

Electronic Supplementary Information

Scalable Synthesis of Two-Dimensional Nano-Sheet Materials with
Chlorophyll Extracts: Enhancing the Hydrogen Evolution Reaction

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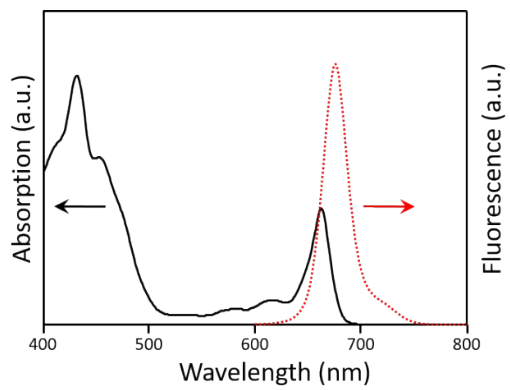


Figure S1. The UV-vis (black solid line) and fluorescence spectrum (red dot line; an excitation wavelength at 450 nm) of the chlorophyll extracts solution.

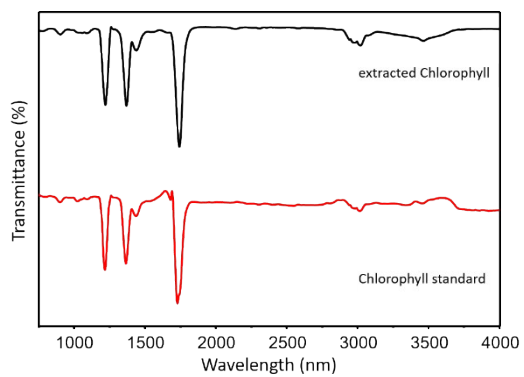


Figure S2. ATR-FTIR spectrum of the extracted chlorophyll (black line) and chlorophyll standard (red line).

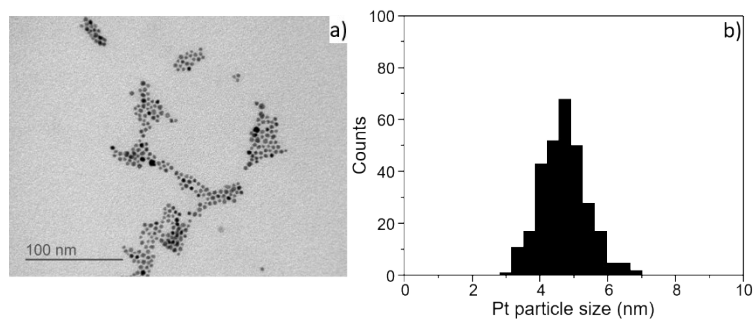


Figure S3. (a) The TEM images of the synthesized PtNPs. (b) The PtNPs size distributions.

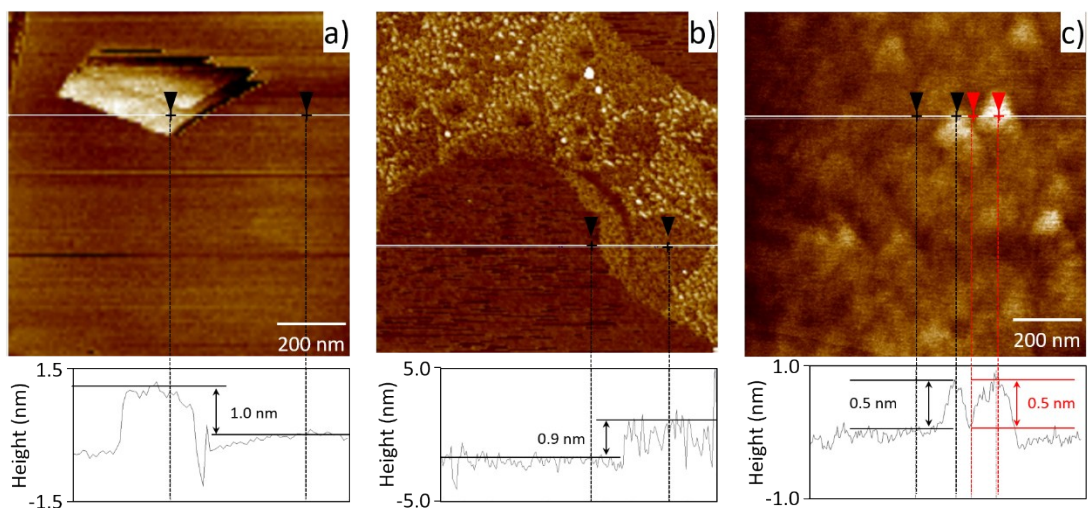


Figure S4. AFM image of the exfoliated (a) graphene, (b) MoS₂ and (c) h-BN transferred onto Si substrate.

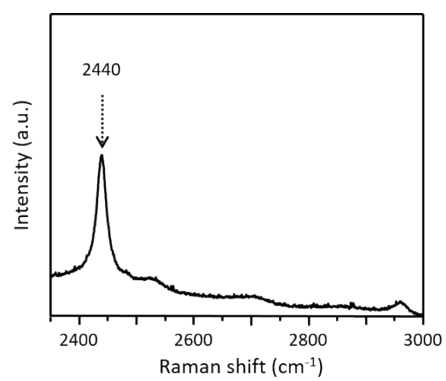


Figure S5. Raman spectrum of chlorophyll extracts.

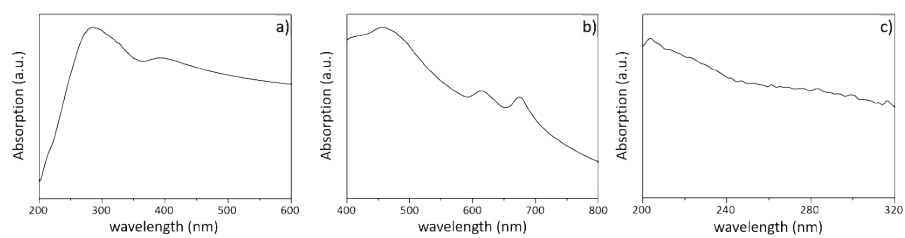


Figure S6. UV-vis spectrum of the exfoliated (a) graphene, (b) MoS₂ and (c) h-BN suspension.

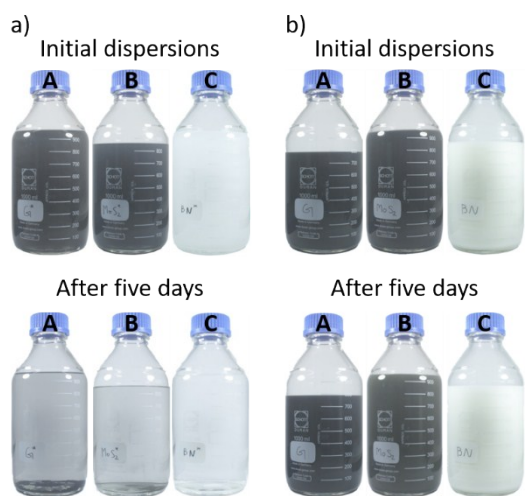


Figure S7. Comparative stability of the suspension of the exfoliated graphene (bottle A), MoS₂ (bottle B), and h-BN (bottle C). (a) without and (b) with chlorophyll extracts.

Initial dispersions



After five days

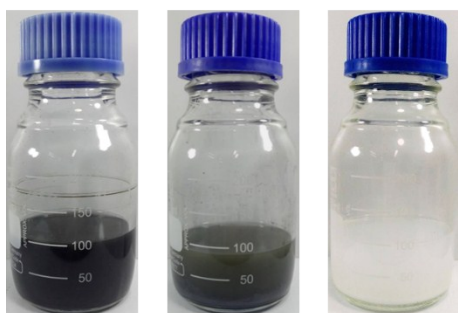


Figure S8. Stability of the suspension of the commercial available chlorophyll-assisted exfoliated graphene (left), MoS₂ (middle), and h-BN (right) suspensions.

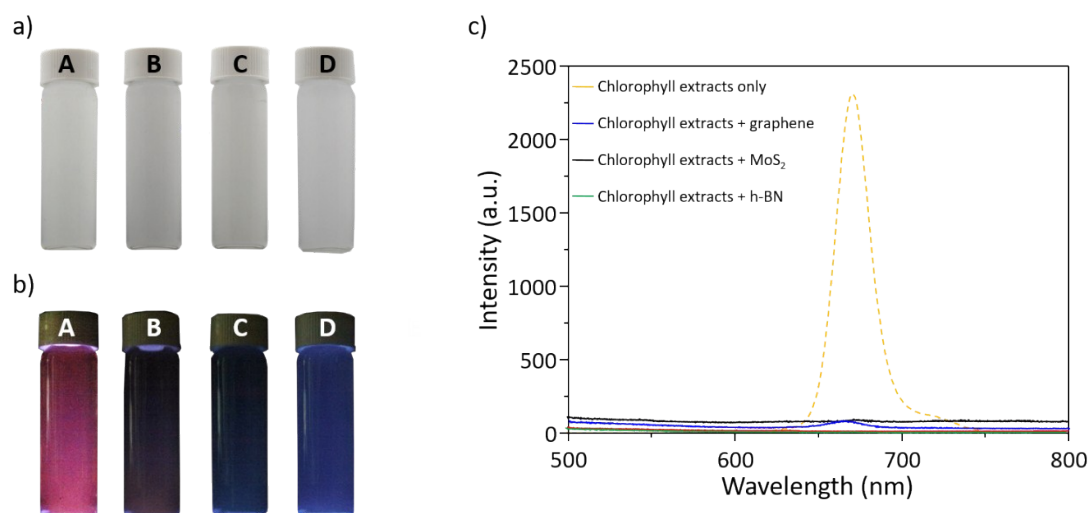


Figure S9. (a) Photographs and (b) Fluorescence of chlorophyll extracts (bottle A), chlorophyll extracts + graphene (bottle B), chlorophyll extracts + MoS₂ (bottle C), and chlorophyll extracts + h-BN (bottle D). (c) The fluorescence spectra of chlorophyll extracts and chlorophyll extracts mixed with different 2D material solutions.

Initial dispersions



After five days



Figure S10. Stability of chlorophyll extracts-assisted exfoliated graphene in solvents. Stable homogeneous suspensions of chlorophyll-assisted exfoliated graphene in various solvents after five days, from left to right: tetrahydrofuran, ethyl acetate, ethanol, hexane, and toluene.

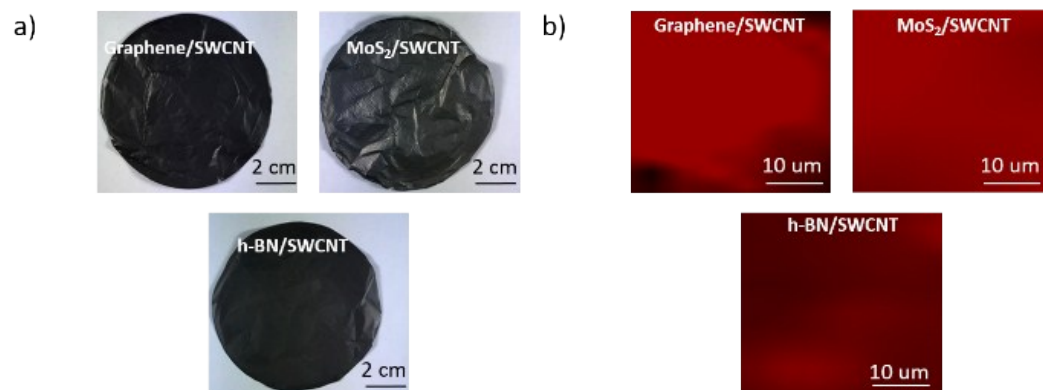


Figure S11. (a) Photograph of free-standing composite paper of graphene/SWCNT, MoS₂/SWCNT, and h-BN/SWCNT. (b) Raman mapping image of the four composite papers by extracting the frequency of the characteristic peak of each 2D material. The Raman 2D mapping area is $30 \times 30 \mu\text{m}$.

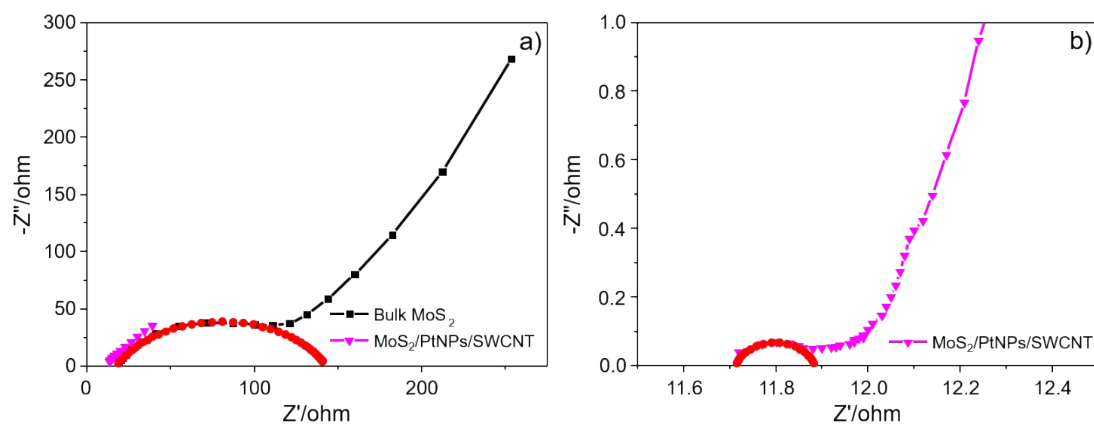


Figure S12. EIS spectra of the bulk MoS₂ (black square) and MoS₂/PtNPs/SWCNT (pink triangle) at low frequency with -0.1 V vs RHE in 0.5 M H₂SO₄ electrolyte. Red dots indicate fitting curve of the bulk MoS₂ and MoS₂/PtNPs/SWCNT paper.

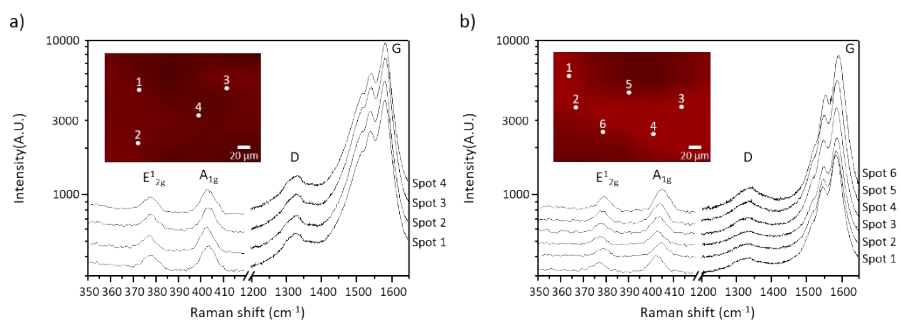


Figure S13. Raman spectra of the MoS₂/PtNPs/SWCNT paper were recorded a) before and b) after 100 h stability tests at a constant potential of -50 mV in 0.5 M H₂SO₄ solution.

Table S1. Summary of literature reported exchange current density of various HER catalysts.

Catalyst	Onset potential (mV)	Tafel slope (mV/dec)	Exchange current density (mA/cm ²)	Year	Journal	Ref.
MoS ₂ /PtNPs/SWCNT paper	-11	38	7.1 x 10 ⁻¹	This work		
Chlorophyll extracts - assisted exfoliated MoS ₂ thin sheets	-58	46	1.4 x 10 ⁻¹	This work		
P-doped 2H-MoS ₂	-103	49	N/A	2017	<i>Adv. Funct. Mater.</i>	1
Hydrothermal synthesis stepped edge-MoS ₂ on carbon fiber	~-75	59	2 x 10 ⁻¹	2017	<i>Energy Environ. Sci.</i>	2
Molybdenum Disulfide-Black Phosphorus	~-40	68	6.6 x 10 ⁻¹	2017	<i>Nano Lett.</i>	3
strained MoS ₂ with S-vacancy	~-140	60	2~4 x 10 ⁻²	2016	<i>Nat. Mater.</i>	4
2H Basal plane of monolayer MoS ₂	N.A.	~ 50	7~16 x 10 ⁻³	2016	<i>Nat. Mater.</i>	5
ground MoS ₂ microflake in the 900 °C annealing	~-240	76	9 x 10 ⁻²	2016	<i>Nano Lett.</i>	6
MoS ₂ annealed under 500 °C	~-300	147	N/A	2016	<i>Nano Lett.</i>	7
semiconductor phase of MoS ₂ (S-MoS ₂)	~-225	135	4 x 10 ⁻²	2016	<i>Nat. Commun.</i>	8
Metallic-phase MoS ₂ (M-MoS ₂)	~-150	41	1 x 10 ⁻¹	2016	<i>Nat. Commun.</i>	8
edge-terminated MoS ₂	-103	49	9.62 x 10 ⁻³	2015	<i>Nat. Commun.</i>	9
MoS ₂	-237	101	9.1 x 10 ⁻⁴	2015	<i>Nat.</i>	10

					<i>Commun.</i>	
MoS ₂ /CoSe ₂	-11	36	7.3 x 10 ⁻²	2015	<i>Nat. Commun.</i>	¹⁰
Ni-Mo-S/C	~140	85.3	4.89 x 10 ⁻²	2015	<i>Sci. Adv.</i>	¹¹
Defect-rich ultrathin MoS ₂ nanosheets	-120	50	8.91 x 10 ⁻³	2013	<i>Adv. Mater.</i>	¹²
Chlorophyll extracts - assisted exfoliated graphene thin sheets	-183	124	3.3 x 10 ⁻²	This work		
Chlorophyll extracts - assisted exfoliated h-BN thin sheets	-179	159	6 x 10 ⁻²	This work		

Reference:

- (1) Huang, X.; Leng, M.; Xiao, W.; Li, M.; Ding, J.; Tan, T. L.; Lee, W. S. V.; Xue, J.; Activating Basal Planes and S-Terminated Edges of MoS₂ toward More Efficient Hydrogen Evolution. *Adv. Funct. Mater.* **2017**, *27*, 1604943.
- (2) Hu, J.; Huang, B.; Zhang, C.; Wang, Z.; An, Y.; Zhou, D.; Lin, H.; Leung, M. K. H.; Yang, S.; Engineering Stepped Edge Surface Structures of MoS₂ Sheet Stacks to Accelerate the Hydrogen Evolution Reaction. *Energy Environ. Sci.* **2017**, *10*, 593-603.
- (3) He, R.; Hua, J.; Zhang, A.; Wang, C.; Peng, J.; Chen, W.; Zeng, J.; Molybdenum Disulfide-Black Phosphorus Hybrid Nanosheets as a Superior Catalyst for Electrochemical Hydrogen Evolution. *Nano Lett.* **2017**, *17*, 4311-4316.
- (4) Li, H.; Tsai, C.; Koh, A. L.; Cai, L.; Contryman, A. W.; Fragapane, A. H.; Zhao, J.; Han, H. S.; Manoharan, H. C.; Abild-Pedersen, F.; Nørskov, J. K.; Zheng, X.; Activating and Optimizing MoS₂ Basal Planes for Hydrogen Evolution through the Formation of Strained Sulphur Vacancies. *Nat. Mater.* **2016**, *15*, 48-54.
- (5) Voiry, D.; Fullon, R.; Yang, J.; Silva, C. d. C. C. e.; Kappera, R.; Bozkurt, I.; Kaplan, D.; Lagos, M. J.; Batson, P. E.; Gupta, G.; Mohite, A. D.; Dong, L.; Er, D.; Shenoy, V. B.; Asefa, T.; Chhowalla, M.; The Role of Electronic Coupling between Substrate and 2D MoS₂ Nanosheets in Electrocatalytic Production of Hydrogen. *Nat. Mater.* **2016**, *15*, 1003-1009.
- (6) Kiriya, D.; Lobaccaro, P.; Nyein, H. Y. Y.; Taher, P.; Hettick, M.; Shiraki, H.; Sutter-Fella, C. M.; Zhao, P.; Gao, W.; Maboudian, R.; Ager, J. W.; Javey, A.; General Thermal Texturization Process of MoS₂ for Efficient Electrocatalytic Hydrogen Evolution Reaction. *Nano Lett.* **2016**, *16*, 4047-4053.
- (7) Ye, G.; Gong, Y.; Lin, J.; Li, B.; He, Y.; Pantelides, S. T.; Zhou, W.; Vajtai, R.; Ajayan, P. M.; Defects Engineered Monolayer MoS₂ for Improved Hydrogen

Evolution Reaction. *Nano Lett.* **2016**, *16*, 1097-1103.

- (8) Geng, X.; Sun, W.; Wu, W.; Chen, B.; Al-Hilo, A.; Benamara, M.; Zhu, H.; Watanabe, F.; Cui, J.; Chen, T.-p.; Pure and Stable Metallic Phase Molybdenum Disulfide Nanosheets for Hydrogen Evolution Reaction. *Nat. Commun.* **2016**, *7*, 10672.
- (9) Gao, M.-R.; Chan, M. K. Y.; Sun, Y.; Edge-Terminated Molybdenum Disulfide with a 9.4-Å Interlayer Spacing for Electrochemical Hydrogen Production. *Nat. Commun.* **2015**, *6*, 7493.
- (10) Gao, M.-R.; Liang, J.-X.; Zheng, Y.-R.; Xu, Y.-F.; Jiang, J.; Gao, Q.; Li, J.; Yu, S.-H.; An Efficient Molybdenum Disulfide/Cobalt Diselenide Hybrid Catalyst for Electrochemical Hydrogen Generation. *Nat. Commun.* **2015**, *6*, 5982.
- (11) Miao, J.; Xiao, F.-X.; Yang, H. B.; Khoo, S. Y.; Chen, J.; Fan, Z.; Hsu, Y.-Y.; Chen, H. M.; Zhang, H.; Liu, B.; Hierarchical Ni-Mo-S Nanosheets on Carbon Fiber Cloth: A Flexible Electrode for Efficient Hydrogen Generation in Neutral Electrolyte. *Sci. Adv.* **2015**, *1*, e1500259.
- (12) Xie, J.; Zhang, H.; Li, S.; Wang, R.; Sun, X.; Zhou, M.; Zhou, J.; Lou, X. W. D.; Xie, Y.; Defect-Rich MoS₂ Ultrathin Nanosheets with Additional Active Edge Sites for Enhanced Electrocatalytic Hydrogen Evolution. *Adv. Mater.* **2013**, *25*, 5807-5813.

Table S2. EDS analysis of the MoS₂/PtNPs/SWCNT paper.

Element	Atomic (%)	Weight (%)
Platinum	0.03	0.26
Molybdenum	7.04	32.18
Sulfur	12.89	19.69