

Supporting Information:

Intermetallic PdZn Nanoparticles Loaded on Deficient TiO₂ Nanosheet as Support: A Bifunctional Electrocatalyst for Oxygen Reduction in PEMFC and Glycerol Oxidation Reactions

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Table S1

Comparison of electrochemical performances of the different electrocatalysts

Table S2

Comparison for the fuel cell performance and its power densities of different cathode materials

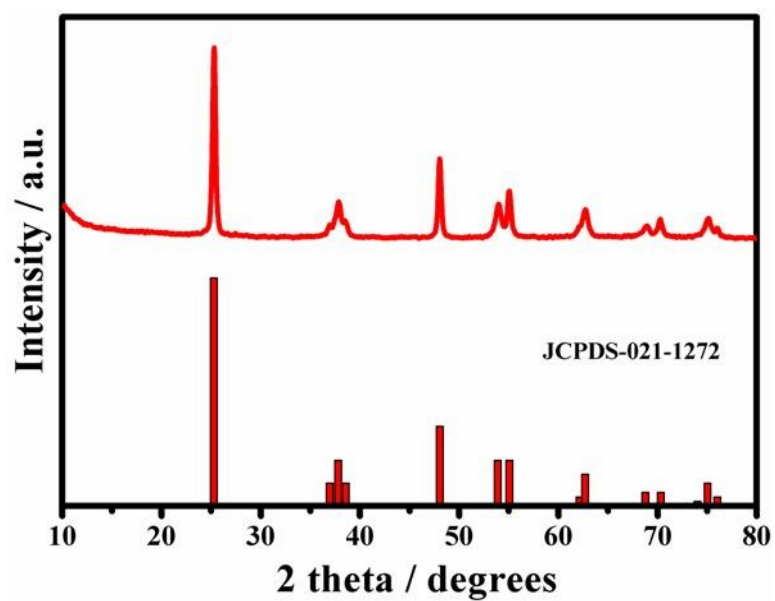


Fig. S1. XRD pattern and its standard pattern of TiO₂ NS (JCPDS-021-1272).

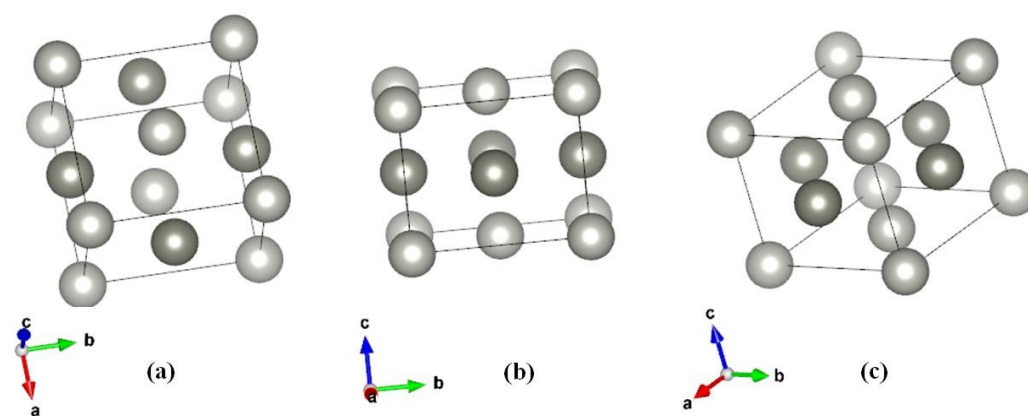


Fig. S2. Crystal structure of PdZn at different angles.

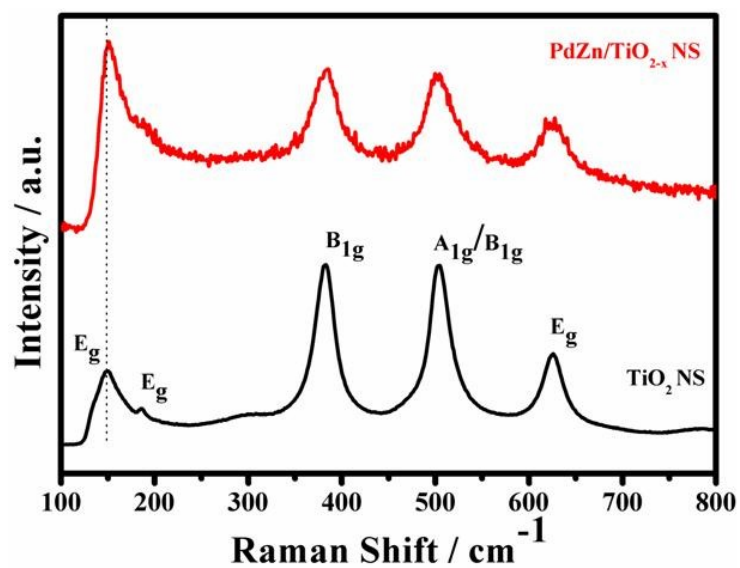


Fig. S3. Raman spectra of TiO_2 NS and PdZn/TiO_{2-x} NS.

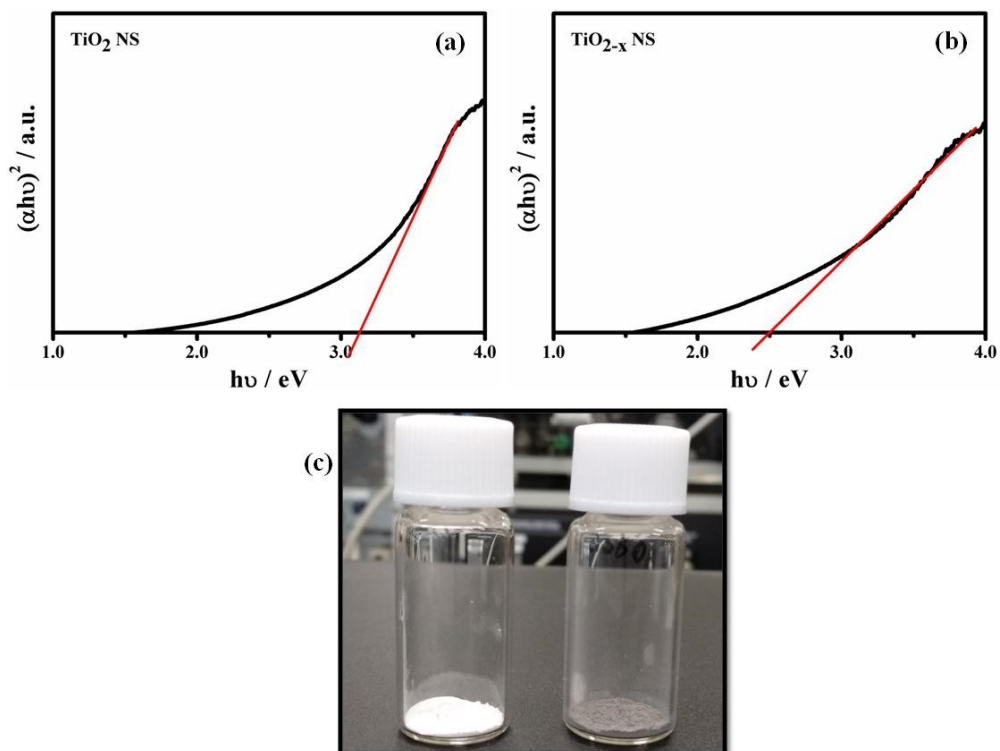


Fig. S4. Tauc plots of (a) TiO_2 NSs and (b) TiO_{2-x} NSs for determining the band gap with the help of UV-vis absorption spectra. (c) Photograph of TiO_2 NSs and TiO_{2-x} NSs powders.

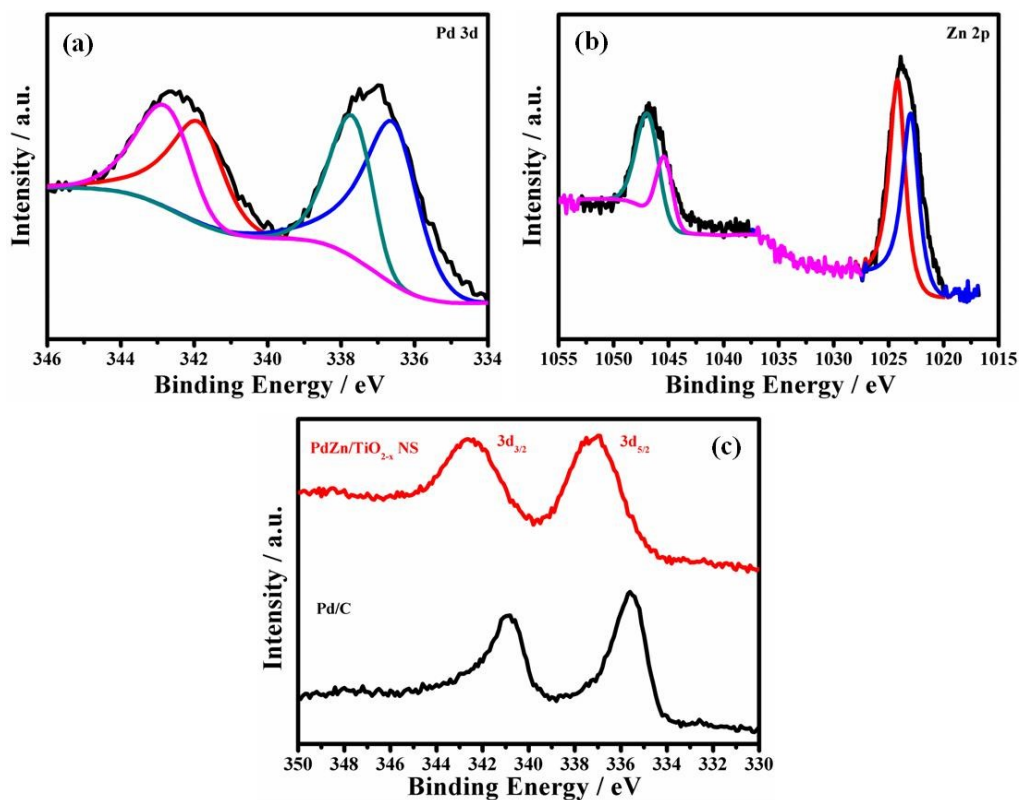


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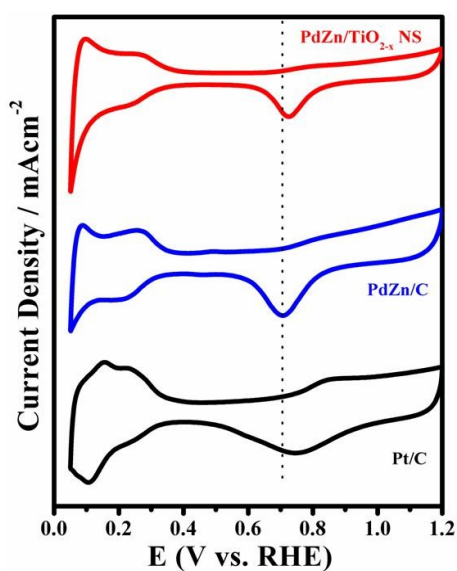


Fig. S6. Cyclic voltammograms of PdZn/TiO_{2-x} NSs, PdZn/C and Pt/C in Ar-saturated 0.1 M HClO₄ at 50 mV s⁻¹.

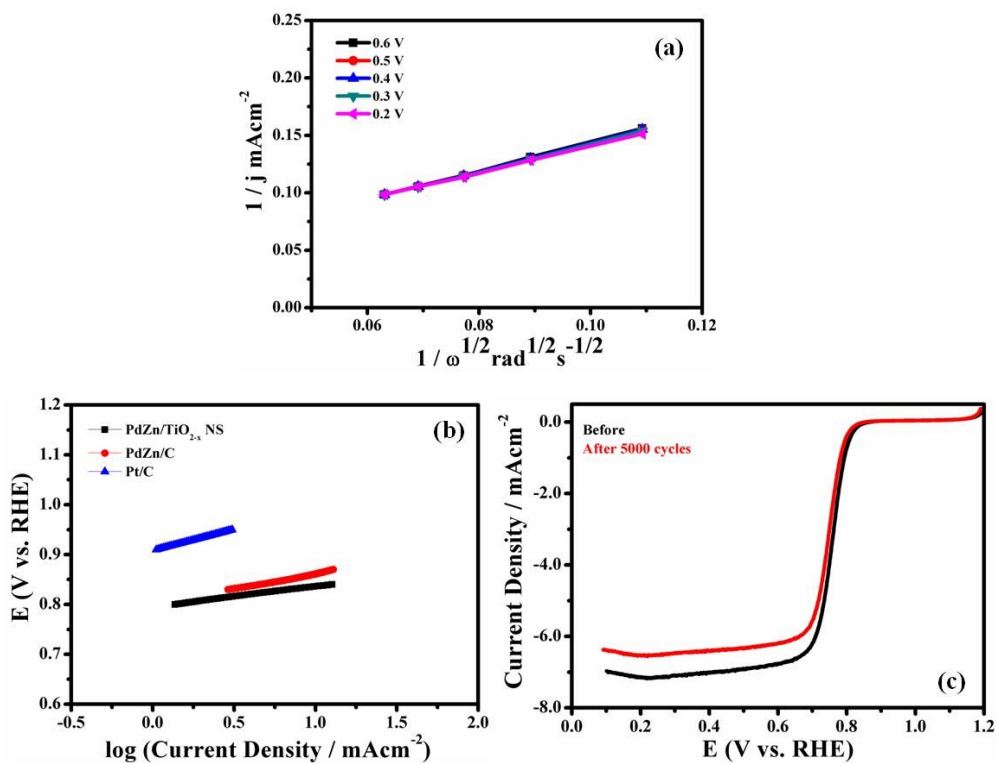


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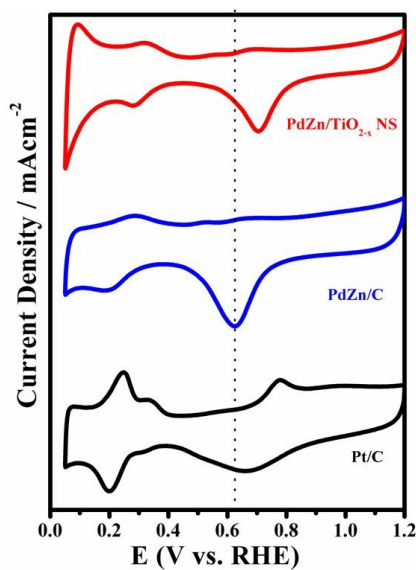


Fig. S8. Cyclic voltammograms of PdZn/TiO_{2-x} NSs, PdZn/C and Pt/C in Ar saturated 1.0 M KOH.

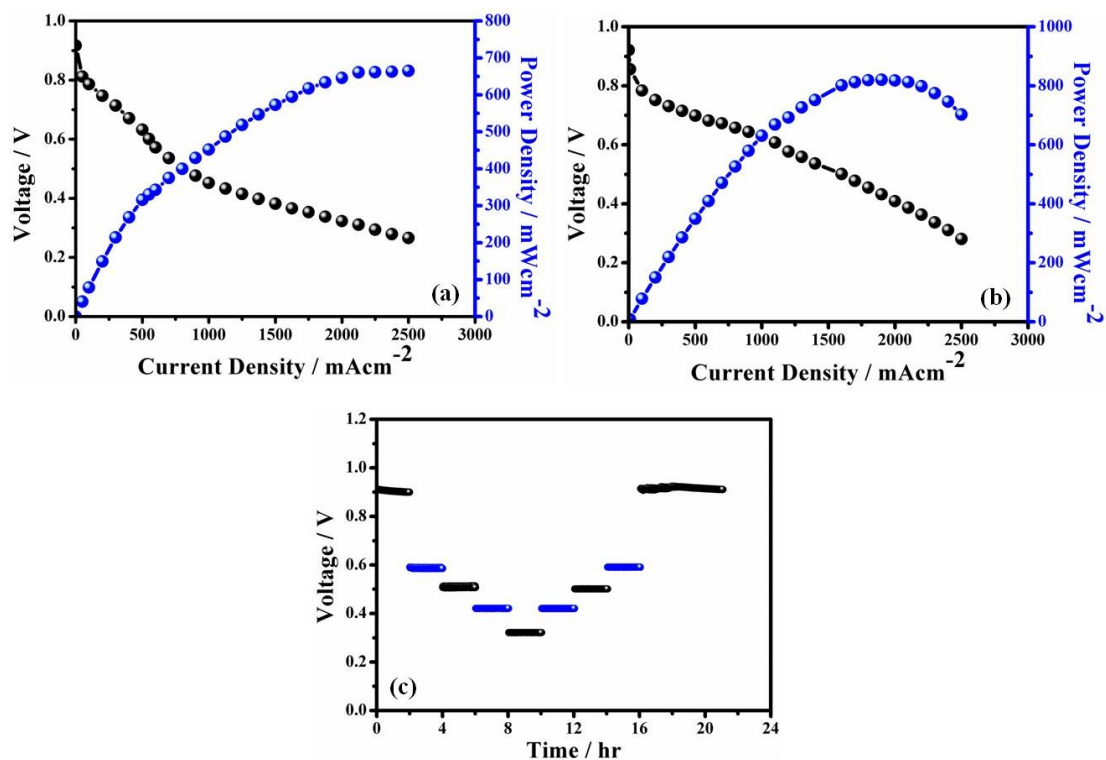


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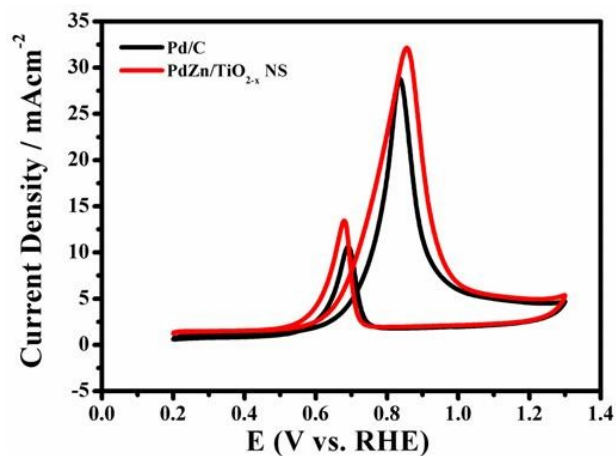


Fig. S10. Cyclic voltammograms of PdZn/TiO_{2-x} NS and Pd/C catalysts in (0.5 M glycerol + 1.0 M KOH) solution.

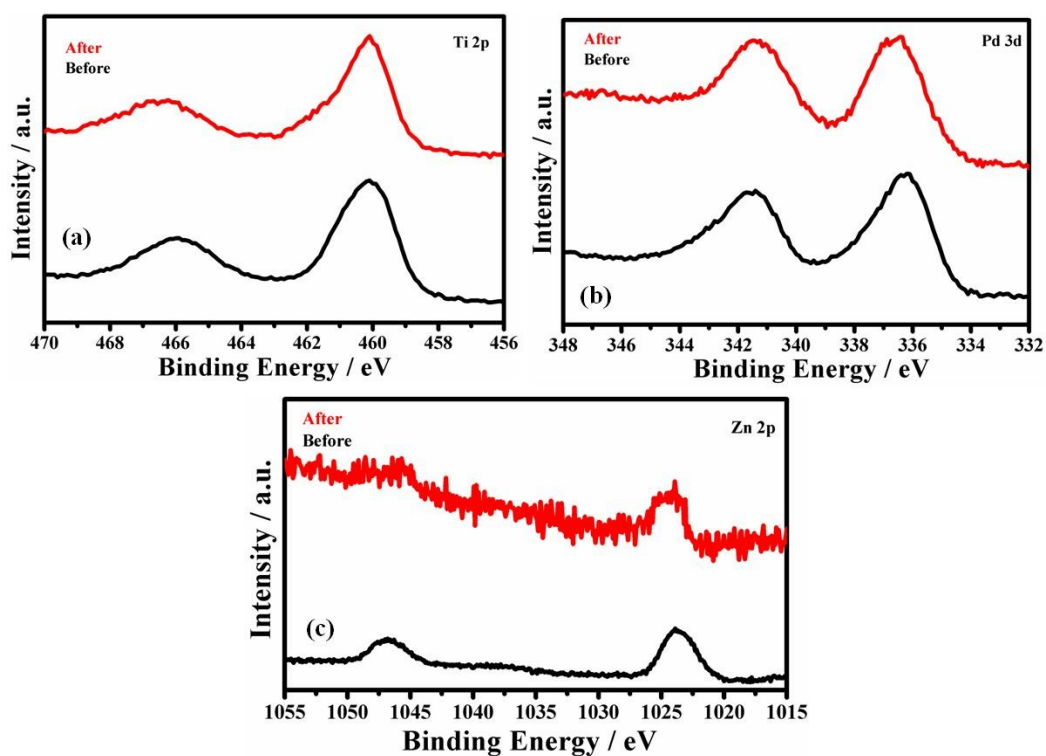


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Table S1

Comparison of electrochemical performances of the different electrocatalysts for oxygen reduction reaction

Catalysts	Onset potential vs RHE in V		E _{1/2} vs RHE in V		References
Pd ₃ Co/C	H ₂ SO ₄	-	H ₂ SO ₄	0.788	[1]
Au ₆₇ Pd ₃₃ /CN	KOH	0.94	KOH	0.83	[2]
Pd/CNS-20%	KOH	0.96	KOH	0.82	[3]
PdCuPt	HClO ₄	0.93	HClO ₄	0.86	[4]
Pd@PdO-Co ₃ O ₄	KOH	0.92	KOH	0.77	[5]
Pd ₃ Fe NPs/CB	KOH	0.87	KOH	0.80	[6]
Pd ₃ Ni NPs/CB	KOH	0.90	KOH	0.81	[6]
Pd/FHNC	HClO ₄	0.82	HClO ₄	0.61	[7]
PdZn/TiO _{2-x} NS	HClO ₄	0.88	HClO ₄	0.76	Present work
	KOH	0.94	KOH	0.834	

Table S2

Comparison for the fuel cell performance and its power densities of different cathode materials

Anode/loading in mg cm⁻²	Cathode/loading in mg cm⁻²	Power Density in mW cm⁻²	Temperature in °C	References
Pt/C (0.2)	fct-FePt/C (0.2)	~ 850	80	[8]
Pt/C (0.4)	PtPd/TiO ₂ (0.4)	520	75	[41] Main manuscript
Pt/C (0.4)	CNT-Pt/TiO ₂ (0.4)	567	75	[42] Main manuscript
Pt/C (0.2)	PANI-Fe-NCS (0.4)	830	80	[9]
Pt/C (0.25)	Pt ₃ Co-N-(G-MWNTs) (0.4)	935	60	[10]
Pt/C (0.25)	Pt ₃ Fe-N-(G-MWNTs)(0.24)	783	60	[10]
Pt/C (0.1)	Pd-Co/gCN (0.5)	190	60	[45] Main manuscript
Pt/C (0.32)	RuTe ₂ /C (0.26)	269	55	[46] Main manuscript
Pt/C (0.231)	Pt ₃ Co/C (0.143)	863	80	[47] Main manuscript
Pt/C (0.2)	PdZn/TiO_{2-x} NS (0.3)	855	80	Present work

References

1. L. An, Y. Chen, J. Shi, J. Cao, B. Liu and J. Yang, *Front. Chem.*, 2018, **6**, 596.
2. W. Yan, Z. Tang, L. Wang, Q. Wang, H. Yang and S. Chen, *Int. J. Hydrogen Energy*, 2017, **42**, 218-227.
3. W. Yan, Z. Tang, L. Li, L. Wang, H. Yang, Q. Wang, W. Wu and S. Chen, *ChemElectroChem*, 2017, **4**, 1349-1355.
4. S. Fu, C. Zhu, J. Song, F. Zhang, M. H. Engelhard, H. Xia, D. Du and Y. Lin, *Nanoscale*, 2017, **9**, 1279-1284.
5. H. C. Li, Y. J. Zhang, X. Hu, W. J. Liu, J. J. Chen and H. Q. Yu, *Adv. Energy Mater.*, 2018, **8**, 1702734.
6. T. Gunji, R. H. Wakabayashi, S. H. Noh, B. Han, F. Mastumoto, F. j. Disalvo and H. D. Arbuna, *Electrochim Acta*, 2018, 283, 1045-1052.
7. S. Zhang, H. Zhou, H. Liao, P. tan, W. Tian and J. Pan, *J. Colloid Interface Sci.*, 2022, **611**, 161-171.
8. J. Lee, J. M. Yoo, Y. Ye, Y. Mun, S. Lee, O. H. Kim, H. W. Rhee, H. I. Lee, Y. E. Sung and J. Lee, *Adv. Energy Mater.*, 2015, **5**, 1402093.
9. X. Fua, F. M. Hassana, P. Zamania, G. Jianga, D. C. Higginsa, J. Y. Choia, X. Wanga, P. Xua, Y. Liua and Z. Chen, *Nano Energy*, 2017, **42**, 249-256.
10. B. P. Vinayan and S. Ramaprabhu, *Nanoscale*, 2013, **5**, 5109-5118.