

*Supporting information for:*

## Ti<sub>3</sub>C<sub>2</sub> Nanosheets with Broad-Spectrum Antioxidant Activity for Cytoprotection against Oxidative Stress

*Hongqi Geng<sup>a,b</sup>, Yaping Ren<sup>b</sup>, Gang Qin<sup>a</sup>, Tao Wen<sup>\*c</sup>, Quan Liu<sup>b</sup>, Haiyan Xu<sup>c</sup>, Weiwei  
He<sup>\*b</sup>*

<sup>a</sup>School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo,  
Henan 454000, P. R. China.

<sup>b</sup>Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan  
Province, College of Chemical and Materials Engineering, Institute of Surface Micro and  
Nano Materials, Xuchang University, Xuchang, Henan 461000, P. R. China.

<sup>c</sup> Institute of Basic Medical Sciences Chinese Academy of Medical Sciences, School of  
Basic Medicine Peking Union Medical College, Beijing 100005, P. R. China.

**\*Corresponding Author**

E-mail: heweiweixcu@gmail.com (W. H.), went@ibms.pumc.edu.cn (T.W)

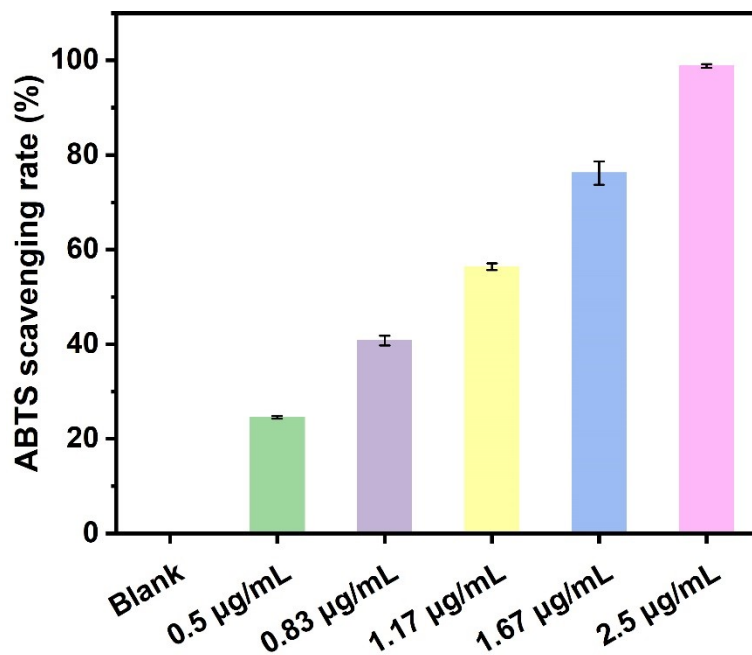


Fig. S1 Histogram of ABTS<sup>•+</sup> radical scavenging rate by Ti<sub>3</sub>C<sub>2</sub> at different concentrations.

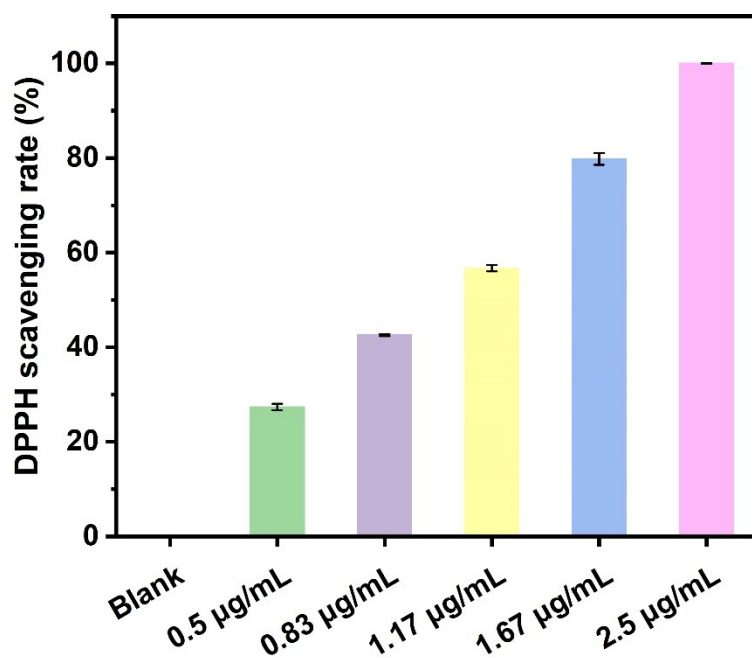
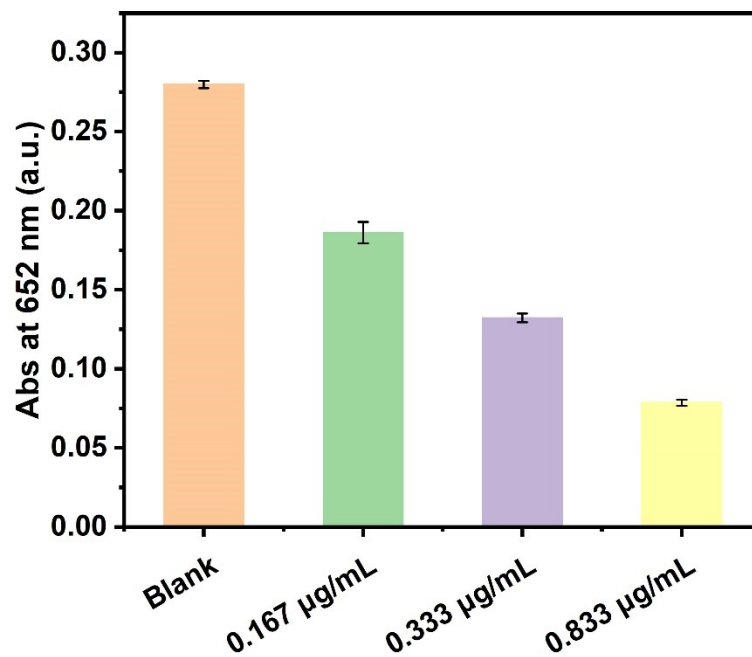


Fig. S2 Histogram of DPPH<sup>•</sup> radical scavenging rate by Ti<sub>3</sub>C<sub>2</sub> at different concentrations.



**Fig. S3** The concentration dependence of  $\bullet\text{OH}$  scavenging activity of  $\text{Ti}_3\text{C}_2$ .

The hydroxyl radicals are generated by light irradiating  $\text{TiO}_2$  NPs and then oxidize TMB to produce typical blue color. The addition of  $\text{Ti}_3\text{C}_2$  can significantly inhibit the oxidation of TMB in a concentration dependent manner, suggesting again their  $\bullet\text{OH}$  scavenging activity.

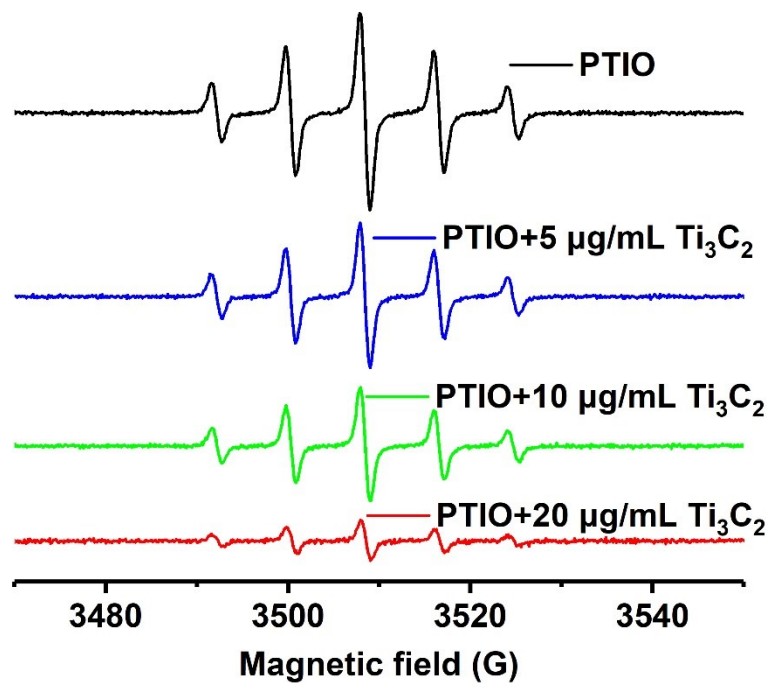


Fig. S4 Scavenging PTIO• radicals activity of  $Ti_3C_2$  dependent on the concentrations.

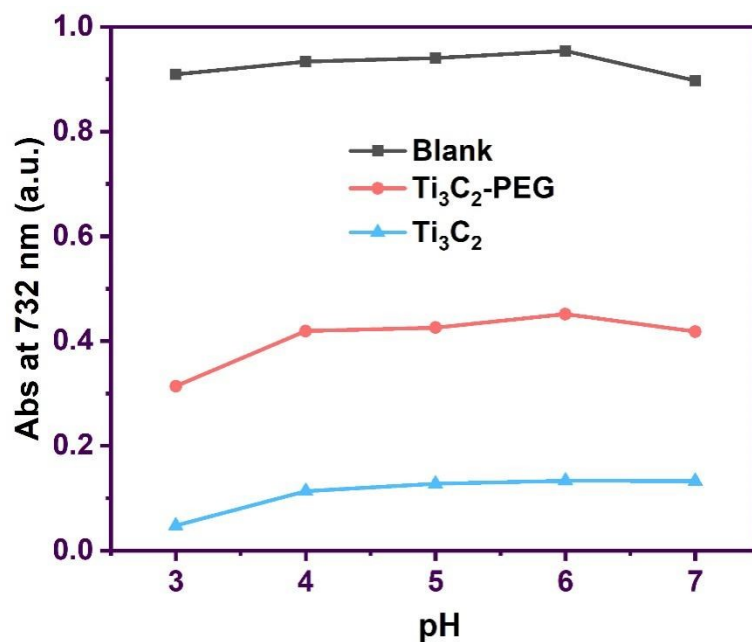


Fig. S5 Histogram of ABTS<sup>+</sup> radical scavenging activity of  $Ti_3C_2$  and  $Ti_3C_2$ -PEG under different pH conditions.

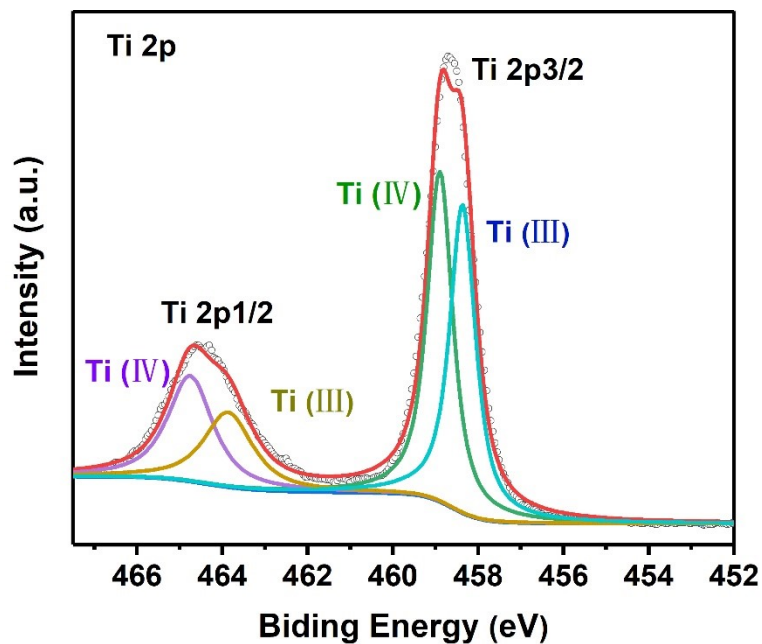


Fig. S6 High resolution XPS spectra of Ti 2p from  $\text{Ti}_3\text{C}_2\text{-B}$ .

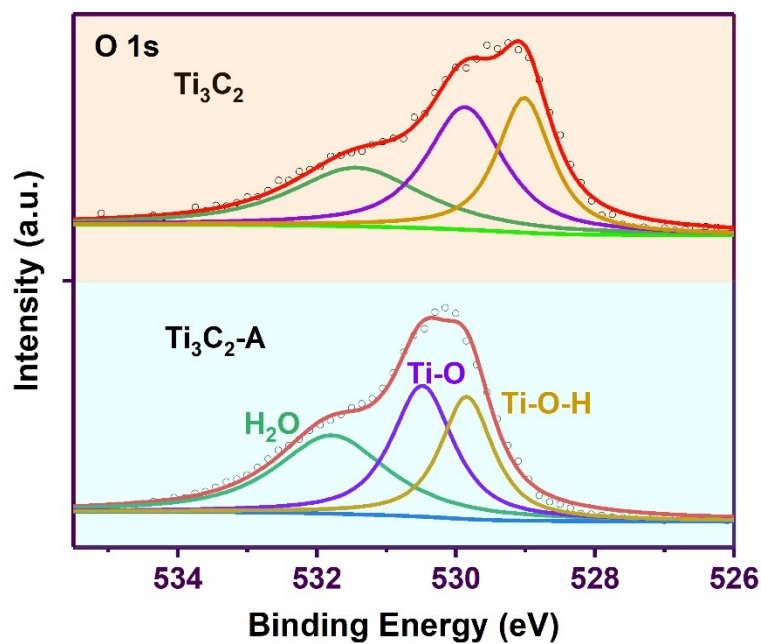


Fig. S7 High resolution XPS spectra of O 1s from  $\text{Ti}_3\text{C}_2$  and  $\text{Ti}_3\text{C}_2\text{-A}$ .

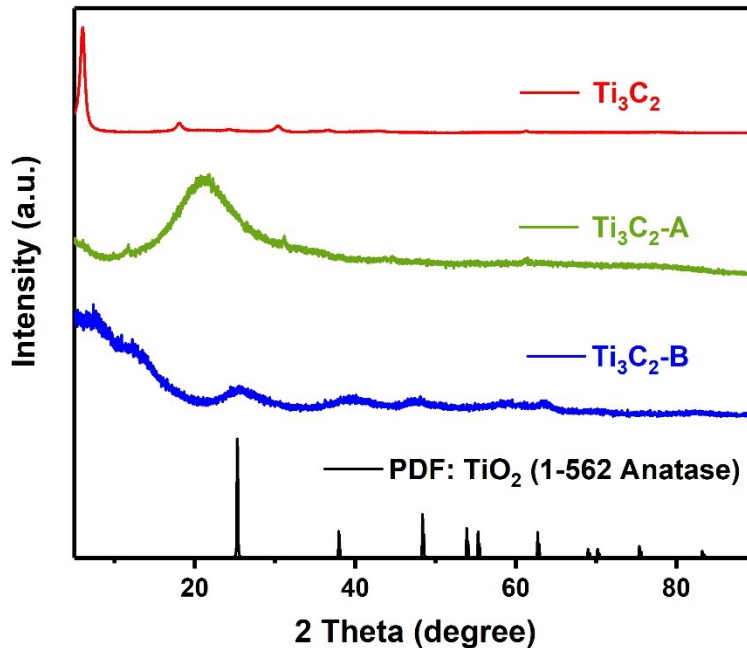
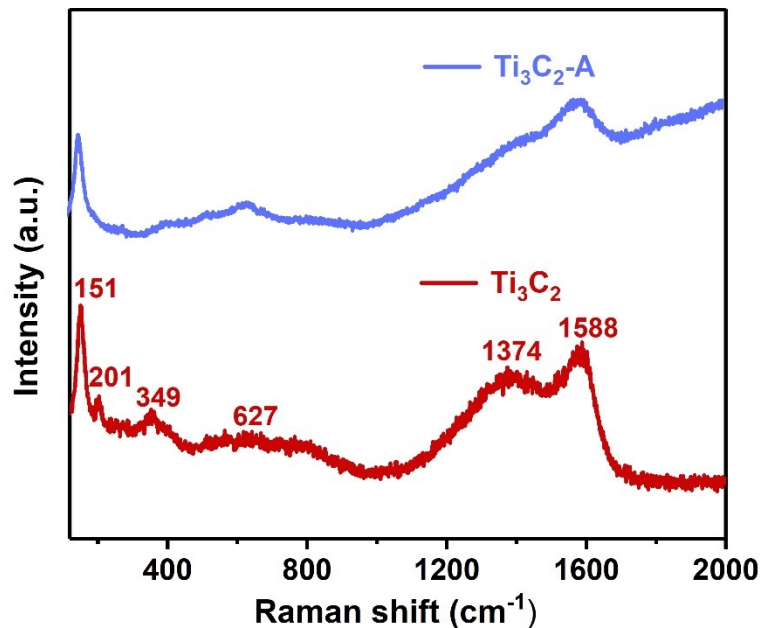


Fig S8. XRD patterns of  $\text{Ti}_3\text{C}_2$ ,  $\text{Ti}_3\text{C}_2\text{-A}$  and  $\text{Ti}_3\text{C}_2\text{-B}$  nanosheets.

It can be seen from XRD that  $\text{Ti}_3\text{C}_2$  has good crystallinity. The characteristic peak (002) at  $6.4^\circ$  disappeared after oxidation with either  $\text{ABTS}^{++}$  or  $\text{H}_2\text{O}_2$ . The obvious change of XRD patterns indicate the crystal structure change in  $\text{Ti}_3\text{C}_2$  after oxidation. For the  $\text{Ti}_3\text{C}_2$  after oxidation of  $\text{H}_2\text{O}_2$  ( $\text{Ti}_3\text{C}_2\text{-B}$ ), the characteristic peaks corresponding to anatase appeared, reflecting the formation of  $\text{TiO}_2$  particles.



**Fig. S9** Raman spectra of Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>-A.

The changes of Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>-A were also validated by Raman spectra (Figure S9). The typical peaks at 151, 201, 349 and 627 cm<sup>-1</sup> can be distinguished to the vibrational modes: Eg of Ti<sub>3</sub>C<sub>2</sub>F<sub>2</sub>, Eg of Ti<sub>3</sub>C<sub>2</sub>(OH)<sub>2</sub>, Eg of Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> and the vibrational modes of nonstoichiometric titanium carbide, respectively.<sup>21, 22</sup> These indicate the existence of groups -F, -O and -OH. The in-phase vibration of the graphene (G band) at 1588 cm<sup>-1</sup> as well as the disorder band caused by the graphene edges (D band) at approximately 1374 cm<sup>-1</sup> are clearly exhibited in Ti<sub>3</sub>C<sub>2</sub>.<sup>23</sup> After oxidation with free radicals, the G-band disappeared, which was suspected to be due to the change of the layered hexagonal structure of Ti<sub>3</sub>C<sub>2</sub>.

**Table S1** Comparison of antioxidant nanomaterials for their antioxidant capability.

Antioxidants	Free radical species							References
	•OH	O <sub>2</sub> <sup>•-</sup>	H <sub>2</sub> O <sub>2</sub>	ABTS <sup>•+</sup>	DPPH•	PTIO•	•NO	
Pt	√	√	√	√	√	N/A	×	1-4
Prussian Blue	√	√	√	√	√	N/A	×	5-7
PtRu	×	√	√	N/A	√	N/A	N/A	8
CO <sub>3</sub> O <sub>4</sub>	×	√	√	N/A	N/A	N/A	N/A	9, 10
Au/N-C	√	√	√	√	√	N/A	N/A	11
Carbogenic Nanozyme	√	√	√	N/A	√	N/A	√	12
Mn <sub>3</sub> O <sub>4</sub>	×	√	√	N/A	N/A	N/A	N/A	13, 14
CeO <sub>2</sub>	√	√	√	N/A	√	N/A	√	15-18
V <sub>2</sub> C	√	√	√	N/A	N/A	N/A	N/A	19
N-Ti <sub>2</sub> C-QDs	√	N/A	N/A	N/A	×	N/A	N/A	20
Ti <sub>3</sub> C <sub>2</sub>	√	√	√	√	√	√	√	This work

**Table S2** Comparison of DPPH free radical scavenging ability of Ti<sub>3</sub>C<sub>2</sub> with reported antioxidant.

Antioxidants	DPPH radical dosage	Antioxidants content (µg/mL)	Reaction time (min)	Scavenging efficiency (%)	References
cationic heteroleptic Pd(II) complex (3)	1 mL (0.073 mg/mL)	75	30	76%	24
(Z)-tributylstannyl 4-(4-methoxyphenylamino)-4-oxobut-2-enoate (2)	180 µl 0.032 mg/mL	N/A	60	55%	25
epigallocatechin gallate@TiO <sub>2</sub>	9.9 mL (25 mg/mL)	8.5	N/A	80%	26
TiO <sub>2</sub> NPs	1 mL (0.394 mg/mL)	100	30	85%	27
Ti <sub>3</sub> C <sub>2</sub> NSs	2.5 mL (0.1 mg/mL)	2.5	2	100%	This work



## References

1. S. Onizawa, K. Aoshiba, M. Kajita, Y. Miyamoto and A. Nagai, *Pulm. Pharmacol. Ther.*, 2009, **22**, 340-349.
2. M. Kajita, K. Hikosaka, M. Iitsuka, A. Kanayama, N. Toshima and Y. Miyamoto, *Free Radic. Res.*, 2007, **41**, 615-626.
3. S. Kato, R. Hokama, H. Okayasu, Y. Saitoh, K. Iwai and N. Miwa, *J. Nanosci. Nanotechno.*, 2012, **12**, 4019-4027.
4. Y. Liu, H. Wu, M. Li, J. Yin and Z. Nie, *Nanoscale*, 2014, **6**, 11904-11910.
5. W. Zhang, S. Hu, J. Yin, W. He, W. Lu, M. Ma, N. Gu and Y. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 5860-5865.
6. H. Oh, J. S. Lee, D. Sung, J. H. Lee, S. H. Moh, J. M. Lim and W. I. Choi, *Nanomedicine*, 2019, **14**, 2567-2578.
7. A. Sahu, J. Jeon, M. S. Lee, H. Yang and G. Tae, *Mater. Sci. Eng. C*, 2021, **119**, 111596.
8. C. Liu, Y. Yan, X. Zhang, Y. Mao, X. Ren, C. Hu, W. He and J. Yin, *Nanoscale*, 2020, **12**, 3068-3075.
9. J. Dong, L. Song, J. Yin, W. He, Y. Wu, N. Gu and Y. Zhang, *ACS Appl. Mater. Inter.*, 2014, **6**, 1959-1970.
10. J. Mu, Y. Wang, M. Zhao and L. Zhang, *Chem. Commun.*, 2012, **48**, 2540-2542.
11. J. Zhao, H. Wang, H. Geng, Q. Yang, Y. Tong and W. He, *ACS Appl. Nano Mater.*, 2021, **4**, 7253-7263.
12. X. Mu, H. He, J. Wang, W. Long, Q. Li, H. Liu, Y. Gao, L. Yang, Q. Ren, S. Sun, J. Wang, J. Yang, Q. Liu, Y. Sun, C. Liu, X. Zhang and W. Hu, *Nano Lett.*, 2019, **19**, 4527-

4534.

13. N. Singh, M. A. Savanur, S. Srivastava, P. D'Silva and G. Muges, *Angew. Chem. Int. Ed.*, 2017, **56**, 14267-14271.
14. N. Singh, M. A. Savanur, S. Srivastava, P. D'Silva and G. Muges, *Nanoscale*, 2019, **11**, 3855-3863.
15. C. Walkey, S. Das, S. Seal, J. Erlichman, K. Heckman, L. Ghibelli, E. Traversa, J. F. McGinnis and W. T. Self, *Environ. Sci-Nano*, 2015, **2**, 33-53.
16. Q. Maqbool, *RSC Adv.*, 2017, **7**, 56575-56585.
17. M. Das, S. Patil, N. Bhargava, J. Kang, L. M. Riedel, S. Seal and J. J. Hickman, *Biomaterials*, 2007, **28**, 1918-1925.
18. D. Schubert, R. Dargusch, J. Raitano and S. W. Chan, *Biochem. Bioph. Res. Commun.*, 2006, **342**, 86-91.
19. W. Feng, X. Han, H. Hu, M. Chang, L. Ding, H. Xiang, Y. Chen and Y. Li, *Nat. Commun.*, 2021, **12**, 2203.
20. J. Guo, L. Zhao, Y. Li and J. Zhang, *ACS Appl. Nano Mater.*, 2021, **4**, 12308-12315.
21. A. Sarycheva and Y. Gogotsi, *Chem. Mater.*, 2020, **32**, 3480-3488.
22. B. Wang, A. Zhou, F. Liu, J. Cao, L. Wang and Q. Hu, *J. Adv. Ceram.*, 2018, **7**, 237-245.
23. B. Wang, M. Wang, F. Liu, Q. Zhang, S. Yao, X. Liu and F. Huang, *Angew. Chem.*, 2020, **132**, 1930-1934.
24. S. Z. Khan, Z. Khan, I. Ahmad, S. Khan, S. Khan, M. Ahmed, M. Inam, F. Belanger-Gariepy and Z. U. Rehman, *Inorg. Chem. Commun.*, 2021, **123**, 108316.
25. I. Ahmad, Z. U. Rehman, A. Waseem, M. Tariq, C. MacBeth, J. Bacsá, D.

Venkataraman, A. Rajakumar, N. Ullah and S. Tabassum, *Inorganica Chim. Acta*, 2020, **505**, 119433.

26. Q. Li, M. Duan, L. Liu, X. Chen, Y. Fu, J. Li, T. Zhao and D. J. McClements, *J. Agric. Food Chem.*, 2021, **69**, 9661-9670.

27. N. Ajmal, K. Saraswat, M. A. Bakht, Y. Riadi, M. J. Ahsan and M. Noushad, *Green Chem. Lett. Rev.*, 2019, **12**, 244-254.