Electronic Supplementary Information

Adsorption Driven Formate Reforming into Hydride and Tandem Hydrogenation of Nitrophenol to Amine over PdO_x Catalysts

Xiaohui Zhu [a,b], Shipan Liang[b], Shuang Chen[b], Xiangdong Liu*[a,b] and Renhong Li*[a,b]

[a]*College of Textile Science and Engineering (International Institute of Silk), Zhejiang Sci-Tech University, Hangzhou, Zhejiang Province (China).*
[b]*School of Materials Science & Engineering, Zhejiang Sci-Tech University, Hangzhou, Zhejiang Province (China)*

**Corresponding author:*

E-mail: lirenhong@zstu.edu.cn (R.H. Li); liuxd2007@yeah.net (X.D.Liu)

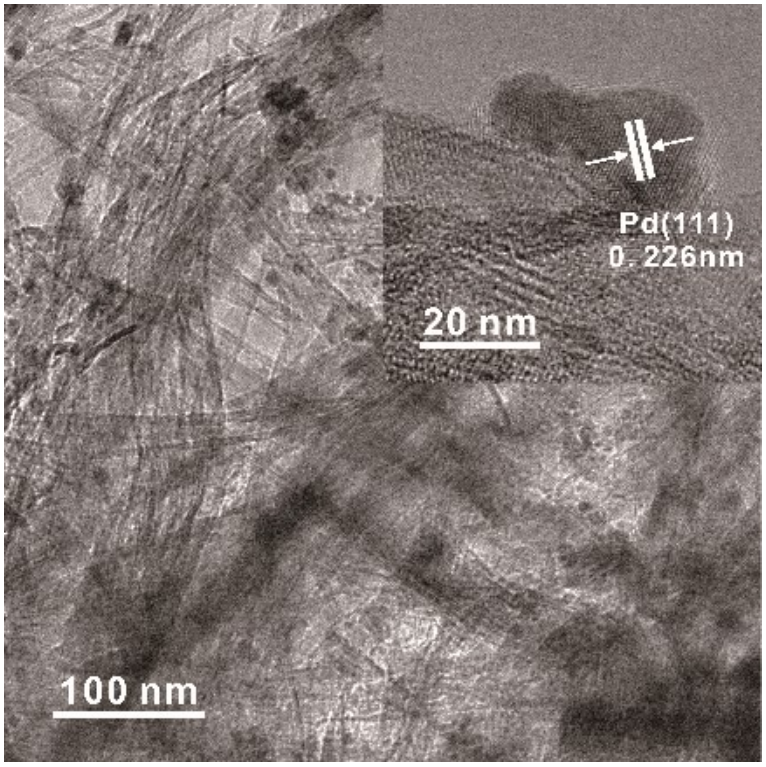

Figure S1 TEM image of 1.0 wt% Pd/TiNTs sample calcined under N_2 (inset shows the HR-TEM image of a single Pd NP).

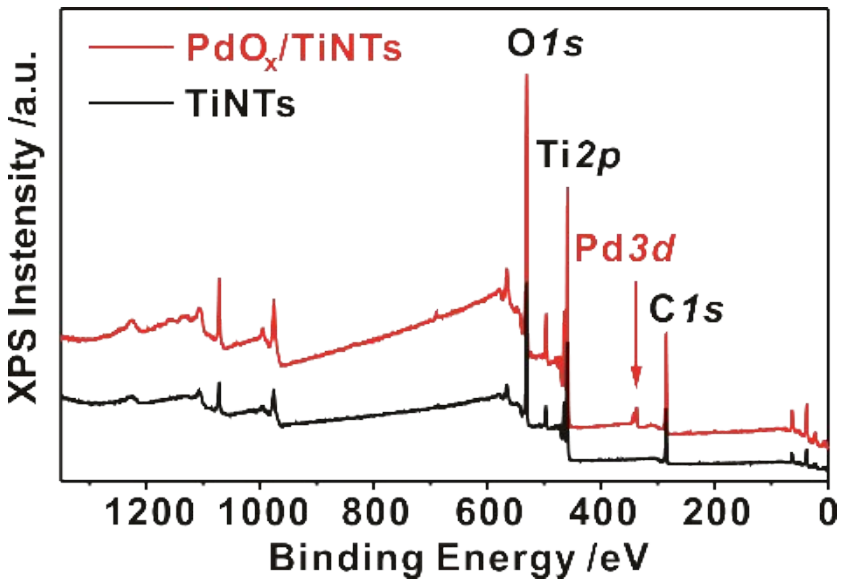

Figure S2 Full XPS spectral of PdO_x/TiNTs and TiNTs.

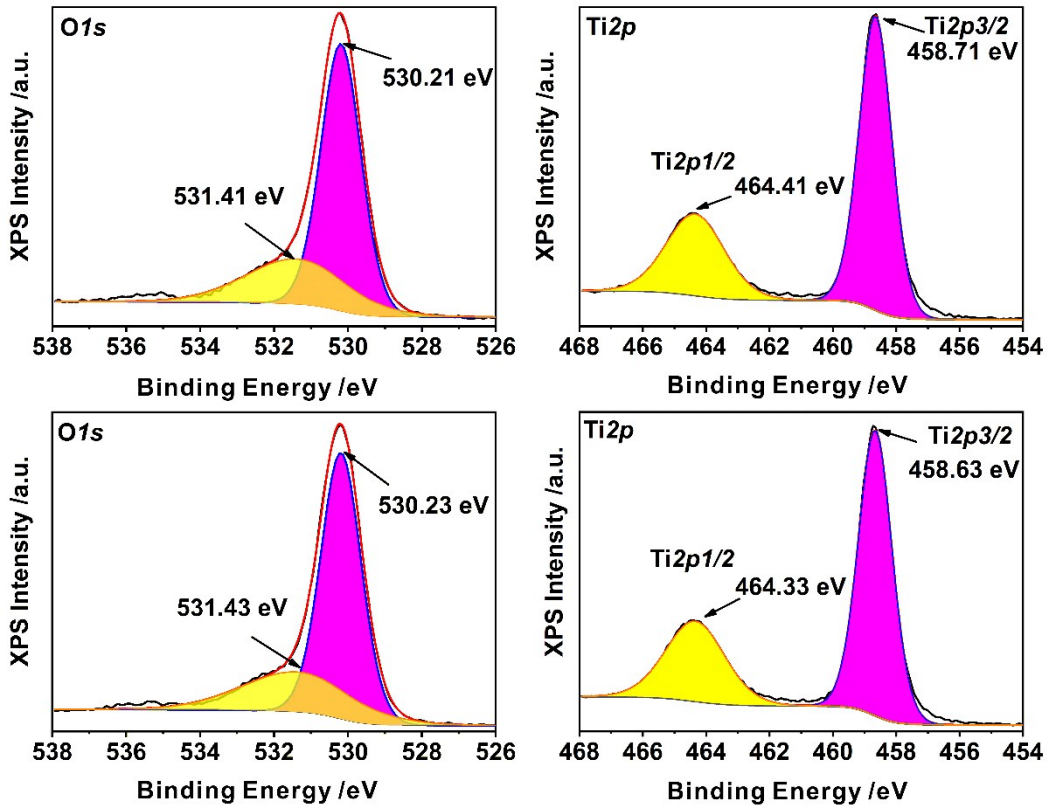

Figure S3 High resolution Ti*2p* and O*1s* XPS spectra of 1.0 wt% Pd/TiNTs samples calcined under N_2 or O_2.

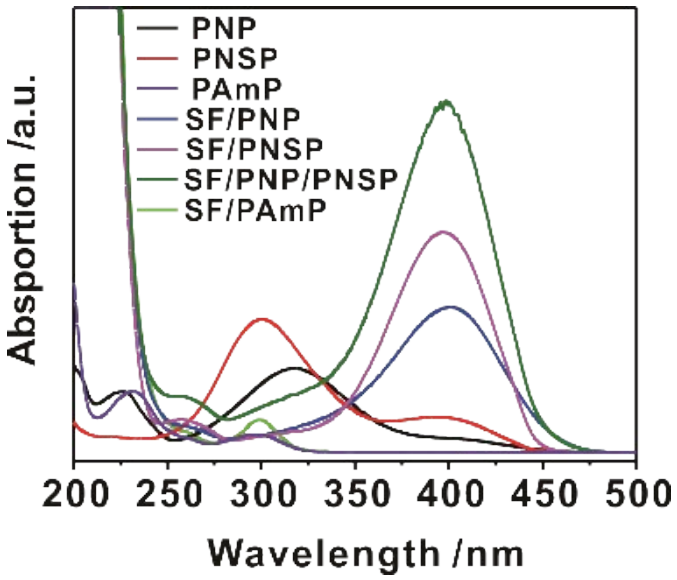

Figure S4 UV-Vis spectra of different solution.

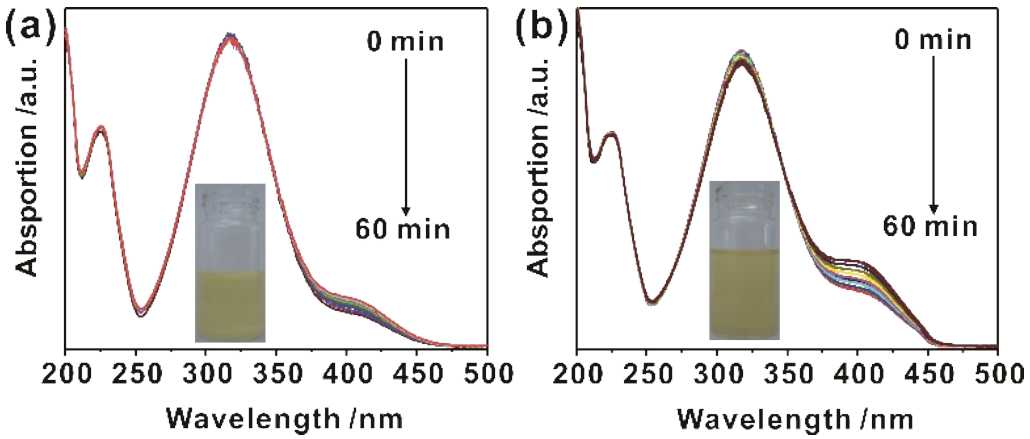

Figure S5 UV-Vis spectral of PNP reduction reaction in the absence of SF: (a) pure TiNTs and (b) PdO_x/TiNTs.

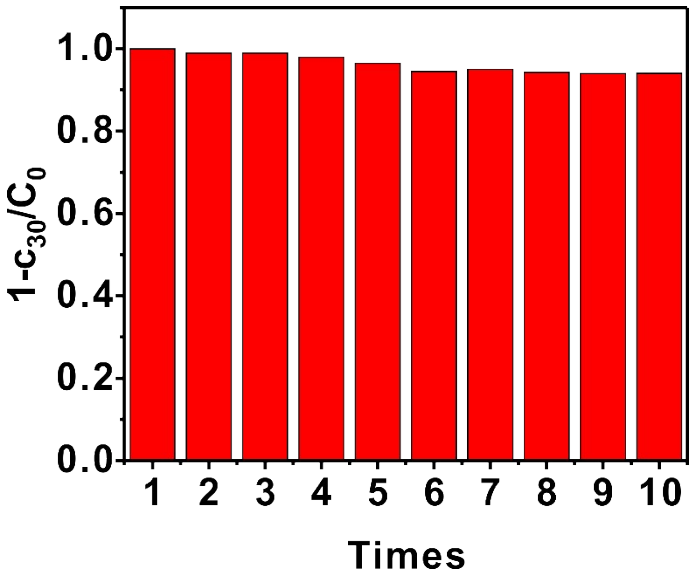

Figure S6 Recycle experiments of PdO_x/TiNTs. C_0 and C_{30} indicate the concentration of PNP solution at 0 and 30 min, respectively.

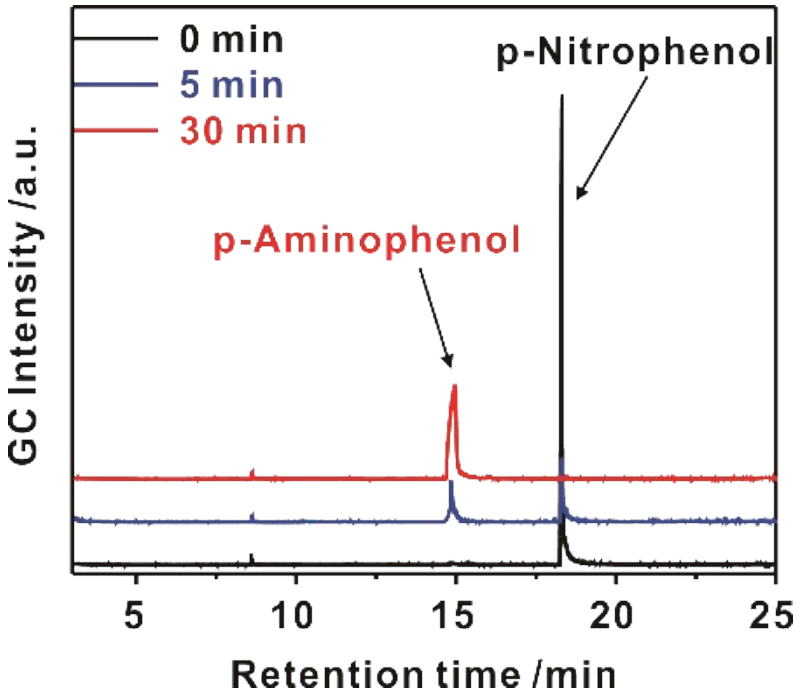

Figure S7 GC spectra of PNP reduction reaction at 0, 5, and 30 min. Extractive solvent: ethyl acetate.

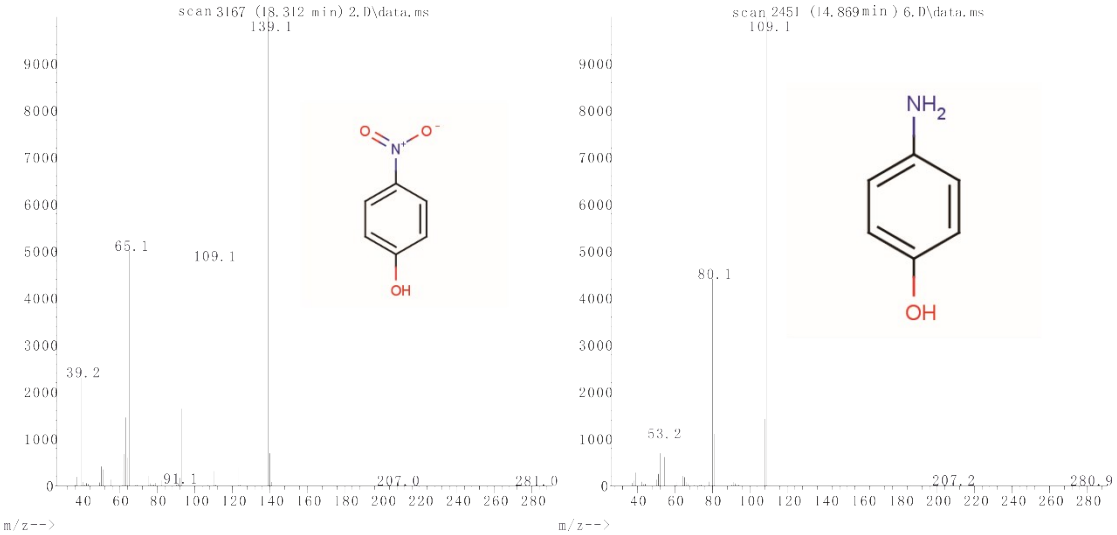

Figure S8 GC-MS spectra of the corresponding GC retention time positions shown in Figure S7.

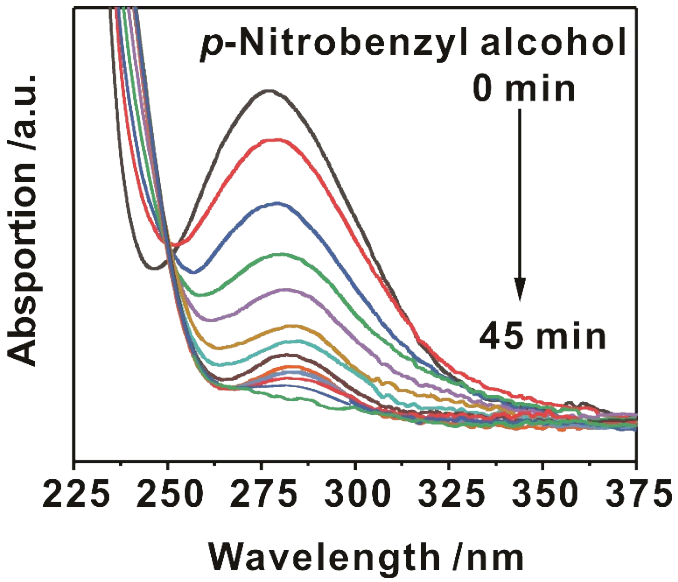

Figure S9 UV-Vis spectra of *p*-nitrobenzyl alcohol as a function of reaction time.

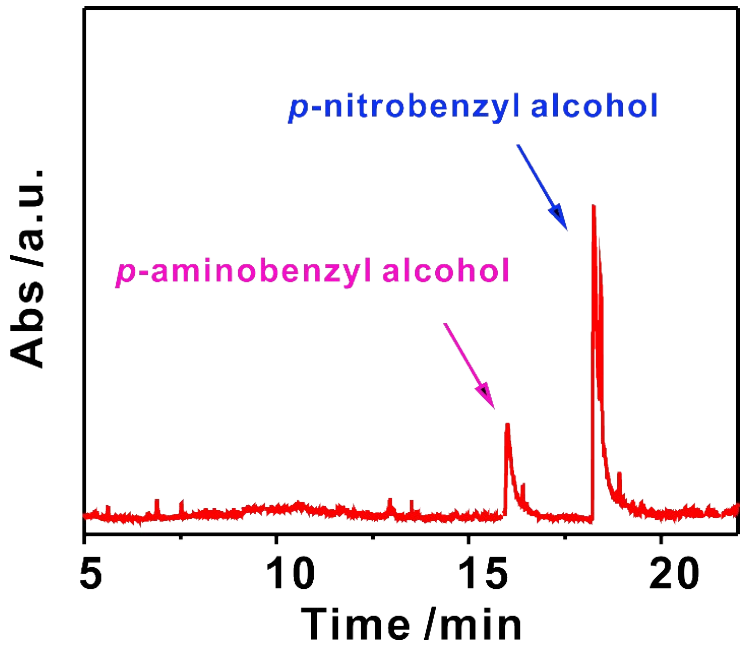

Figure S10 GC spectra of *p*-nitrobenzyl alcohol after 5 min reaction. Extractive solvent: ethyl acetate.

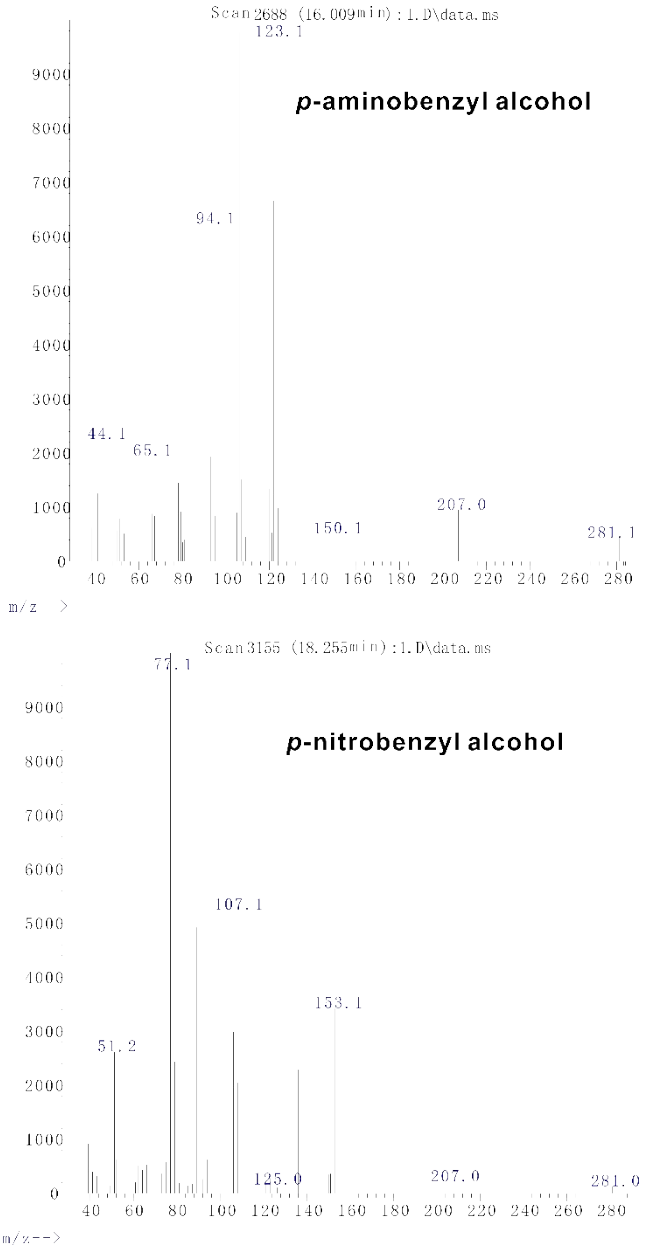

Figure S11 GC-MS spectra of GC retention time positions shown in Figure S10.

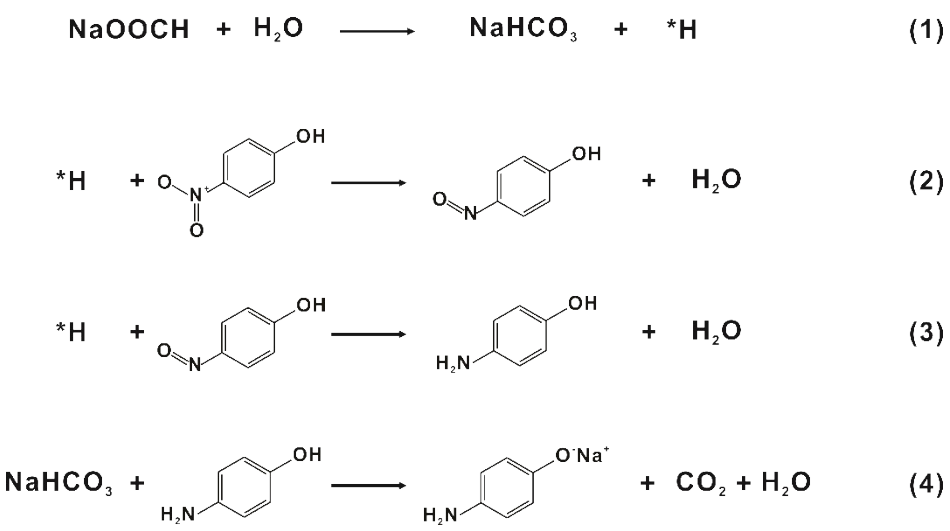

Figure S12 Schematic diagram of PdO_x/TiNTs catalyze PNP in the presence of SF under ambition conditions.

Table S1 Comparison of the catalyst properties during reduction PNP to PAmP under ambient conditions.

Entry	Catalysts	Hydrogen source	Temperature (°C)	TOF (h^{-1})	Selectivity (%)	Rference
1	PdO_x/TiNTs	NaOOCH	25	45.6	~100	This work
2	Pd/TiNTs	NaOOCH	25	17.4	~100	
3	7% Ca/Co_3O_4	$NaBH_4$	35	0.66	-	Ref. 1[1]
4[a]	$Pt_{55}Pd_{38}Bi_7$	$NaBH_4$	20	1.92	-	Ref. 2[2]
5[a]	$Ni_{70}Pd_{30}$	N_2H_2 H_2O	25	4.98	~99	Ref.3 [3]
6	Cu NCs[b]	$NaBH_4$	40	3.6	-	Ref. 4[4]
7	N-NG[c]	$NaBH_4$	25	0.9	~100	Ref. 5[5]

a. Calculation based on Pd,

b. Cu NCs: faceted copper nanocrystals,

c. N-doped graphene.

Table S2 Acidity (Ka) and acidity coefficient (p*k*a) of different standard solutions.

Entry	K_a	pk_a
1	NaOOCH	7.0-8.5 (0.1 M)
2	$NaHCO_3$	10.321
3	PNP	7.15
4	PAmP	5.48

References

1. B. M. Mogudi, P. Ncube, N. Bingwa, et al., *Appl. Catal. B-Environ.*, 2017, **218**, 240-248.
2. Y.-Y. Shen, Y. Sun, L.-N. Zhou, et al., *Journal of Materials Chemistry A*, 2014, **2**, 2977-2984.
3. D. Bhattacharjee, K. Mandal and S. Dasgupta, *RSC Advances*, 2016, **6**, 64364-64373.
4. P. Zhang, Y. Sui, G. Xiao, et al., *J. Mater. Chem. A*, 2013, **1**, 1632-1638.
5. X.-k. Kong, Z.-y. Sun, M. Chen, et al., *Energy & Environmental Science*, 2013, **6**, 3260-3266.