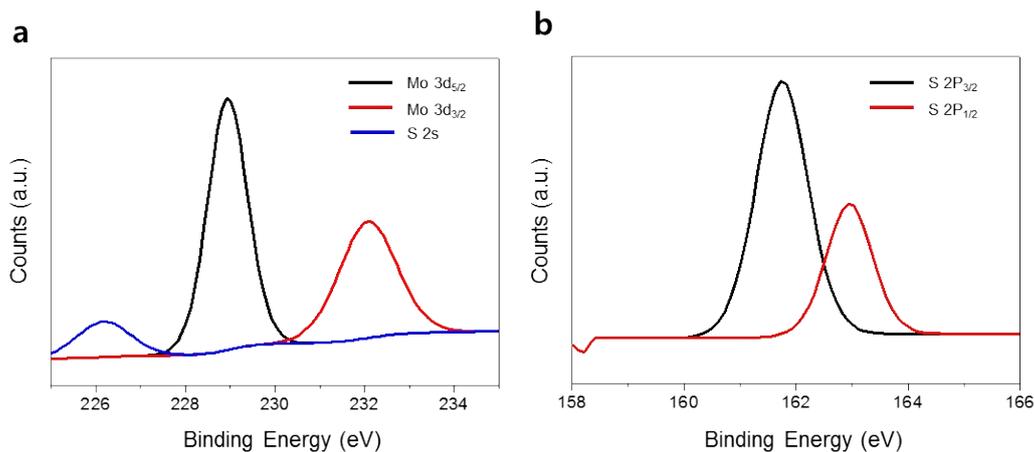


Fig. S3. XPS spectra for MoS₂ bilayer grown by our method. (a) Mo 3d 5/2, 3/2 and S 2s state. (b) S 2p 3/2 and 1/2, which mean that our synthesis method shows similar peak position compared with previously reports.¹

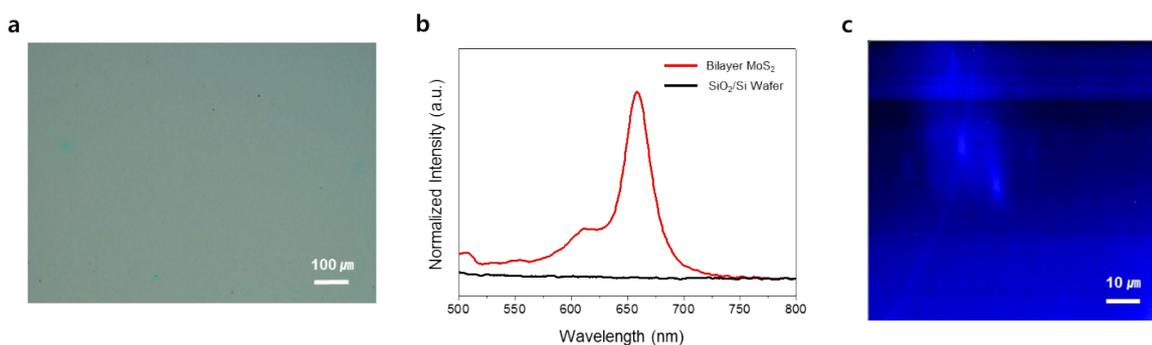


Fig. S4. A photograph and PL measurement of the pristine bilayer MoS₂ on SiO₂/Si wafer. (a) Optical microscope image of the bilayer MoS₂ synthesized by our MOCVD on SiO₂/Si wafer. (b) PL spectrum of the bilayer MoS₂ obtained at (a) compared with a bare SiO₂/Si wafer. (c) PL mapping of the bilayer MoS₂ obtained at (a).

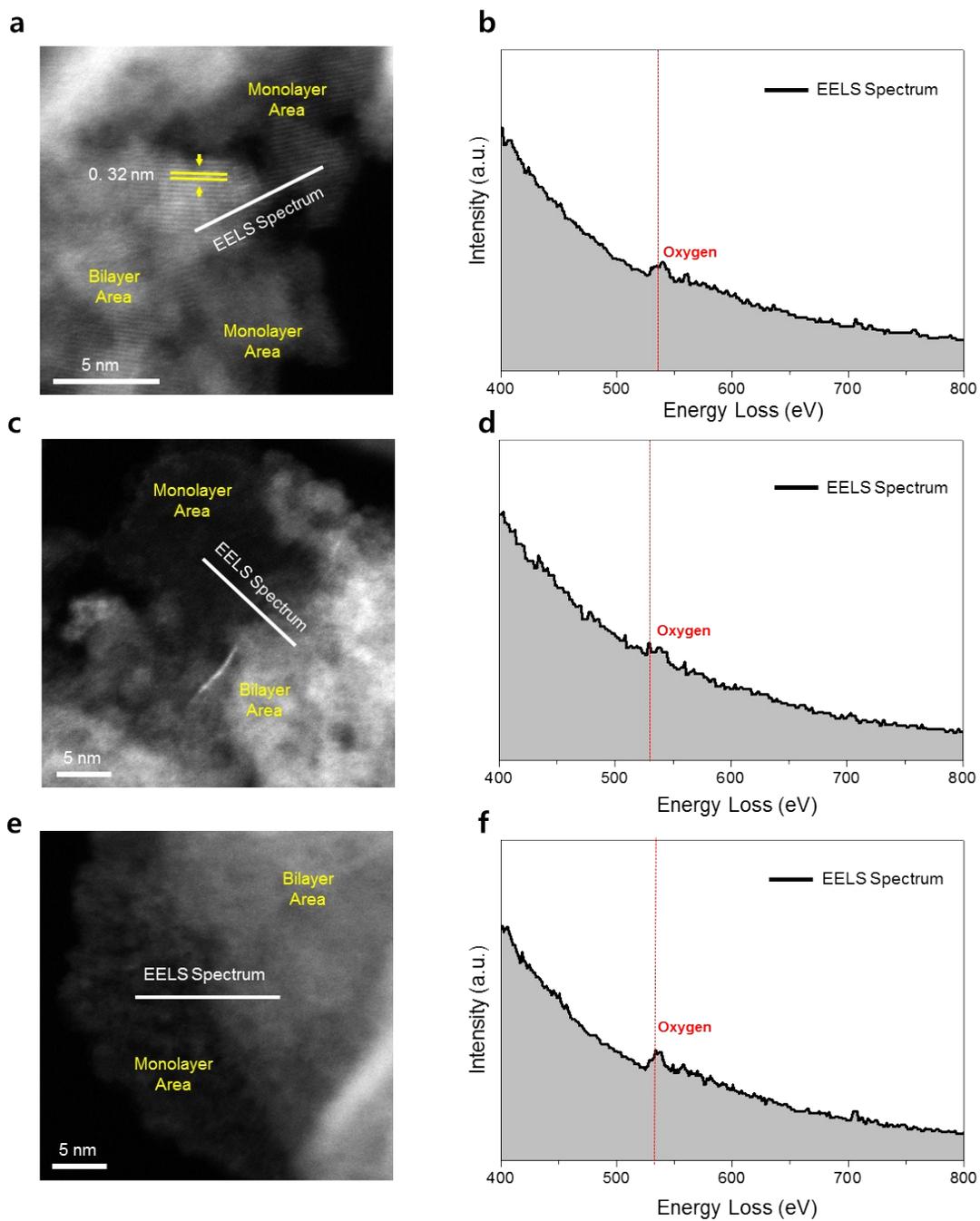


Fig. S5. CS-TEM analysis after UV-ozone treatment on the bilayer MoS₂. (a,c,f) CS-STEM HADDF images after UV-ozone treatment at various locations. (b,d,f) EELS spectrum at line profile in (a), (c) and (e), respectively.

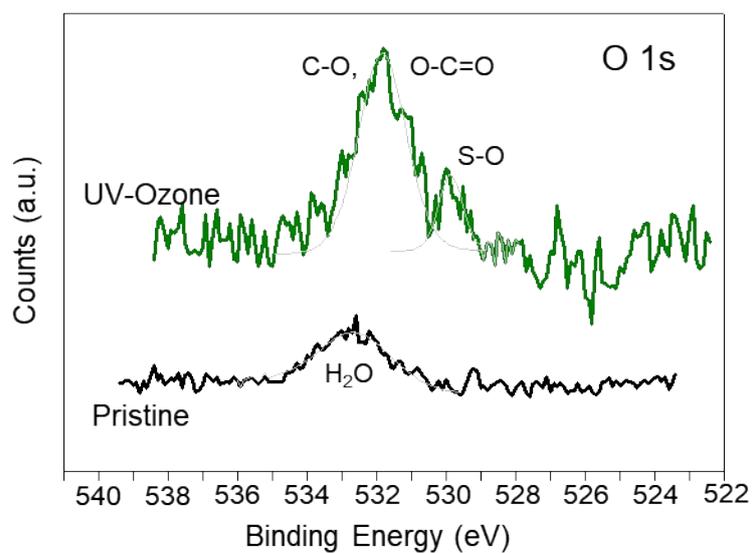


Fig. S6. XPS spectra of pristine bilayer MoS₂ and UV-ozone treated bilayer MoS₂ for O1s.

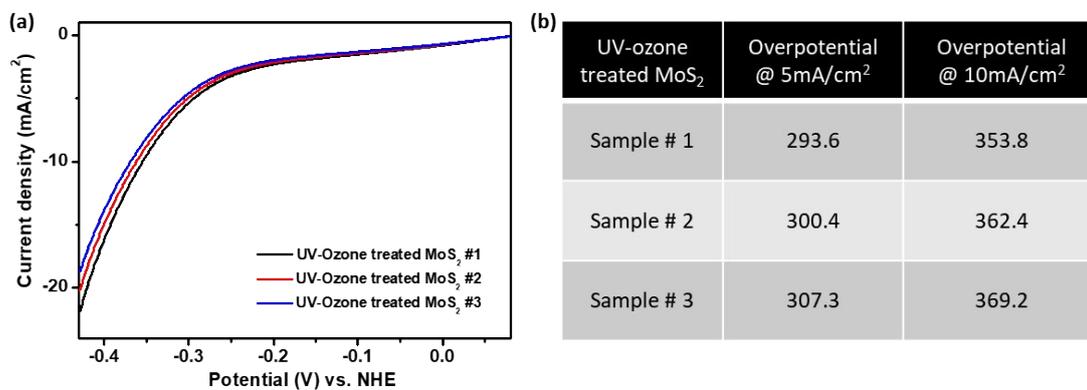


Fig. S7. (a) The reproducibility of electrochemical HER activity for UV-ozone treated MoS₂. (b) The overpotentials at current density of 5 mA/cm² and 10mA/cm² for each samples in Fig S7a.

Table S1. Exciton life-time values depending on UV-ozone exposure time. Computational DFT theory and exfoliation experimental values are studied in previously report.^{2,3}

	Pristine	Less exposure	Optimization exposure (5 sec)	Over exposure
Exciton Life -Time (ns)	1.34 (DFT theory : 1.3 Exfoliated MoS ₂ : 0.71) ²	1.83	2.36	0.35

Table S2. HER performance comparison. References were focused on pure film types excluding chemically exfoliated MoS₂ combined with other materials and functional groups.

	Overpotential (mV) @ 10 mA/cm ²	Overpotential (mV) @ 5 mA/cm ²	Tafel slope (mV/dec)	Electrode & Electrolyte
Bilayer MoS ₂ by MOCVD (Our work)	N/A	N/A	231	Glassy carbon 0.5 M H ₂ SO ₄
UV-Ozone treated MoS ₂ (Our work)	362.4 ± 7.7	300.4 ± 6.9	135	Glassy carbon 0.5 M H ₂ SO ₄
2H-MoS ₂ nanosheets ⁴	377	314	75~85	Glassy carbon 0.5 M H ₂ SO ₄
Nanosphere MoS ₂ ⁵	> 400	348	140	Glassy carbon 0.5 M H ₂ SO ₄
Strain-induced MoS ₂ ⁶	405	365	135	Ag electrode 0.5 M H ₂ SO ₄
Monolayer 2H-MoS ₂ ⁷	N/A	454	98	FTO electrode 0.5 M H ₂ SO ₄
Oxygen plasma treated MoS ₂ ⁸	618	526	171	Glassy carbon 0.5 M H ₂ SO ₄
Hydrogen annealed MoS ₂ ⁸	> 600	558	147	Glassy carbon 0.5 M H ₂ SO ₄
Monolayer MoS ₂ (by CVD) ⁸	N/A	N/A	342	Glassy carbon 0.5 M H ₂ SO ₄
Multilayer MoS ₂ @ MWNT ⁹	N/A	>300	92.7	FTO electrode 0.5 M H ₂ SO ₄
Monolayer MoS ₂ @ nanoporous Au ¹⁰	> 400	> 400	46	Nanoporous Au 0.5M H ₂ SO ₄

REFERENCES

1. K. Kang, S. E. Xie, L. J. Huang, Y. M. Han, P. Y. Huang, K. F. Mak, C. J. Kim, D. Muller, J. Park, *Nature*, 2015, **520**, 656-660.
2. M. Palummo, M. Bernardi, J. C. Grossman, *Nano Lett.*, 2015, **15**, 2794-2800.
3. H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, L. Huang, *ACS Nano* 2013, **7**, 1072-1080.
4. D. Voiry, M. Salehi, R. Silva, T. Fujita, M. W. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nano Lett.*, 2013, **13**, 6222-6227.
5. S. M. S. Kumar, K. Selvakumar, J. Karthikeyan, R. Thangamuthu, J. Karthikeyan, R. Thangamuthu, P. Murugan, P. Rajput, S. N. Jha, D. Bhattacharyya, N. Navascues, S. Irusta, *ChemistrySelect*, 2017, **2**, 4667-4672.
6. J. H. Lee, W. S. Jang, S. W. Han, H. K. Baik, *Langmuir*, 2014, **30**, 9866-9873.
7. K. Chang, X. Hai, H. Pang, H. B. Zhang, L. Shi, G. G. Liu, H. M. Liu, G. X. Zhao, M. Li, J. H. Ye, *Adv. Mater.*, 2016, **28**, 10033-10041.
8. G. L. Ye, Y. J. Gong, J. H. Lin, B. Li, Y. M. He, S. T. Pantelides, W. Zhou, R. Vajtai, P. M. Ajayan, *Nano Lett.*, 2016, **16**, 1097-1103.
9. E. Ahn, B. S. Kim, *ACS Appl. Mater. Interfaces*, 2017, **9**, 8688-8695.
10. Y. W. Tan, P. Liu, L. Y. Chen, W. T. Cong, Y. Ito, J. H. Han, X. W. Guo, Z. Tang, T. Fujita, A. Hirata, M. W. Chen, *Adv. Mater.*, 2014, **26**, 8023-+.