Supporting Information

Molybdenum Diselenide Nanolayers Prepared on Carbon Black as an Efficient and Stable Electrocatalyst for Hydrogen Evolution Reaction

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Mild Oxidation of Carbon Black

CB was mildly oxidized before use through a specific strategy established by us previously[1]. In details, CB (1.0 g) was mixed with 23 mL concentrated H_2SO_4 (98%) in a 250 mL round-bottom flask. The mixture was stirred at room temperature for 24 hours. Then, the flask was heated in an oil bath at 50 °C, and 100 mg of $NaNO_3$ was added to the suspension. After the $NaNO_3$ was dissolved, 300 mg of $KMnO_4$ was slowly added into the mixture, keeping the temperature below 55 °C. The mixture was stirred for 30 min and then 50 mL water was slowly added in 15 min to dilute the reaction system. Afterwards, the flask was removed from the oil bath followed by adding 140 mL of water and 6 mL of 30% H_2O_2 to end the reaction. The resulting suspension was then repeatedly centrifuged and washed with 5% HCl solution and water, and then purified by dialysis with a large amount of water until pH reached neutral. The final oxidized CB precipitate was obtained by centrifugation at 5000 rpm for 5 min and dried under air at 50 ^{o}C in an oven. The typical yield of oxidized CB was ca. 95%.

Preparation of the Working Electrode

The $MoSe_2$/CB composite modified GC electrodes were prepared as follows. The composite powder (4 mg) was dispersed in 1 mL of isopropanol along with 80 μL of Nafion solution (5 wt%, Dupont) by ultrasonicated for about 30 min to form a homogeneous ink with final catalyst concentration of 4 mg·mL^{-1}. Then, the suspension was dropped onto the surface of GC electrode and allowed to dry in air to obtain the $MoSe_2$/CB modified GC electrode. The loadings of 0.08 mg·cm^{-2}, 0.16 mg·cm^{-2}, 0.32 mg·cm^{-2}, 0.48 mg·cm^{-2}, 0.64 mg·cm^{-2} and 0.80 mg·cm^{-2} were obtained by adding 4 μL, 8 μL, 16 μL, 24 μL, 32 μL and 40 μL onto the GC electrode, respectively. When using carbon fiber paper as the working electrode, the loading of catalyst was 1 mg·cm^{-2}.

Supplementary Figures

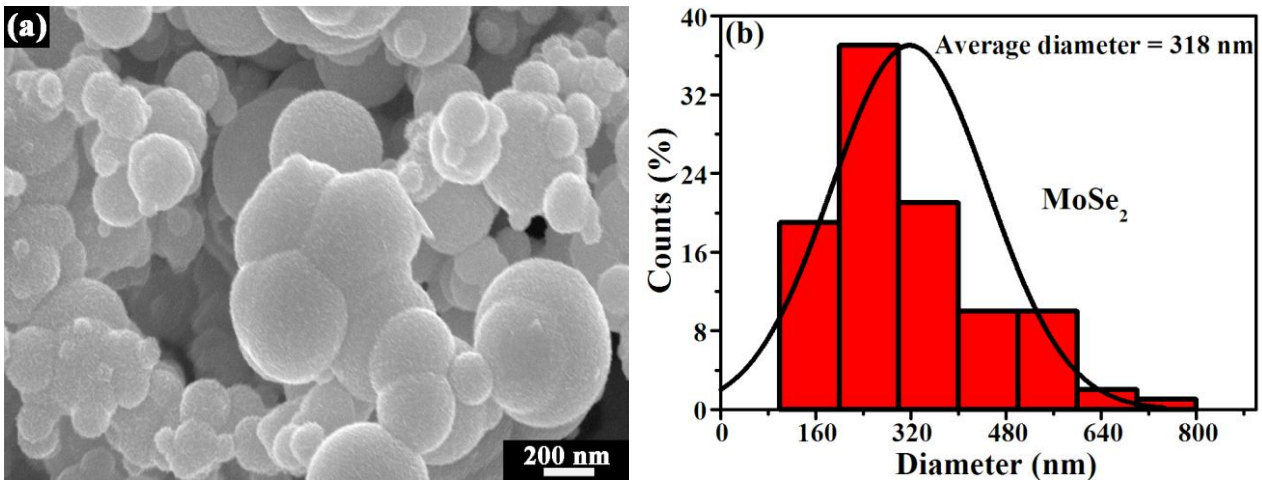

Figure S1. (a) Typical SEM image of pure $MoSe_2$ nanospheres. (b) Size distribution histogram of pure $MoSe_2$ microspheres.

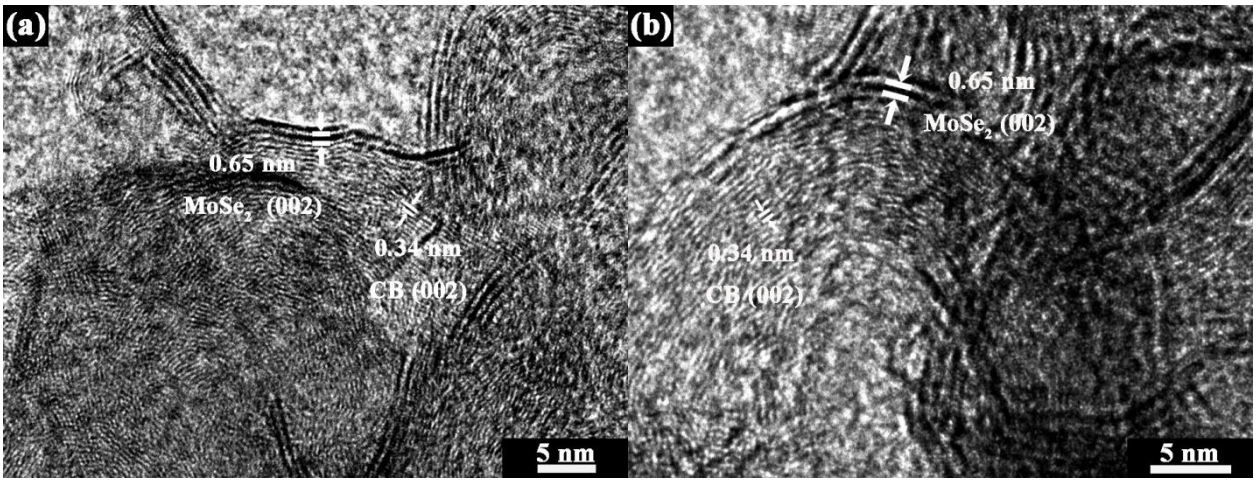

Figure S2. Typical high-resolution TEM images of the $MoSe_2$/CB-50% composite.

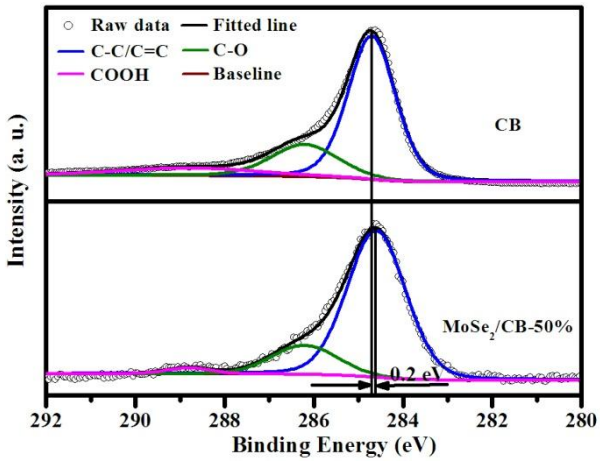

Figure S3. Comparison of high resolution C 1s spectrum of oxidized CB and $MoSe_2$/CB composite. The the position of the C 1s line of the $MoSe_2$/CB composite attributed to C=C/C-C is downshifted by ca. 0.2 eV compared to that of the oxidized CB, indicating the charge transfer from CB to $MoSe_2$.[2-4]

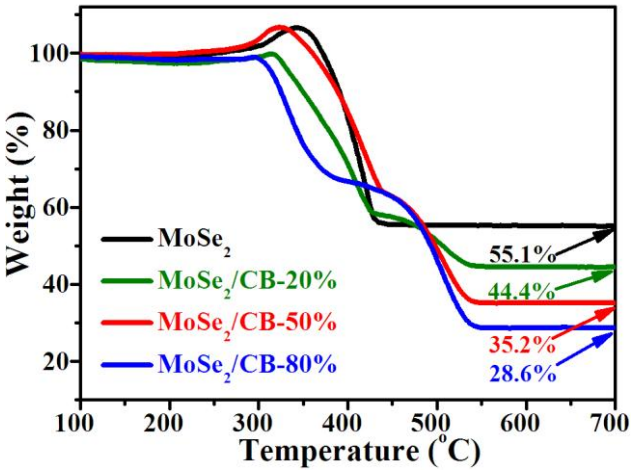

Figure S4. TGA curves of pure $MoSe_2$ and the $MoSe_2$/CB composite powders with three different CB contents.

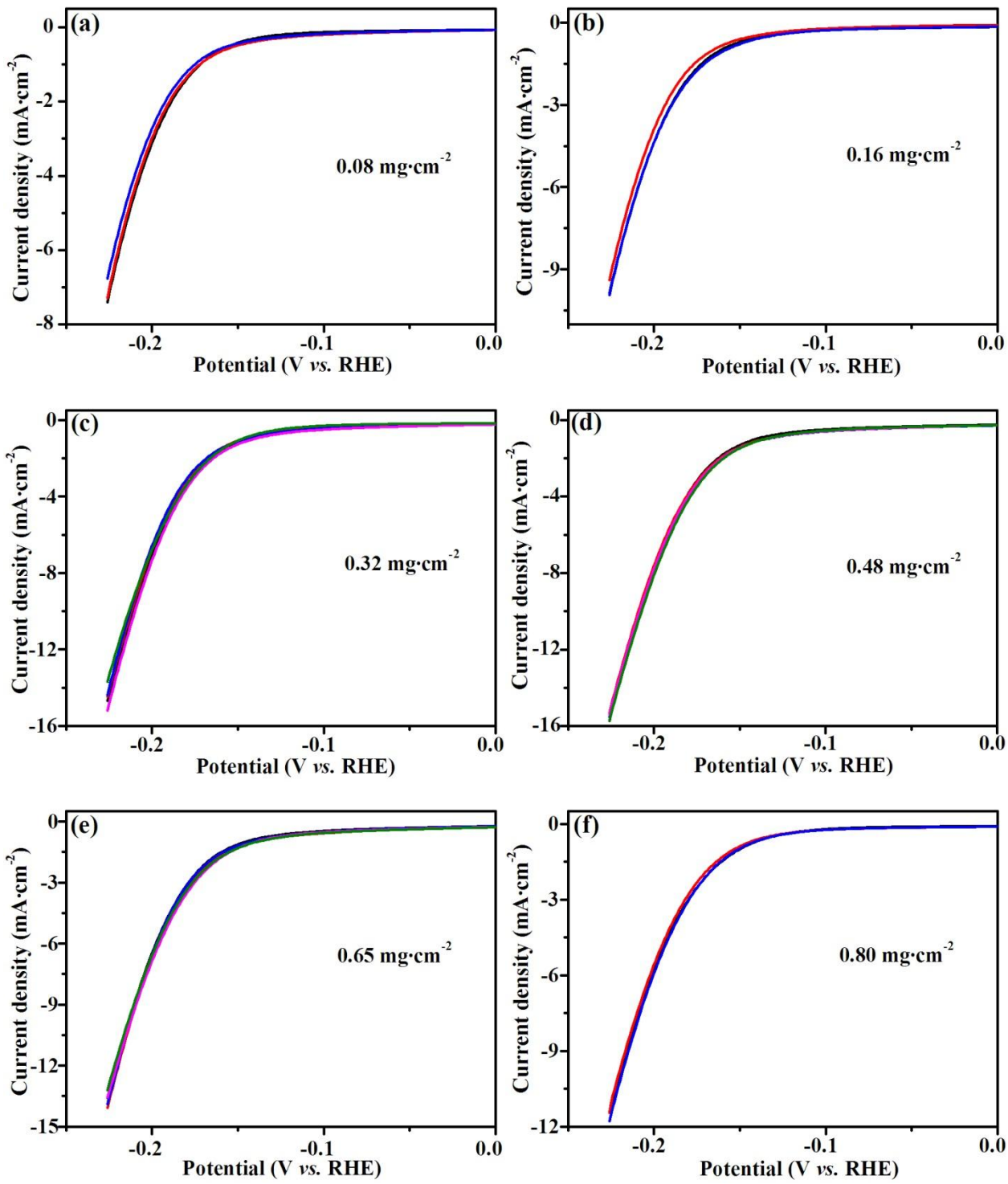

Figure S5. Multiple measurement results of each loading for $MoSe_2$/CB-50% on glassy carbon electorde.

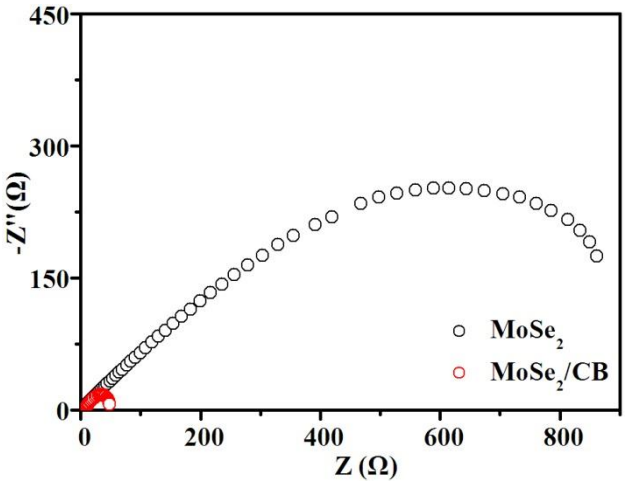

Figure S6. Electrochemical impedance spectroscopies of $MoSe_2$/CB and pure $MoSe_2$ at η = 0.18 V.

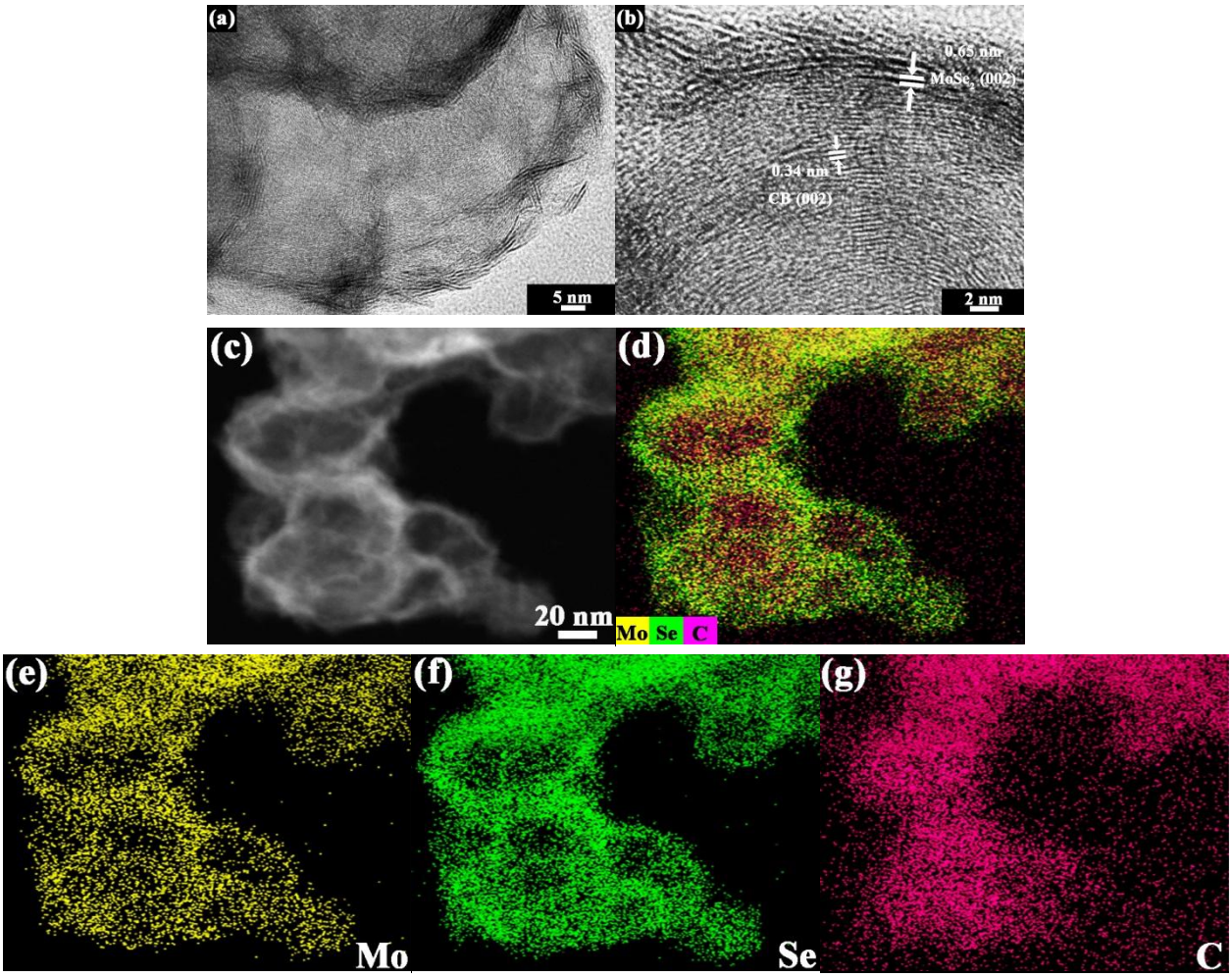

Figure S7. Typical TEM and high-resolution TEM images of the $MoSe_2$/CB-50% composite (a, b), and TEM image (c), integrated STEM-EDX mapping image of the $MoSe_2$/CB-50% composite (d) and the corresponding elemental mapping images of Mo (e), Se (f), C (g) in the $MoSe_2$/CB-50% composite after 2500 cycles.

References

(1) Xue, N.; Diao, P. Composite of Few-Layered MoS_2 Grown on Carbon Black: Tuning the Ratio of Terminal to Total Sulfur in MoS_2 for Hydrogen Evolution Reaction. *J. Phys. Chem. C* **2017**, *121*, 14413-14425.

(2) Koroteev, V.; Bulusheva, L.; Asanov, I.; Shlyakhova, E.; Vyalikh, D.; Okotrub, A. Charge Transfer in the MoS_2/Carbon Nanotube Composite. *J. Phys. Chem. C* **2011**, *115*, 21199-21204.

(3) Zheng, X.; Xu, J.; Yan, K.; Wang, H.; Wang, Z.; Yang, S. Space-Confined Growth of MoS_2 Nanosheets within Graphite: The Layered Hybrid of MoS_2 and Graphene as an Active Catalyst for Hydrogen Evolution Reaction. *Chem. Mater.* **2014**, *26*, 2344-2353.

(4) Zhu, H.; Du, M.; Zhang, M.; Zou, M.; Yang, T.; Wang, S.; Yao, J.; Guo, B. S-Rich Single-Layered MoS_2 Nanoplates Embedded in N-Doped Carbon Nanofibers: Efficient Co-Electrocatalysts for the Hydrogen Evolution Reaction. *Chem. Commun.* **2014**, *50*, 15435-15438.