Supplementary Information for

Assembling of Bi Atoms on TiO_2 Nanorods Boosts Photoelectrochemical Water Splitting of Semiconductor

Yajun Pang[a, b,⊥], Wenjie Zang[b,⊥], Zongkui Kou[b, *], Lei Zhang[b], Guangqing Xu[a, c, *], Jun Lv[a, c], Xiaorui Gao[b], Zhenghui Pan[b], John Wang[b, *], Yucheng Wu[a, c]

[a] School of Materials Science and Engineering, and Key Laboratory of Advanced Functional Materials and Devices of Anhui Province, Hefei University of Technology, Hefei 230009, China.

[b] Department of Materials Science and Engineering, National University of Singapore, Singapore 117574, Singapore.

[c] China International S&T Cooperation Base for Advanced Energy and Environmental Materials, Hefei 230009, China

*Corresponding authors

E-mail: msekz@nus.edu.sg (Z. Kou); gqxu1979@hfut.edu.cn (G. Xu); msewangj@nus.edu.sg (J. Wang).

[⊥]These authors contributed equally to this work.

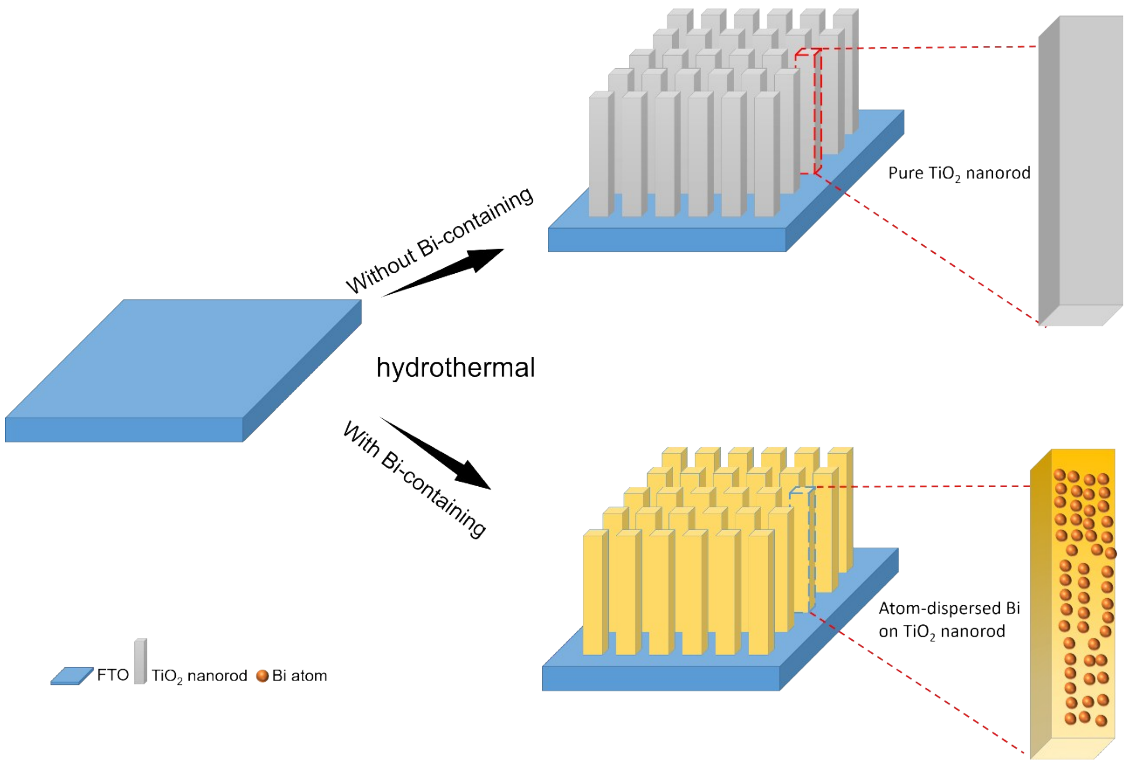

Figure S1. Schematic showing the formation of pure TiO_2 and atom-dispersed Bi on TiO_2 nanorods.

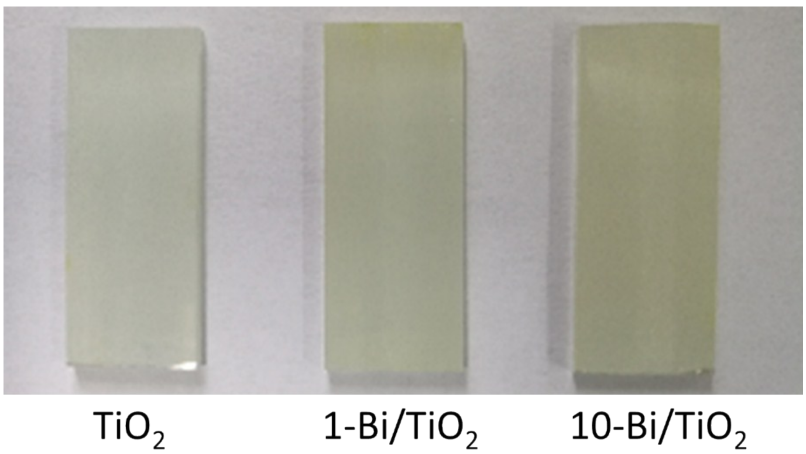

Figure S2. Optical photos of TiO_2, 1-Bi/TiO_2, and 10-Bi/TiO_2.

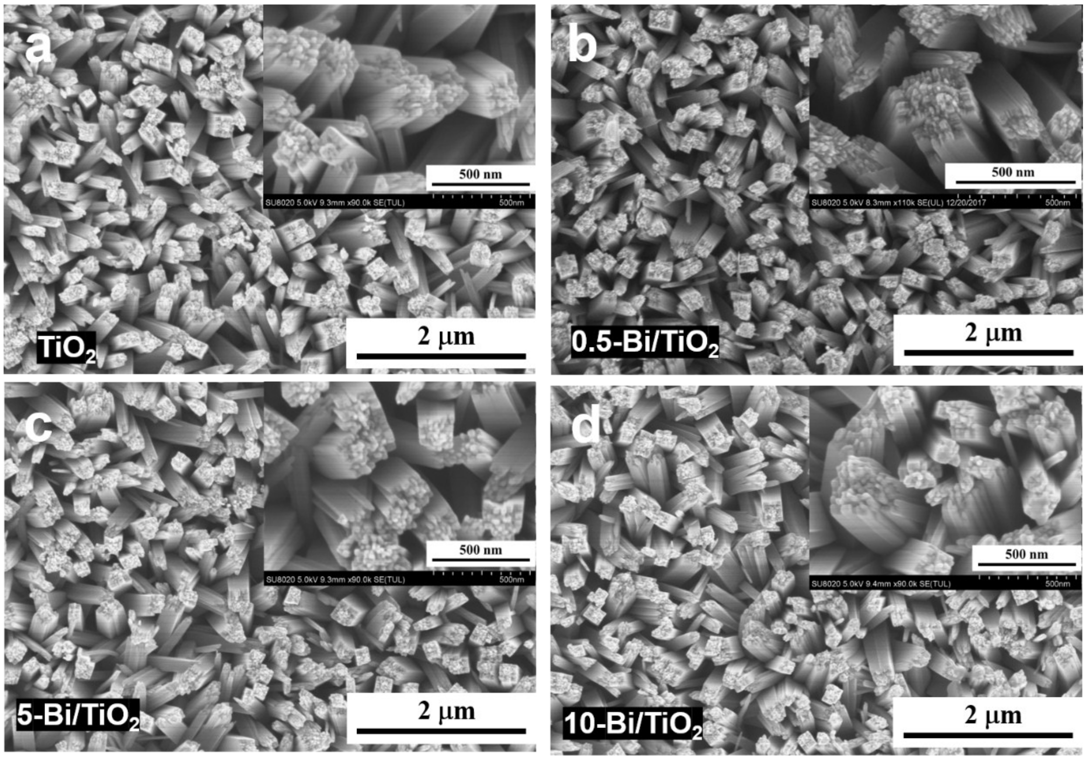

Figure S3. Additional SEM images as-prepared (a) TiO_2, (b) 0.5-Bi/TiO_2, (c) 5-Bi/TiO_2, and (d) 10-Bi/TiO_2, respectively.

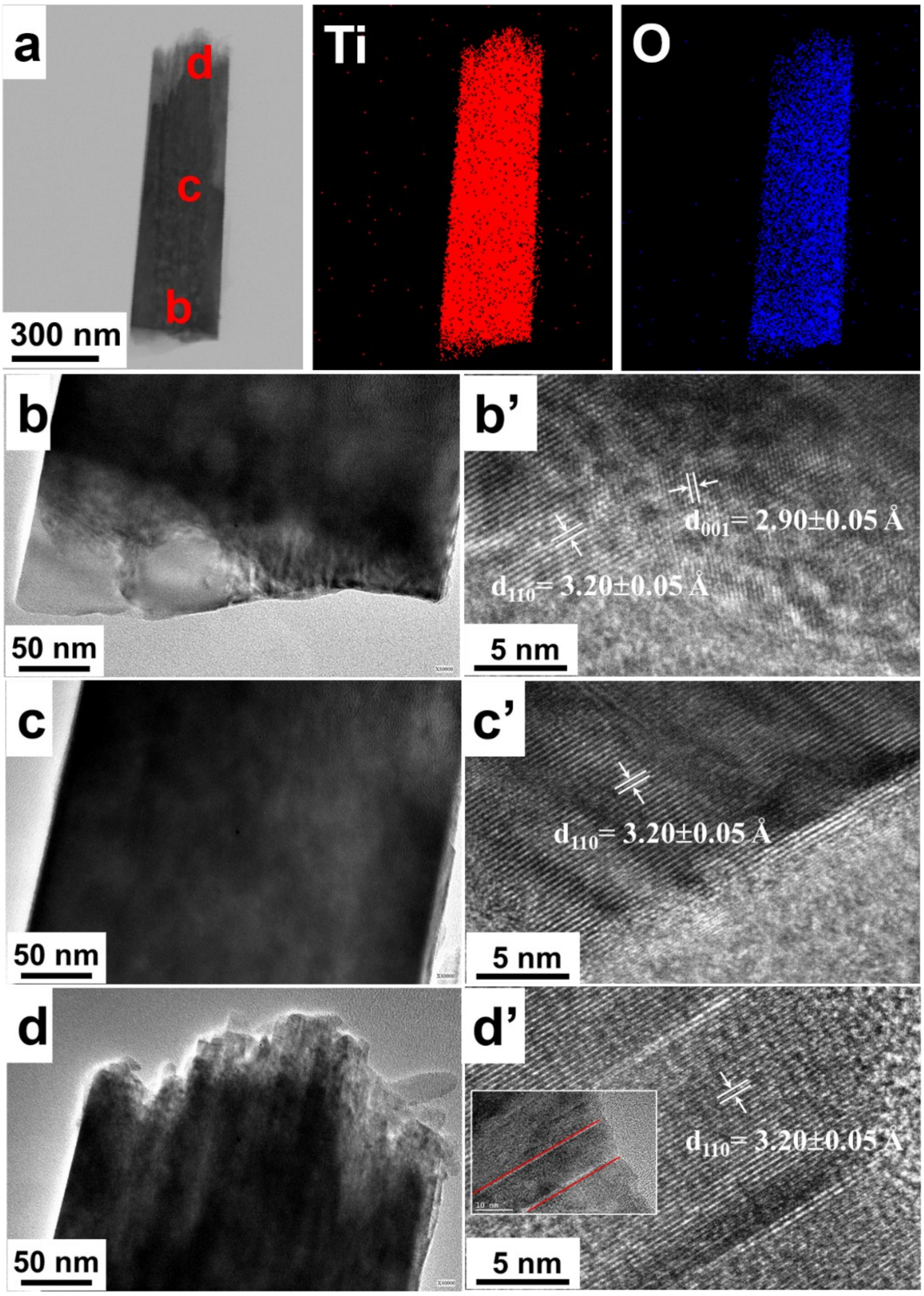

Figure S4. (a) TEM image and corresponding elemental mappings of Ti, and O in Bi/TiO_2 nanorods; (b-d) additional HR-TEM images of Bi/TiO_2 sample.

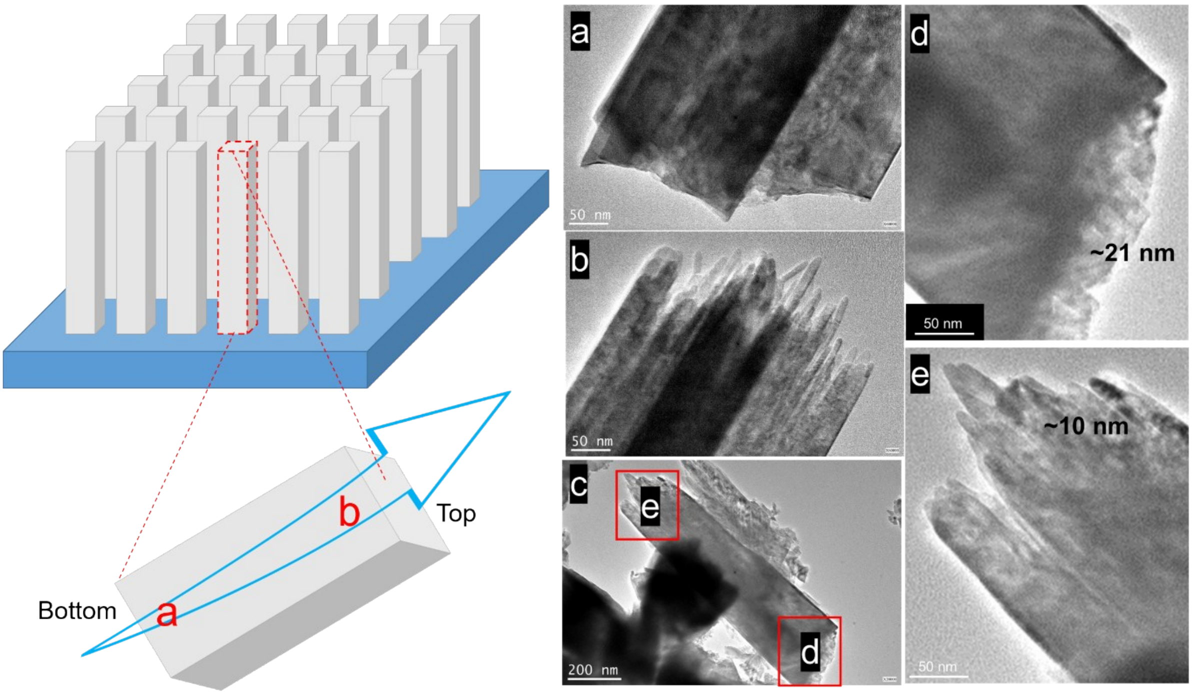

Figure S5. Schematic diagram and HR-TEM images of pristine TiO_2 for understanding gradient distribution for Bi/TiO_2.

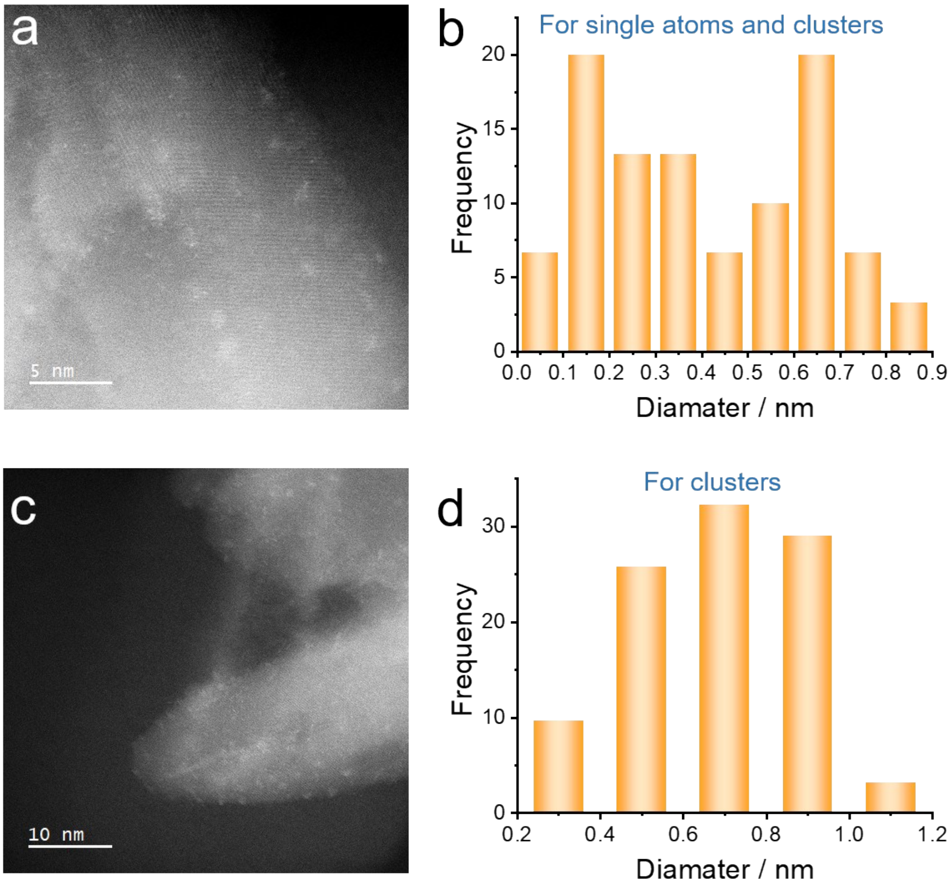

Figure S6. Size distribution of Bi atoms and cluster on Bi/TiO_2 NRs.

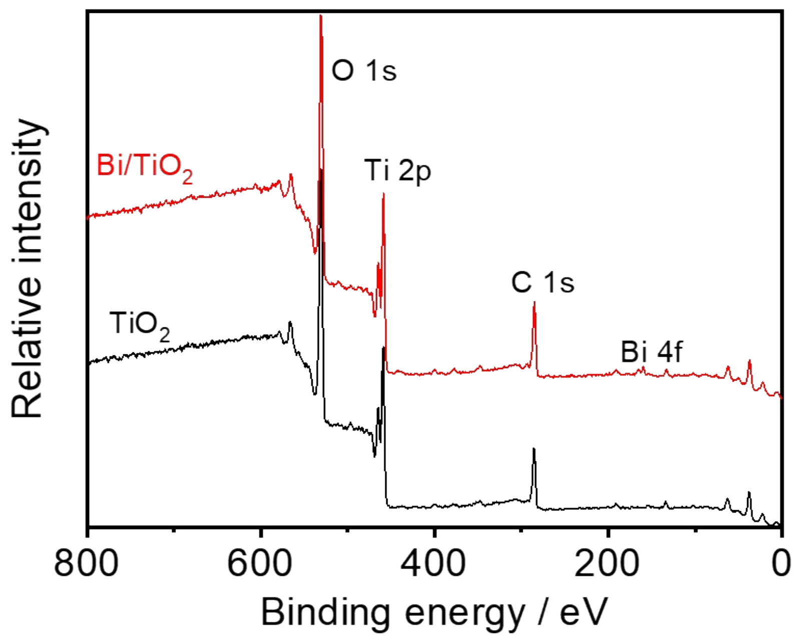

Figure S7. Broad scan XPS patterns of TiO_2 and 1-Bi-TiO_2.

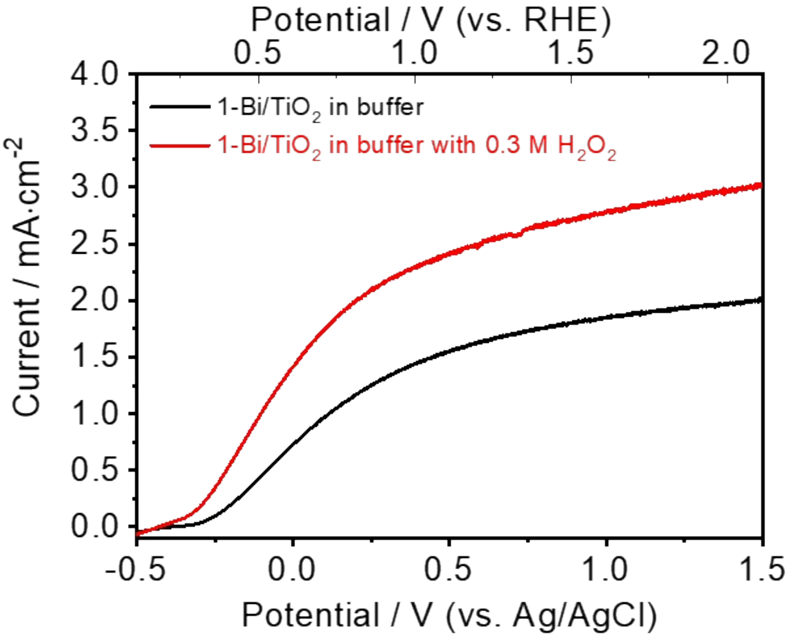

Figure S8. Linear sweep voltammogram (LSV) measurements of 1-Bi/TiO_2 NRs electrode in buffer solution without and with 0.3 M H_2O_2.

Table S1. A comparison study between this work and previously reported active TiO_2 NRs-based photoanodes toward PEC water splitting.

Photoanode material	Current intensity	Reference
TiO_2 nanorod@nanobowl arrays	1.24 mA cm^{-2} at 1.23 V_{RHE}	[1]
Au/TiO_2 NR photonic crystals	1.65 mA cm^{-2} at 1.23 V_{RHE}	[2]
TiO_2/BTO core/shell nanowire	1.30 mA cm^{-2} at 1.23 V_{RHE}	[3]
TiO_2/CdS/Co-Pi nanowire array	0.78 mA cm^{-2} at 0 $V_{Ag/AgCl}$	[4]
TiO_2-STO core-shell nanowire	1.43 mA cm^{-2} at 1.23 V_{RHE}	[5]
A-V-Si: TiO_2 nanorod	0.83 mA cm^{-2} at 1.23 V_{RHE}	[6]
C/N-TiO_2	~1 mA cm^{-2} at 1.23 V_{RHE}	[7]
TiO_2@$Ta_2O_xN_y$	1.32 mA cm^{-2} at 1.23 V_{RHE}	[8]
NH_2-MIL-125(Ti)/TiO_2 nanorod	1.63 mA cm^{-2} at 1.23 V_{RHE}	[9]
$BiFeO_3$/Sn:TiO_2 nanorod	~1.5 mA cm^{-2} at 1.23 V_{RHE}	[10]
TNCuPc/TiO_2	~1.10 mA cm^{-2} at 1.23 V_{RHE}	[11]
Bi/TiO_2 nanorod	1.65 mA cm^{-2} at 1.23 V_{RHE}	This work

References

[1] W. Wang, J. Dong, X. Ye, Y. Li, Y. Ma and L. Qi, *Small* 2016, **12**, 1469.

[2] X. Zhang, Y. Liu, S. T. Lee, S. Yang and Z. Kang, *Energy Environ. Sci.* 2014, **7**, 1409.

[3] W. Yang, Y. Yu, M. B. Starr, X. Yin, Z. Li, A. Kvit, S. Wang, P. Zhao and X. Wang, *Nano Lett.* 2015, **15**, 7574.

[4] G. Ai, H. Li, S. Liu, R. Mo and J. Zhong, *Adv. Funct. Mater.* 2015, **25**, 5706.

[5] F. Wu, Y. Yu, H. Yang, L. N. German, Z. Li, J. Chen, W. Yang, L. Huang, W. Shi, L. Wang and X. Wang, *Adv. Mater.* 2017, **29**, 1701432.

[6] C. Chen, Y. Wei, G. Yuan, Q. Liu, R. Lu, X. Huang, Y. Cao and P. Zhu, *Adv. Funct. Mater.* 2017, **27**, 1701575.

[7] X. Song, W. Li, D. He, H. Wu, Z. Ke, C. Jiang, G. Wang and X. Xiao, *Adv. Energy Mater.* 2018, **8**, 1800165.

[8] H. Zhang, L. Ma, J. Ming, B. Liu, Y. Zhao, Y. Hou, Z. Ding, C. Xu, Z. Zhang and J. Long, *Appl. Catal., B* 2019, **243**, 481.

[9] J. Yoon, D. Kim, J. Kim, H. Jangand J. Lee, *Appl. Catal., B* 2019, **244**, 511.

[10] J. Huang, Y. Wang, X. Liu, Y. Li, X. Hu, B. He, Z. Shu, Z. Li and Y. Zhao, *Nano Energy* 2019, **59**, 33.

[11] X. Li, T. Zhang, Y. Chen, Y. Fu, J. Su and L. Guo, *Chem. Eng. J.* 2020, **382**, 122783.