Metal and F Dual-doping to Synchronously Improve Electronic Transport Rate and Lifetime for TiO_2 Photoanode to Enhance Dye-Sensitized Solar Cells Performances

Yandong Duan,‡[ab] Jiaxin Zheng,‡[a] Ming Xu,[a] Xiaohe Song,[a] Nianqing Fu,[bc] Yanyan Fang,[b] Xiaowen Zhou,[b] Yuan Lin*[ab] and Feng Pan *[a]

[a]School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, China

[b]Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[c]Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

† Electronic supplementary information (ESI) available. See DOI:

‡ Y. D. Duan and J. X. Zheng contributed equally to this work.

* Corresponding author: linyuan@iccas.ac.cn Tel: 86-10-82615031 Fax: 86-10-82617315
* Corresponding author: panfeng@pkusz.edu.cn Tel: 86-755-26033200

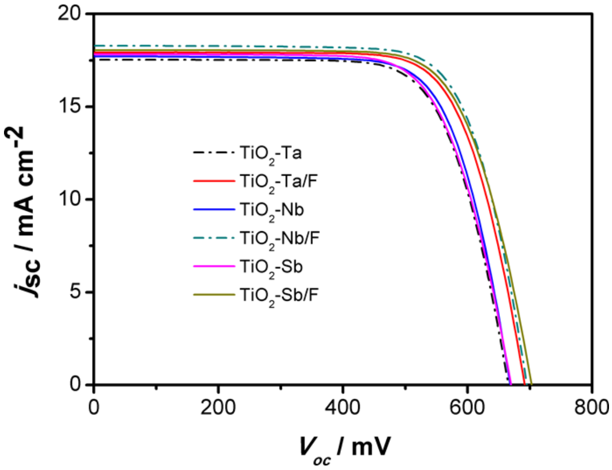

Fig. S1 Photocurrent-voltage characteristics of DSSCs based on the doped TiO_2 photoanodes under illumination AM1.5. ($(C_4H_9O)_5Ta$, $(C_4H_9O)_5Nb$, and $(CH_3CO_2)_3Sb$ are tantalum butoxide, niobium butoxide, and antimony triacetate, respectively. The optimized molar ratios of Ta, Nb and Sb to Ti were 1:100. The molar ratio of F to Ti in TiO_2-F, TiO_2-Ta/F, TiO_2-Nb/F, and TiO_2-Sb/F samples was 0.75:100.

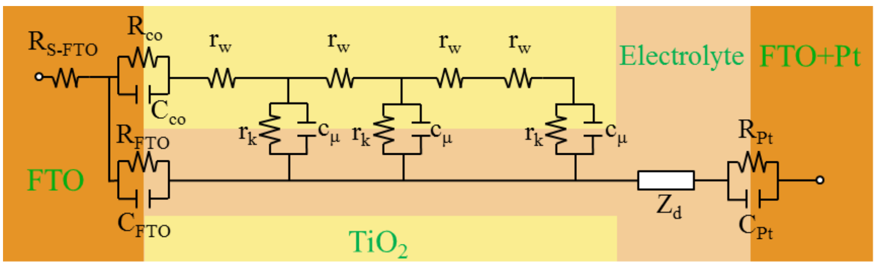

Fig. S2 The general transmission line model of DSSCs.

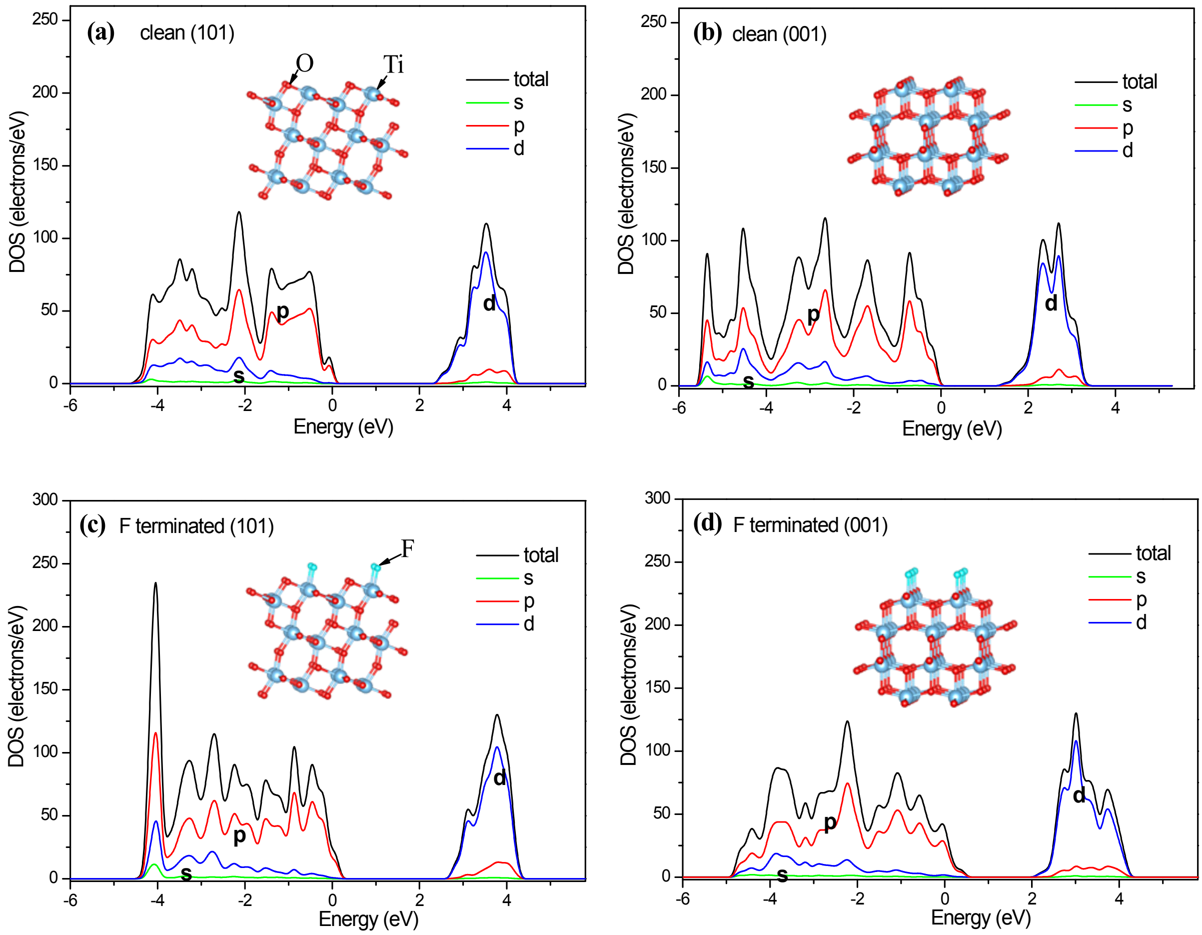

Fig. S3 Calculated total and partial density of states (DOS) for surfaces of anatase. (a) clean (101); (b) clean (001); (c) F terminated (101); (d) F terminated (001). The insets are the clean surface and F adsorbed surface models for anatase.

Table S1 Comparison of different doping element for TiO_2/SnO_2/ZnO and photovoltaic performance of the DSSCs based on these samples.

Ref.	Doping element	CB shift	Injection efficiency	Transport rate	Electron Lifetime	Dye loading	η (%)[a]
DSSCs based on doped-TiO_2 photoanode							
1	W^{6+}			↑	↓		6.64/7.42
2	W^{6+}	positive		↓	↑		3.37/4.2
3	W^{6+}			↑	↑	↑	4.14/8.71
4	Zn^{2+}			↑		↑	5.18/5.73
5	Mg^{2+}	positive	↑	↑		→	6.35/7.12
6	Mg^{2+}	negative		↑	↓		---
7	V^{5+}			↑	↓	↓	6.01/6.81
8	Ce^{4+}/Ce^{3+}	positive	↑			→	6.4/7.12
9	Sb^{3+}	positive	↑	↑		→	7.36/8.13
10	Ru^{3+}			↑			4.3/5.2
11	Ag+			↓	↑	↑	4.74/6.13
12	Zn^{2+}	negative		↑			6.7/7.6
13	Zn^{2+}				↑		0.58/4.63
14	Zn^{2+}	negative		↑	↓(1sun)		7.8/8.3
		negative		↑	↑(0.1sun)		6.2/7.6
15	Ta^{5+}				↑		4.8/6.7
16	Nb			↓	↑		2.40/3.21
17	Nb		↑	↑	↑		6.8/8.0
18	Nb	positive	↑	↑			6.6/7.8
19	Nb			↑	↑		---
20	Nb^{5+}		↑		↑	↑	7.4/8.1
21	Eu^{3+}	negative			↑		2.60/3.43
22	Cu^{2+}	negative			↑		5.8/8.1
23	Cr^{3+}	negative			↑		7.1/8.4
24	Zr^{4+}	negative					7.0/8.1
25	Ni	negative		↑	↑	↑	5.2/6.75
26	Li^{+}				↑		1.96/2.60
b	Sn^{4+}/F^{-}	negative		↑	↑	→	7.22/8.89
b	Ta^{5+}	positive		↑	↓	→	7.22/8.3
b	Ta^{5+}/F^{-}	positive		↑	↑	→	7.22/8.78
b	Nb^{5+}	positive		↑	↓	→	7.22/8.4
b	Nb^{5+}/F^{-}	positive		↑	↑	→	7.22/9.02
b	Sb^{3+}	positive	↑	↑	↓	→	7.22/8.36
b	Sb^{3+}/F^{-}	Positive		↑	↑	→	7.22/8.87
b	F-			↓	↑	→	7.22/8.31
25	B^{3+}	positive	↑		↑		3.02/3.44
26	S^{6+}	positive	↑	↑			5.56/6.91
27	F-			↑	↑	→	5.62/6.31

28	I^-				↑	↑	4.9/7.0
29	N		↑		↓		7.14/8.32
30	N					↑	7/8
31	Zr^{4+}/N			↑	↑	↑	9.6/12.62
32	N/F^-	positive	↑	↑	↑		6.71/8.20
DSSCs based on doped-SnO_2 photoanode							
33	Sb^{3+}			↑			2.8/3.5
34	Mg^{2+}			↑	↑	↑	0.85/2.03
35	Zn^{2+}	negative			↑	↑	1.13/4.15
36	Zn^{2+}			↑			---/3.00
37	N	negative			↑	↑	1.07/2.31
DSSCs based on doped-ZnO photoanode							
38	Eu^{3+}	positive	↑	↑	↓	↑	4.5/5.7
39	Mg^{2+}	negative		↑	↑		1.97/4.11
40	Al^{3+}		↑		↑		0.205/0.298
41	Sn^{4+}			↑		↑	1.49/1.82
42	B^{3+}				↑	↑	4.1/7.2
43	N^{3-}		↑		↑		0.67/2.64
44	N^{3-}					↑	2.2/5.0
45	I^-				↑		2.3/4.5
46	F-				↑	↑	1.04/3.43

[a]Photon-to-electron conversion efficiency of DSCs with pure TiO_2 and the doped TiO_2.

[b]Data in our work.

[c] ↑ , increase; ↓ , decrease; →, no change.

Table S2 Flat band potential (E_{fb}) and donor density (N_d) of TiO_2 and the doped TiO_2 films

Samples	E_{fb} / V vs. SCE	N_d ($\times 10^{19}$)/cm^{-3}
TiO_2	-0.530	0.93
TiO_2-Sn	-0.577	1.18
TiO_2-F	-0.515	0.90
TiO_2-Sn/F	-0.575	1.17

Table S3 Photovoltaic characteristics of the DSSCs based on TiO_2 and the doped TiO_2 photoanodes.

Samples	Doping sources	j_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)	Dye loading ($\times 10^{-7}$ mol cm^{-2})
	None	14.82±0.11	686±7	0.71±0.01	7.22±0.10	1.14±0.04
TiO_2-Ta	$(C_4H_9O)_5Ta$	17.53±0.10	667±6	0.71±0.01	8.30±0.10	1.14±0.05
TiO_2-Ta/F	$(C_4H_9O)_5Ta+TiF_4$	17.92±0.10	690±6	0.71±0.01	8.78±0.12	1.10±0.05
TiO_2-Nb	$(C_4H_9O)_5Nb$	17.71±0.12	668±7	0.71±0.00	8.40±0.12	1.13±0.05
TiO_2-Nb/F	$(C_4H_9O)_5Nb+TiF_4$	18.28±0.12	695±7	0.71±0.01	9.02±0.11	1.16±0.04
TiO_2-Sb	$(CH_3CO_2)_3Sb$	17.82±0.11	670±5	0.70±0.02	8.36±0.11	1.15±0.03
TiO_2-Sb/F	$(C_4H_9O)_5Nb+TiF_4$	18.05±0.14	702±7	0.70±0.02	8.87±0.15	1.12±0.04
TiO_2-F	TiF_4	16.67±0.11	702±5	0.71±0.01	8.31±0.11	1.16±0.04

References

1. Z. Tong, T. Peng, W. Sun, W. Liu, S. Guo and X. Z. Zhao, *J. Phys. Chem. C*, 2014, **118**, 16892-16895.
2. X. Zhang, F. Liu, Q. L. Huang, G. Zhou and Z. S. Wang, *J. Phys. Chem. C*, 2007, **115**, 12665-12671.
3. P. S. Archana, A. Gupta, M. M. Yusoff and R. Jose, *Phys. Chem. Chem. Phys.*, 2014, **16**, 7448-7454.
4. A. H. G. Niaki, A. M. Bakhshayesh and M. R. Mohammadi, *Sol. Energy*, 2014, **103**, 210-222.
5. Q. Liu, *Electrochimi. Acta*, 2014, **129**, 459-462.
6. C. N. Zhang, S. Chen, L. e. Mo, Y. Huang, H. Tian, L. Hu, Z. Huo, F. Kong, S. Dai and X. Pan, *J. Phys. Chem. C*, 2011, 16418-16424.
7. H. Seo, Y. Wang, D. Ichida, G. Uchida, N. Itagaki, K. Koga, M. Shiratani, S. H. Nam and J. H. Boo, *Jpn. J. Appl. Phys.*, 2013, **52**, 11NM02.
8. J. Zhang, W. Q. Peng, Z. H. Chen, H. Chen and L. Y. Han, *J. Phys. Chem. C*, 2012, **116**, 19182-19190.
9. M. Wang, S. L. Bai, A. F. Chen, Y. D. Duan, Q. P. Liu, D. Q. Li and Y. Lin, *Electrochimica Acta*, 2012, **77**, 54-59.
10. S. G. So, K. Lee and P. Schmuki, *Phys. Status Solidi-R*, 2012, **6**, 169-171.
11. E. M. Jin, X. G. Zhao, J. Y. Park and H. B. Gu, *Nanoscale Res. Lett.*, 2012, **7**, 97.
12. F. Z. Huang, Q. Li, G. J. Thorogood, Y. B. Cheng and R. A. Caruso, *J. Mater. Chem.*, 2012, **22**,

17128-17132.

13. Y. Zhang, L. L. Wang, B. K. Liu, J. L. Zhai, H. M. Fan, D. J. Wang, Y. H. Lin and T. F. Xie, *Electrochimica Acta*, 2011, **56**, 6517-6523.
14. K. P. Wang and H. Teng, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9489-9496.
15. R. Ghosh, Y. Hara, L. Aibabaei, K. Hanson, S. Rangan, R. Bartynski, T. J. Meyer and R. Lopez, *ACS Appl. Mater. Inter.*, 2012, **4**, 4566-4570.
16. M. Yang, D. Kim, H. Jha, K. Lee, J. Paul and P. Schmuki, *Chem. Commun.*, 2011, **47**, 2032-2034.
17. T. Nikolay, L. Larina, O. Shevaleevskiy and B. T. Ahn, *Energy Environ. Sci.*, 2011, **4**, 1480-1486.
18. X. Lü, X. Mou, J. Wu, D. Zhang, L. Zhang, F. Huang, F. Xu and S. Huang, *Adv. Funct. Mater.*, 2010, **20**, 509-515.
19. P. S. Archana, R. Jose, M. M. Yusoff and S. Ramakrishna, *Appl. Phys. Lett.*, 2011, **98**.
20. A. K. Chandiran, F. d. r. Sauvage, M. Casas-Cabanas, P. Comte, S. M. Zakeeruddin and M. Graetzel, *J. Phys. Chem. C*, 2010, **114**, 15849-15856.
21. J. H. Huang, P. Y. Hung, S. F. Hu and R. S. Liu, *J. Mater. Chem.*, 2010, **20**, 6505-6511.
22. T. R. C. K. Wijayarathna, G. M. L. P. Aponsu, Y. P. Y. P. Ariyasinghe, E. V. A. Premalal, G. K. R. Kumara and K. Tennakone, *Nanotechnology*, 2008, **19**, -.
23. C. Kim, K. S. Kim, H. Y. Kim and Y. S. Han, *J. Mater. Chem.*, 2008, **18**, 5809-5814.
24. M. Dürr, S. Rosselli, A. Yasuda and G. Nelles, *J. Phys. Chem. B*, 2006, **110**, 21899-21902.
25. A. Subramanian and H. W. Wang, *Appl. Surf. Sci.*, 2012, **258**, 6479-6484.
26. Q. Sun, J. Zhang, P. Q. Wang, J. Zheng, X. N. Zhang, Y. Z. Cui, J. W. Feng and Y. J. Zhu, *J. Renew Sustain Ener.*, 2012, **4**, 023104.
27. L. Song, H. Bin Yang, X. Wang, S. Y. Khoo, C. C. Wong, X. W. Liu and C. M. Li, *ACS Appl. Mater. Inter.*, 2012, **4**, 3712-3717.
28. Q. Q. Hou, Y. Z. Zheng, J. F. Chen, W. L. Zhou, J. Deng and X. Tao, *J. Mater. Chem.*, 2011, **21**, 3877-3883.
29. W. Guo, Y. Shen, G. Boschloo, A. Hagfeldt and T. Ma, *Electrochim. Acta*, 2011, **56**, 4611-4617.
30. T. Ma, M. Akiyama, E. Abe and I. Imai, *Nano lett.*, 2005, **5**, 2543-2547.
31. J. Y. Park, K. H. Lee, B. S. Kim, C. S. Kim, S. E. Lee, K. Okuyama, H. D. Jang and T. O. Kim, *Rsc Adv.*, 2014, **4**, 9946-9952.
32. J. Yu, Y. Yang, R. Fan, L. Li and X. Li, *J. Phys. Chem. C*, 2014, **118**, 8795-8802.

33. J. P. Correa Baena and A. G. Agrios, *J. Phys. Chem. C*, 2014. **118**, 17028-17035.

34. H. C. Pang, H. B. Yang, C. X. Guo and C. M. Li, *ACS Appl. Mater. Inter.*, 2012, **4**, 6261-6265.

35. Z. D. Li, Y. Zhou, T. Yu, J. G. Liu and Z. G. Zou, *Crystengcomm*, 2012, **14**, 6462-6468.

36. X. C. Dou, D. Sabba, N. Mathews, L. H. Wong, Y. M. Lam and S. Mhaisalkar, *Chem. Mater.*, 2011, **23**, 3938-3945.

37. Z. D. Li, Y. Zhou, J. C. Song, T. Yu, J. G. Liu and Z. G. Zou, *J. Mater. Chem. A*, 2013, **1**, 524-531.

38. J. X. Zhao, X. H. Lu, Y. Z. Zheng, S. Q. Bi, X. Tao, J. F. Chen and W. Zhou, *Electrochem. Commun.*, 2013, **32**, 14-17.

39. C. J. Raj, K. Prabakar, S. N. Karthick, K. V. Hemalatha, M.-K. Son and H. J. Kim, *J. Phys. Chem. C*, 2013, **117**, 2600-2607.

40. R. B. Tao, T. Tomita, R. A. Wong and K. Waki, *J. Power Sources*, 2012, **214**, 159-165.

41. S. Ameen, M. S. Akhtar, H. K. Seo, Y. S. Kim and H. S. Shin, *Chem. Eng. J.*, 2012, **187**, 351-356.

42. K. Mahmood and H. J. Sung, *J. Mater. Chem. A*, 2014, **2**, 5408-5417.

43. L. Y. Zhang, Y. L. Yang, R. Q. Fan, H. Y. Chen, R. K. Jia, Y. H. Wang, L. Q. Ma and Y. Z. Wang, *Mater. Sci. Eng. B-Adv.*, 2012, **177**, 956-961.

44. K. Mahmood, B. S. Swain, G. S. Han, B.-J. Kim and H. S. Jung, *ACS Appl. Mater. Inter.*, 2014, **6**, 10028-10043.

45. Y. Z. Zheng, X. Tao, Q. A. Hou, D. T. Wang, W. L. Zhou and J. F. Chen, *Chem. Mater.*, 2011, **23**, 3-5.

46. L. J. Luo, W. Tao, X. Y. Hu, T. Xiao, B. J. Heng, W. Huang, H. Wang, H. W. Han, Q. K. Jiang, J. B. Wang and Y. W. Tang, *J. Power Sources*, 2011, **196**, 10518-10525.