Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supporting Information

Photoelectrochemical devices for solar water splitting – materials and challenges

Chaoran Jiang,[1,2] Savio J. A. Moniz,[1] Aiqin Wang,[2] Tao Zhang,[2] and Junwang Tang[1*]

1. Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK.

2. State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.

∗ Email: Junwang.tang@ucl.ac.uk

References for Additional reading:

TiO_2 photoelectrodes:

1. Y. Gai, J. Li, S.-S. Li, J.-B. Xia and S.-H. Wei, *Physical Review Letters*, 2009, **102**, 036402.

2. D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave and I. P. Parkin, *Nature materials*, 2013, **12**, 798-801.

3. F. Dong, S. Guo, H. Wang, X. Li and Z. Wu, *The Journal of Physical Chemistry C*, 2011, **115**, 13285-13292.

4. J. Varley, A. Janotti and C. Van de Walle, *Advanced Materials*, 2011, **23**, 2343-2347.

5 W. Q. Fang, Z. Huo, P. Liu, X. L. Wang, M. Zhang, Y. Jia, H. Zhang, H. Zhao, H. G. Yang and X. Yao, *Chemistry-A European Journal*, 2014, **20**, 11439-11444.

6 P. Triggs and F. Levy, *physica status solidi (b)*, 1985, **129**, 363-374.

7. M. Altomare, K. Lee, M. S. Killian, E. Selli and P. Schmuki, *Chemistry – A European Journal*, 2013, **19**, 5841-5844.

8. M. Yang, D. Kim, H. Jha, K. Lee, J. Paul and P. Schmuki, *Chemical Communications*, 2011, **47**, 2032-2034.

α-Fe_2O_3 photoanodes:

9. Y. Zhang, S. Jiang, W. Song, P. Zhou, H. Ji, W. Ma, W. Hao, C. Chen and J. Zhao, *Energy & Environmental Science*, 2015, **8**, 1231-1236.

10. Y. Hou, F. Zuo, A. Dagg and P. Feng, *Angewandte Chemie*, 2013, **125**, 1286-1290.

11. B. Klahr, S. Gimenez, F. Fabregat-Santiago, J. Bisquert and T. W. Hamann, *Journal of the American Chemical Society*, 2012, **134**, 16693-16700.

12. K. M. H. Young, B. M. Klahr, O. Zandi and T. W. Hamann, *Catalysis Science & Technology*, 2013, **3**, 1660-1671.

13. A. G. Joly, J. R. Williams, S. A. Chambers, G. Xiong, W. P. Hess and D. M. Laman, *Journal of applied physics*, 2006, **99**, 053521.

14. Y. Ling, G. Wang, J. Reddy, C. Wang, J. Z. Zhang and Y. Li, *Angewandte Chemie*, 2012, **124**, 4150-4155.

15. S. Kumari, A. P. Singh, D. Deva, R. Shrivastav, S. Dass and V. R. Satsangi, *International journal of hydrogen energy*, 2010, **35**, 3985-3990.

16. N. T. Hahn and C. B. Mullins, *Chemistry of Materials*, 2010, **22**, 6474-6482.

17. J. S. Jang, J. Lee, H. Ye, F.-R. F. Fan and A. J. Bard, *The Journal of Physical Chemistry C*, 2009, **113**, 6719-6724.

18. Y.-S. Hu, A. Kleiman-Shwarsctein, A. J. Forman, D. Hazen, J.-N. Park and E. W. McFarland, *Chemistry of Materials*, 2008, **20**, 3803-3805.

19. C. Jorand Sartoretti, B. D. Alexander, R. Solarska, I. A. Rutkowska, J. Augustynski and R. Cerny, *The Journal of Physical Chemistry B*, 2005, **109**, 13685-13692.

20. A. Kleiman-Shwarsctein, Y.-S. Hu, A. J. Forman, G. D. Stucky and E. W. McFarland, *The Journal of Physical Chemistry C*, 2008, **112**, 15900-15907.

21. Y. Ling, G. Wang, D. A. Wheeler, J. Z. Zhang and Y. Li, *Nano Letters*, 2011, **11**, 2119-2125.

22. P. M. Chee, P. P. Boix, H. Ge, Y. Fang, J. Barber and L. H. Wong, 2015, **7**, 6852-6859.

23. F. Le Formal, N. Tetreault, M. Cornuz, T. Moehl, M. Gratzel and K. Sivula, *Chemical Science*, 2011, **2**, 737-743.

$BiVO_4$ photoanodes:

24. Z.-F. Huang, L. Pan, J.-J. Zou, X. Zhang and L. Wang, *Nanoscale*, 2014, **6**, 14044-14063.

25. D. K. Zhong, S. Choi and D. R. Gamelin, *Journal of the American Chemical Society*, 2011, **133**, 18370-18377.

26. Y. Pihosh, I. Turkevych, K. Mawatari, T. Asai, T. Hisatomi, J. Uemura, M. Tosa, K. Shimamura, J. Kubota, K. Domen and T. Kitamori, *Small*, 2014, **10**, 3692-3699.

CdS photoanodes:

27. E. Rabinovich and G. Hodes, *The Journal of Physical Chemistry C*, 2013, **117**, 1611-1620.

28. K. Wu, Z. Chen, H. Lv, H. Zhu, C. L. Hill and T. Lian, *Journal of the American Chemical Society*, 2014, **136**, 7708-7716.

29. K. Wu, Z. Chen, H. Lv, H. Zhu, C. L. Hill and T. Lian, *Journal of the American Chemical Society*, 2014, **136**, 7708-7716.

III-V photoanodes:

30. J. A. Del Alamo, *Nature*, 2011, **479**, 317-323.

31. K. Sun, Y. Kuang, E. Verlage, B. S. Brunschwig, C. W. Tu and N. S. Lewis, *Advanced Energy Materials*, 2015, **5**, 1402276.

Cu_2O photocathodes:

32. J. Luo, L. Steier, M.-K. Son, M. Schreier, M. T. Mayer and M. Grätzel, *Nano Letters*, 2016, **16**, 1848-1857.

33. M. Wang, L. Sun, Z. Lin, J. Cai, K. Xie and C. Lin, *Energy & Environmental Science*, 2013, **6**, 1211-1220.

34. C. G. Morales‐Guio, L. Liardet, M. T. Mayer, S. D. Tilley, M. Grätzel and X. Hu, *Angewandte Chemie International Edition*, 2015, **54**, 664-667.

Group IIIA Metal Phosphides:

35. J. Sun, C. Liu and P. Yang, *Journal of the American Chemical Society*, 2011, **133**, 19306-19309.

36. A. Paracchino, V. Laporte, K. Sivula, M. Grätzel and E. Thimsen, *Nature materials*, 2011, **10**, 456-461.

37. Y. Lin, R. Kapadia, J. Yang, M. Zheng, K. Chen, M. Hettick, X. Yin, C. Battaglia, I. D. Sharp, J. W. Ager and A. Javey, *The Journal of Physical Chemistry C*, 2015, **119**, 2308-2313.

Stabilisation of Silicon photoelectrodes:

(i) Transition metal oxides used as a co-catalyst as well as protection layer:

38. J. J. H. Pijpers, M. T. Winkler, Y. Surendranath, T. Buonassisi and D. G. Nocera, 2011, **108**, 10056-10061.

39. K. Sun, M. T. McDowell, A. C. Nielander, S. Hu, M. R. Shaner, F. Yang, B. S. Brunschwig and N. S. Lewis, *The Journal of Physical Chemistry Letters*, 2015, **2**, 592-598.

(ii) Ultra thin metal films used as co-catalyst as well as a protection layer:

40. J. A. Turner, 2012, **227**, 2012-2014.

(iii) Amorphous TiO_2 as a protection layer:

41. M. R. Shaner, S. Hu, K. Sun and N. S. Lewis, *Energy & Environmental Science*, 2015, **8**, 203-207.

Co-catalysts:

42. L. Trotochaud, J. K. Ranney, K. N. Williams and S. W. Boettcher, *Journal of the American Chemical Society*, 2012, **134**, 17253-17261.

43. A. Singh, S. L. Y. Chang, R. K. Hocking, U. Bach and L. Spiccia, *Energy & Environmental Science*, 2013, **6**, 579-586.

44. L. Wang, F. Dionigi, N. T. Nguyen, R. Kirchgeorg, M. Gliech, S. Grigorescu, P. Strasser and P. Schmuki, *Chemistry of Materials*, 2015, 150309165528004.

45. H.-J. Lewerenz and L. Peter, *Photoelectrochemical Water Splitting: Materials, Processes and Architectures*, RSC publishing, Cambridge, 2013.

46. S. Giménez and J. Bisquert, *Photoelectrochemical Solar Fuel Production*, Springer, Switzerland, 2016.

Materials	Type of system	Oxidation co-catalyst	Reduction co-catalyst	Photoanode	Photocathode	Photovoltaic	Device Life time	Electrolyte	STH (%)	Ref
WO_3 //Si|-Pt	Photoanode/ photocathode	-	Pt	WO_3	Si	----	-	1M HCl	-	47
Co-Pi /$BiVO_4$// Cu_2O/ RuO_2	Photoanode/ photocathode	Co-Pi	RuO_2	$BiVO_4$	Cu_2O	----	2mins 20% current loss	$K_{3-x}H_xPo4$ buffer (pH=6)	0.5%	48
RuO_2/WO_3|2jn Si|-Pt	PV-PEC	RuO_2	Pt	WO_3	------	2jn S	----	0.33M H_3PO_4	3%	49
WO3-|DSSC|-Pt	PV-PEC	---	Pt	WO_3	-----	DSSC	8h	1M $HClO_4$	3.10%	50
Co-Pi|3jn-Si| NiMoZn	PV + electrolyser	Co-Pi	NiMoZn	----	-----	3jn-Si	3h	0.5MK-Bi +1.5M KNO_3	4.7%	51
NiB|3jn-Si|NiMoZn	PV + electrolyser	Ni-B	NiMoZn	----	-----	3 jn-Si	168 h	0.5MKB/0.5M K_2SO_4	9.8%	52

Pt|1jn-GaAs|1jn-GaInP_2|-Pt	PV + electrolyser	Pt	Pt	----	---	1jn-GaAs+1jn-GaInP_2	9h	2M KOH	16.5%	53
P-Si/SnO_2/Fe_2O_3- Pt	Heterojunction PEC	Pt		-----	pSi/SnO_2/Fe_2O_3 core /Shell/shell nanowire	---	2h	0.25M Na_2SO_4	-----	54
CoO_x/WO_3/C_3N_4/-Pt	Heterojunction PEC	CoO_x	Pt	WO_3+ C_3N_4	----	----	300s	0.01M Na_2SO4	0.11%	55

Table S1*: Overview of the reported efficient PEC cells and the corresponding performance*

Notation in column 1: (1) cocatalyst/photoelectrode// the other photoelectrode/the other cocatalyst; (2) cocatalyst/photoelectrode|PV cell|-couther electrode; (3) cocatalyst|PV cell|the other cocatalyst; (4) Co-catalysts/ seconductor1/semiconductor2/-counter electrode. Notation in column 7: “jn” stands for junction.

References for table S1:

47. R. H. Coridan, M. Shaner, C. Wiggenhorn, B. S. Brunschwig and N. S. Lewis, *The Journal of Physical Chemistry C*, 2013, **117**, 6949-6957.
48. P. Bornoz, F. F. Abdi, S. D. Tilley, B. Dam, R. Van De Krol, M. Graetzel and K. Sivula, *The Journal of Physical Chemistry C*, 2014, **118**, 16959-16966.
49. N. Gaillard, Y. Chang, J. Kaneshiro, A. Deangelis and E. Miller, Proceedings of SPIE at the University of Hawai, 2010, 7770.
50. J. Brillet, J.-H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, M. Graetzel and K. Sivula, *Nature Photonics*, 2012, **6**, 824-828.
51. S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers and D. G. Nocera, 2011, **334**,645-648.
52. C. R. Cox, J. Z. Lee, D. G. Nocera and T. Buonassisi, *Proceedings of the National Academy of Sciences*, 2014, **111**, 14057-14061.
53. O. Khaselev, A. Bansal and J. Turner, *International Journal of Hydrogen Energy*, 2001, **26**, 127-132.
54. A. Kargar, S. J. Kim, P. Allameh, C. Choi, N. Park, H. Jeong, Y. Pak, G. Y. Jung, X. Pan, D. Wang and S. Jin, *Advanced Functional Materials*, 2015, **25**, 2609-2615.
55. Y. Hou, F. Zuo, A. P. Dagg, J. Liu and P. Feng, *Advanced materials*, 2014,**26**, 5043-5049.

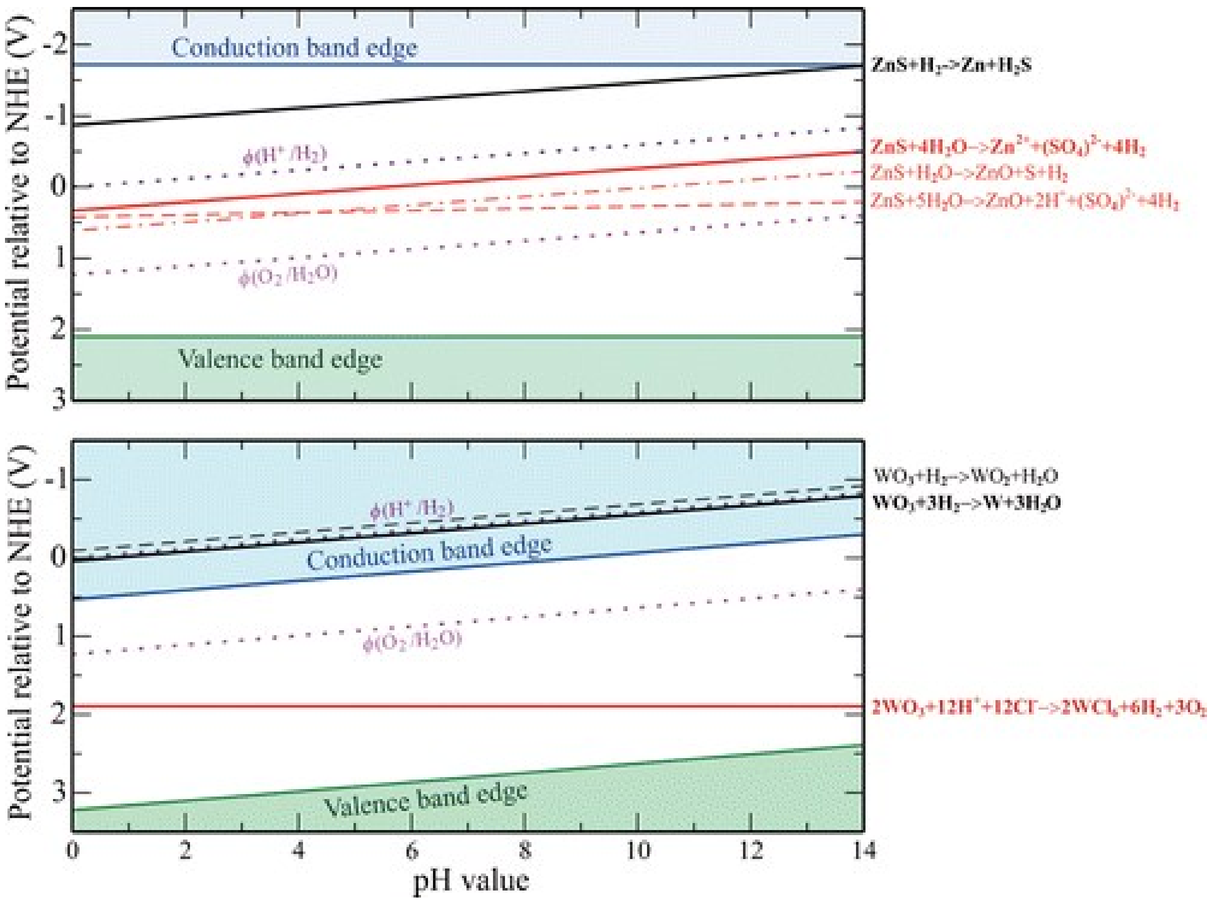

Figure S1: pH value dependence of the reduction and oxidation potentials of ZnS (top) and WO_3 (bottom), with the corresponding reactions labeled near the lines. The dependence of the water redox potentials and the band edges of ZnS and WO_3 are also plotted. The band edges of WO_3 follow the Nernstian relation with the pH value, while those of ZnS are assumed to be fixed as their dependence on pH value is more complicated. Reproduced from reference 54 with permission of the American Chemical Society.

References for figureS1:

56: S. Chen, L. Wang, *Chemistry of Materials*, 2012, **24**, 3659-3666.