catalysts

Supplementary Materials

Effect of Ag_2S Nanocrystals/Reduced Graphene Oxide interface on Hydrogen Evolution Reaction.

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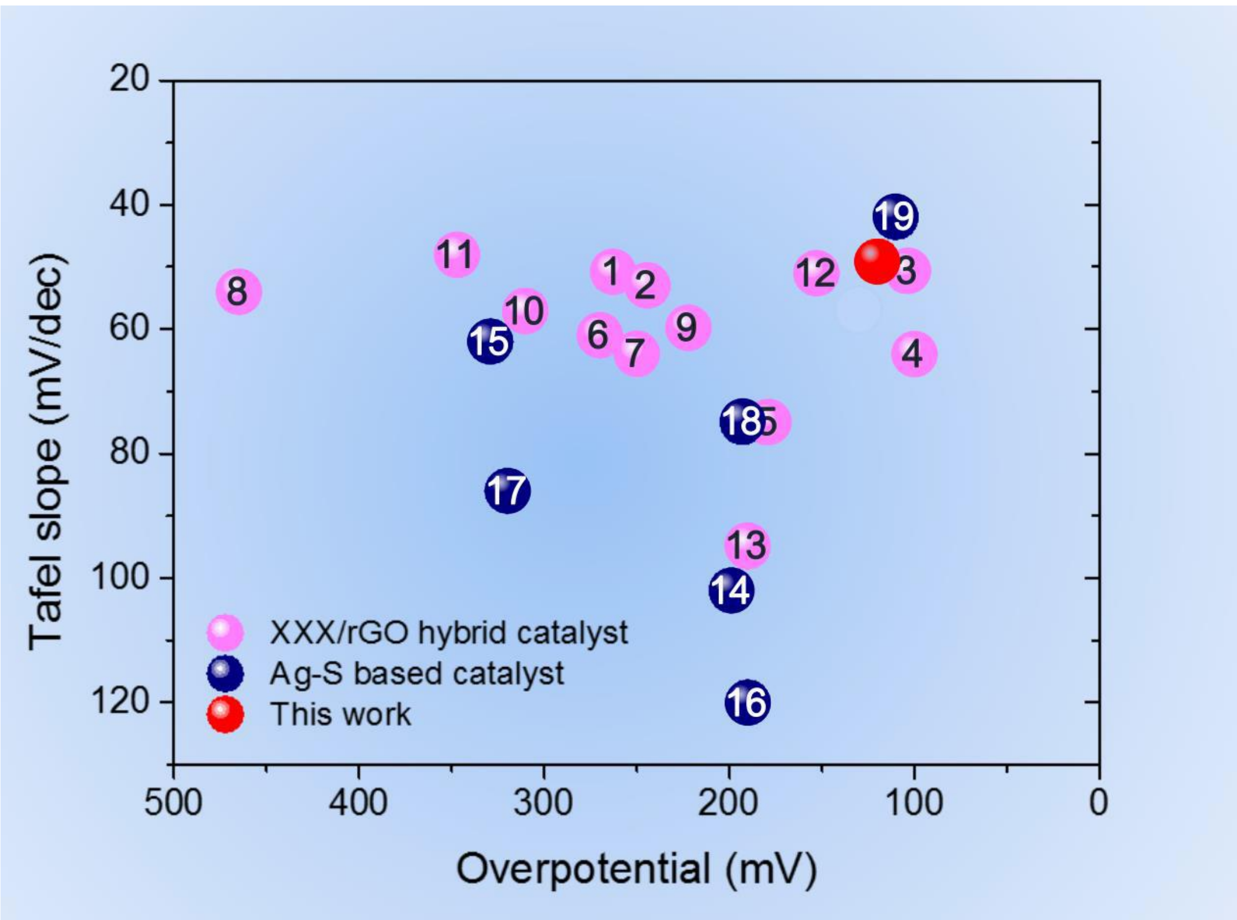
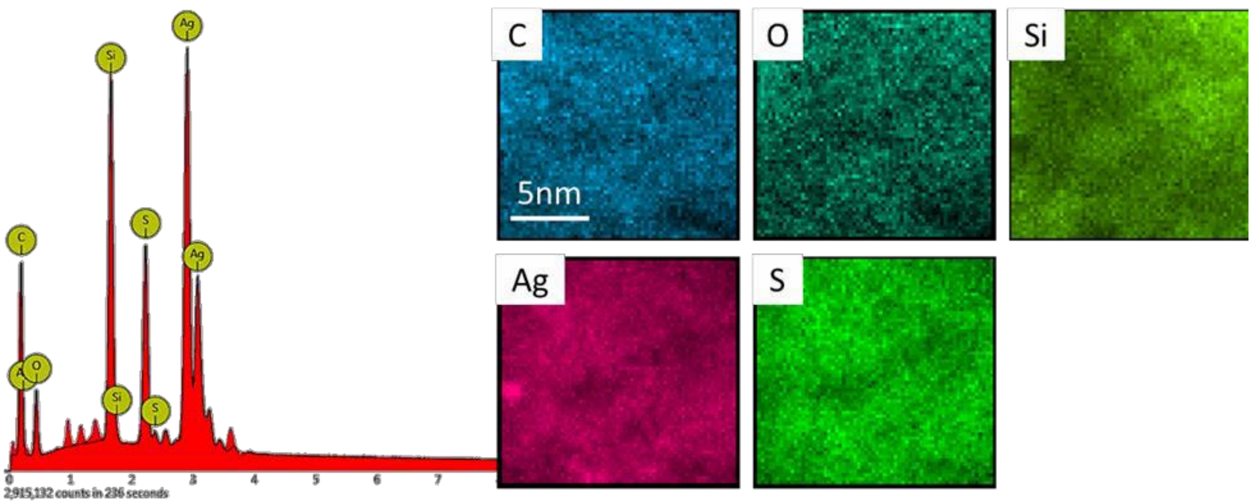


Figure S1. Electrochemical performance of different catalysts. The horizontal axis represents the overpotential. The vertical axis represents the Tafel slope. Performance of rGO-based chalcogenide metal semiconductor composites as electrocatalyst for hydrogen evolution reaction was shown in **Table S2**. Performance of Ag-based chalcogenide metal semiconductor as electrocatalyst for hydrogen evolution reaction is presented in **Table S3**.



Element Name	Atomic Conc.	Weight Conc.
Carbon	55	24
Oxygen	19	11
Silver	12	49
Sulfur	5	7
Silicon	9	9

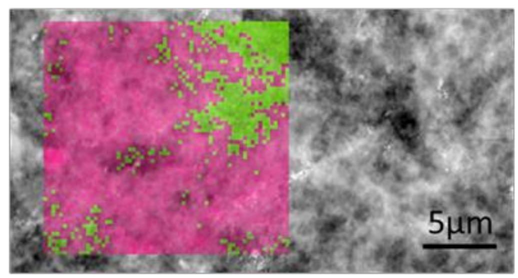


Figure S2. EDS of Ag_2S/rGO hybrid on glass substrate.

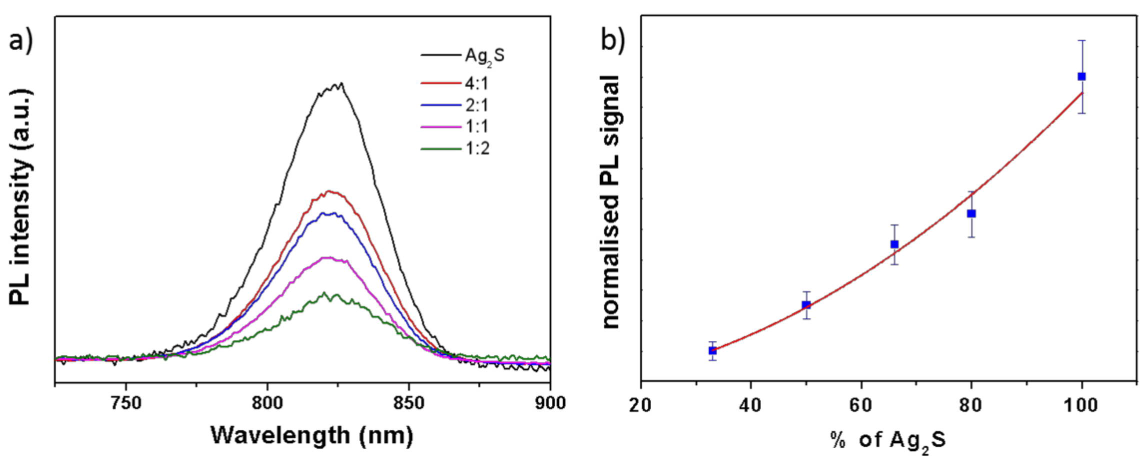


Figure S3. a. Changes in photoluminescence at different weight ratios of Ag_2S to rGO. b. normalized changes in the PL signal as a function of Ag_2S %. The fitting indicates a slight deviation from linearity.

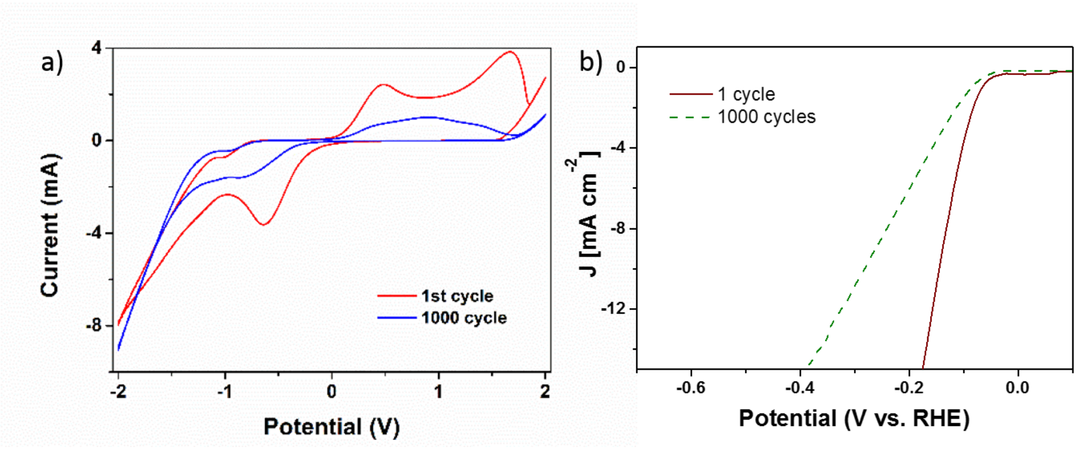


Figure S4. a. Typical CV scans (1st and 1000th) of Ag2S/rGO. **b.** Durability tests of Ag_2S/GO hybrid. The polarization curves were recorded before and after 1000 potential cycles in 0.5 M H_2SO_4 aqueous solution from 0 to −0.7 V (vs RHE).

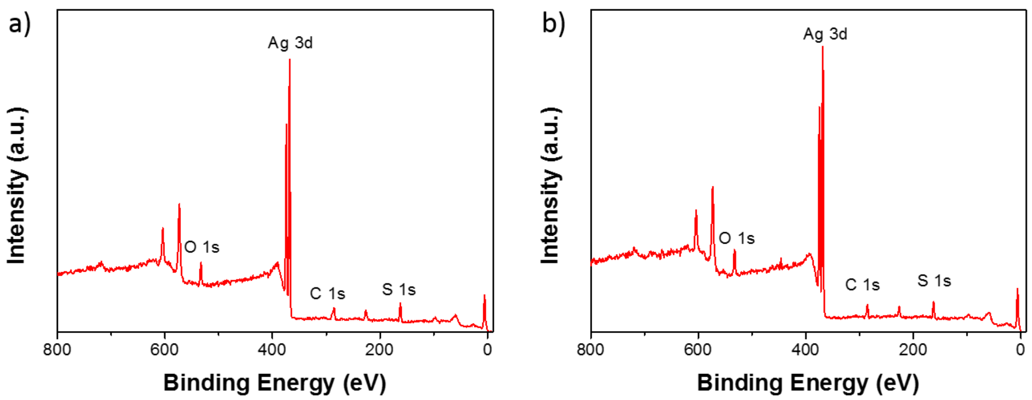


Figure S5. The XPS spectra of the Ag_2S/rGO composite. **a.** Survey XPS spectrum of Ag_2S/rGO composite before electro-catalyst reaction. **b.** Survey XPS spectrum of Ag_2S/rGO composite after electro-catalyst reaction.

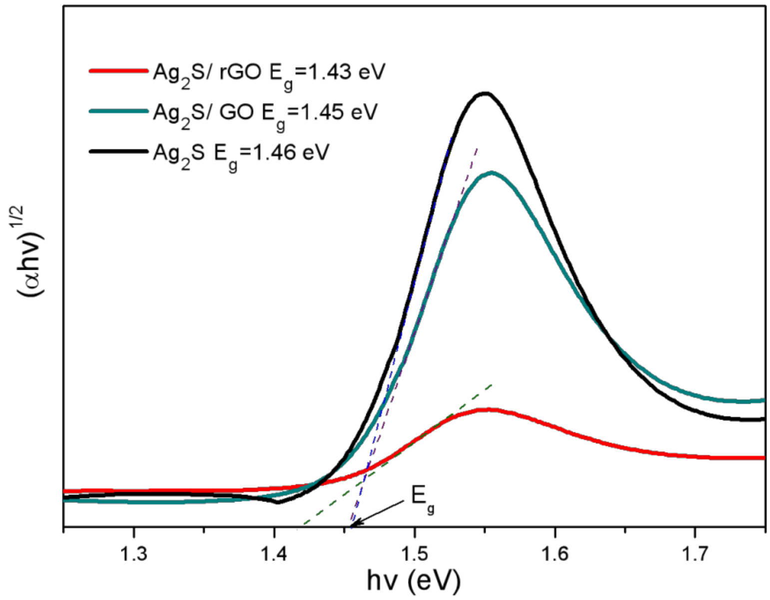


Figure S6. Tauc plots for Ag_2S/rGO, Ag_2S/GO, and Ag_2S used for the extraction of the band gaps.

Table S1. The fluorescence lifetime of the Ag_2S and the Ag_2S/rGO.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ (ns)	Average (ns)
Ag_2S_1	908.3	108.4	3164.2	5.6	11685.1	0.5	7.7	
Ag_2S_2	803.9	115.2	2744.2	6.1	10694.2	0.5	8.0	
Ag_2S_3	776.8	114.5	2727.2	5.9	10618.9	0.5	7.8	7.8
Ag_2S_4	762.5	113.9	2640.2	6.1	10699.2	0.5	7.7	
Ag_2S_5	837.1	113.9	2834.4	6.2	11919.1	0.5	7.6	
Ag_2S/rGO_1	814.2	75.0	3269.4	5.8	17918.0	0.6	4.1	
Ag_2S/rGO_2	1003.6	77.9	4290.3	6.4	23758.3	0.7	4.2	
Ag_2S/rGO_3	834.8	83.9	3020.2	6.9	19141.0	0.6	4.5	4.4
Ag_2S/rGO_4	1068.8	85.2	3819.5	7.1	24718.7	0.6	4.5	
Ag_2S/rGO_5	1077.0	84.3	3807.9	7.1	25250.6	0.6	4.4	

Table S2. The performance of rGO-based chalcogenide metal semiconductor composites as electrocatalyst for hydrogen evolution reaction.

Catalyst type	electrolyte	Overpotential	Tafel slope (mV/dec)	Year	Ref.
$(MoS_2)_x(SnO_2)_{1-x}$/rGO	0.5 M H_2SO_4	263 ±5 mV	50.8 mV/dec	2018	[1]
Mo_3S_{13}-SrGO	0.5 M H_2SO_4	244 mV	53 mV/dec	2018	[2]
$Ni_{0.85}Se$@NGO	0.5 M H_2SO_4	104 mV	50.7 mV/dec	2018	[3]
WSe_2-rGO	0.5 M H_2SO_4	100 mV	64 mV/dec	2018	[4]
CoS_2/RGO	0.5 M H_2SO_4	180 mV	75 mV/dec	2017	[5]
NiSe-RGO-PI/CNT	0.5 M H_2SO_4	270 mV	61 mV/dec	2017	[6]
$FeSe_2$/GO	0.5 M H_2SO_4	250 mV	64 mV/dec	2017	[7]
WS_3@x/rGO	1M KOH	465 mV	54 mV/dec	2017	[8]
MoS_2/rGO	0.5 M H_2SO_4	222 mV	59.8mV/dec	2017	[9]
$MoSe_2$–rGO–M	0.5 M H_2SO_4	310 mV	57 mV/dec	2017	[10]
MoS_2/rGO	0.5 M H_2SO_4	347 mV (η_1)	48 mV/dec	2017	[11]
MoSSe@rGO	0.5 M H_2SO_4	153 mV	51 mV/dec	2016	[12]
MoS_2NF/rGO	0.5 M H_2SO_4	190 mV	95 mV/dec	2014	[13]
Ag_2S/rGO	**0.5 M H_2SO_4**	**120 mV**	**49.1 mV/dec**		**This work**

Table S3. The performance of Ag_2S-based composites for hydrogen evolution reaction.

Catalyst type	electrolyte	Overpotential	Tafel slope (mV/dec)	Year	Ref.
Ag_2S/Ag	0.5 M H_2SO_4	199 mV	102 mV/dec	2017	[14]
Ag_2WS_4	0.5 M H_2SO_4	329 mV	62 mV/dec	2018	[15]
Ag_2S/Ag	0.5 M H_2SO_4	190 mV	120 mV/dec	2018	[16]
Ag_2S	0.5 M H_2SO_4	320 mV	86 mV/dec	2019	[17]
Ag_2S/CuS	0.5 M H_2SO_4	193 mV	75 mV/dec	2016	[18]
Ag_2S/MoS_2	0.5 M H_2SO_4	110 mV	42 mV/dec	2017	[19]
Ag-Ag_2S/MoS_2	0.5 M H_2SO_4	200 mV	—	2014	[20]
Ag_2S/rGO	**0.5 M H_2SO_4**	**120 mV**	**49.1 mV/dec**		**This work**

References

1. S. Ravula, C. Zhang, J. Essner, J. Robertson, J. Lin, G. Baker, Ionic liquid-assisted synthesis of nanoscale $(MoS_2)x(SnO_2)1-x$ on reduced graphene oxide for the electrocatalytic hydrogen evolution reaction, Abstr Pap Am Chem S 255 (2018).

2. C.V. Pham, A. Zana, M. Arenz, S. Thiele, $[Mo_3S_{13}](2-)$ Cluster Decorated Sulfur-doped Reduced Graphene Oxide as Noble Metal-Free Catalyst for Hydrogen Evolution Reaction in Polymer Electrolyte Membrane Electrolyzers, Chemelectrochem 5 (2018) 2672-2680.

3. H.Y. Fu, Y.J. Chen, Z.Y. Ren, Y.T. Xiao, Y.Y. Liu, X. Zhang, G.H. Tian, Highly dispersed of Ni0.85Se nanoparticles on nitrogen-doped graphene oxide as efficient and durable electrocatalyst for hydrogen evolution reaction, Electrochim Acta 262 (2018) 107-114.
4. J.S. Cho, S.K. Park, K.M. Jeon, Y. Piao, Y.C. Kang, Mesoporous reduced graphene oxide/WSe_2 composite particles for efficient sodium-ion batteries and hydrogen evolution reactions, Appl Surf Sci 459 (2018) 309-317.
5. Y.Y. Yang, F. Li, W.Z. Li, W.B. Gao, H. Wen, J. Li, Y.P. Hu, Y.T. Luo, R. Li, Porous CoS_2 nanostructures based on ZIF-9 supported on reduced graphene oxide: Favourable electrocatalysis for hydrogen evolution reaction, Int J Hydrogen Energ 42 (2017) 6665-6673.
6. T.X. Wang, X. Li, Y.M. Jiang, Y.X. Zhou, L.P. Jia, C.M. Wang, Reduced graphene oxide-polyimide/carbon nanotube film decorated with NiSe nanoparticles for electrocatalytic hydrogen evolution reactions, Electrochim Acta 243 (2017) 291-298.
7. J. Theerthagiri, R. Sudha, K. Premnath, P. Arunachalam, J. Madhavan, A.M. Al-Mayouf, Growth of iron diselenide nanorods on graphene oxide nanosheets as advanced electrocatalyst for hydrogen evolution reaction, Int J Hydrogen Energ 42 (2017) 13020-13030.
8. S.M. Tan, M. Pumera, Electrosynthesis of Bifunctional WS_{3-x}/Reduced Graphene Oxide Hybrid for Hydrogen Evolution Reaction and Oxygen Reduction Reaction Electrocatalysis, Chem-Eur J 23 (2017) 8510-8519.
9. W.Y. Sun, P. Li, X. Liu, J.J. Shi, H.M. Sun, Z.L. Tao, F.J. Li, J. Chen, Size-controlled MoS_2 nanodots supported on reduced graphene oxide for hydrogen evolution reaction and sodium-ion batteries, Nano Research 10 (2017) 2210-2222.

10 S.K. Park, G.D. Park, D. Ko, Y.C. Kang, Y. Piao, Aerosol synthesis of molybdenum diselenide-reduced graphene oxide composite with empty nanovoids and enhanced hydrogen evolution reaction performances, Chemical Engineering Journal 315 (2017) 355-363.

11., J.E. Lee, J. Jung, T.Y. Ko, S. Kim, S.I. Kim, J. Nah, S. Ryu, K.T. Nam, M.H. Lee, Catalytic synergy effect of MoS_2/reduced graphene oxide hybrids for a highly efficient hydrogen evolution reaction, Rsc Advances 7 (2017) 5480-5487.

12. B. Konkena, J. Masa, W. Xia, M. Muhler, W. Schuhmann, MoSSe@reduced graphene oxide nanocomposite heterostructures as efficient and stable electrocatalysts for the hydrogen evolution reaction, Nano Energy 29 (2016) 46-53.
13. C.B. Ma, X.Y. Qi, B. Chen, S.Y. Bao, Z.Y. Yin, X.J. Wu, Z.M. Luo, J. Wei, H.L. Zhang, H. Zhang, MoS_2 nanoflower-decorated reduced graphene oxide paper for high-performance hydrogen evolution reaction, Nanoscale 6 (2014) 5624-5629.

14 M. Basu, R. Nazir, C. Mahala, P. Fageria, S. Chaudhary, S. Gangopadhyay, S. Pande, Ag2S/Ag Heterostructure: A Promising Electrocatalyst for the Hydrogen Evolution Reaction, Langmuir : the ACS journal of surfaces and colloids 33 (2017) 3178-3186.

15. F.P. Zhan, Q.H. Wang, Y.B. Li, X. Bo, Q.X. Wang, F. Gao, C. Zhao, Low-Temperature Synthesis of Cuboid Silver Tetrathiotungstate (Ag_2WS_4) as Electrocatalyst for Hydrogen Evolution Reaction, Inorganic chemistry 57 (2018) 5791-5800.
16. C.M. Cova, A. Zuliani, A.R. Puente Santiago, A. Caballero, M.J. Muñoz-Batista, R. Luque, Microwave-assisted preparation of Ag/Ag_2S carbon hybrid structures from pig bristles as efficient HER catalysts, J Mater Chem A 6 (2018) 21516-21523.
17. W. Yu, J. Yin, Y. Li, B. Lai, T. Jiang, Y. Li, H. Liu, J. Liu, C. Zhao, S.C. Singh, J. Chen, B. Lin, H. Idriss, C. Guo, Ag_2S Quantum Dots as an Infrared Excited Photocatalyst for Hydrogen Production, ACS Applied Energy Materials (2019).
18. H.T. Ren, W.C. Xu, S.L. Zhu, Z.D. Cui, X.J. Yang, A. Inoue, Synthesis and properties of nanoporous Ag_2S/CuS catalyst for hydrogen evolution reaction, Electrochim Acta 190 (2016) 221-228.
19. M. Wang, P. Ju, W. Li, Y. Zhao, X.X. Han, Ag_2S nanoparticle-decorated MoS_2 for enhanced electrocatalytic and photoelectrocatalytic activity in water splitting, Dalton transactions 46 (2017) 483-490.
20. X.H. Xia, X.J. Zhao, W.C. Ye, C.M. Wang, Highly porous Ag-Ag_2S/MoS_2 with additional active sites synthesized by chemical etching method for enhanced electrocatalytic hydrogen evolution, Electrochim Acta 142 (2014) 173-181.