Controllable growth on Nano-graphite-supported ZrO$_2$-MnO$_x$ bimetallic oxides for electrocatalytic antibiotics degradation: Boosting mechanism of Mn^{3+}/Mn^{4+} redox cycle

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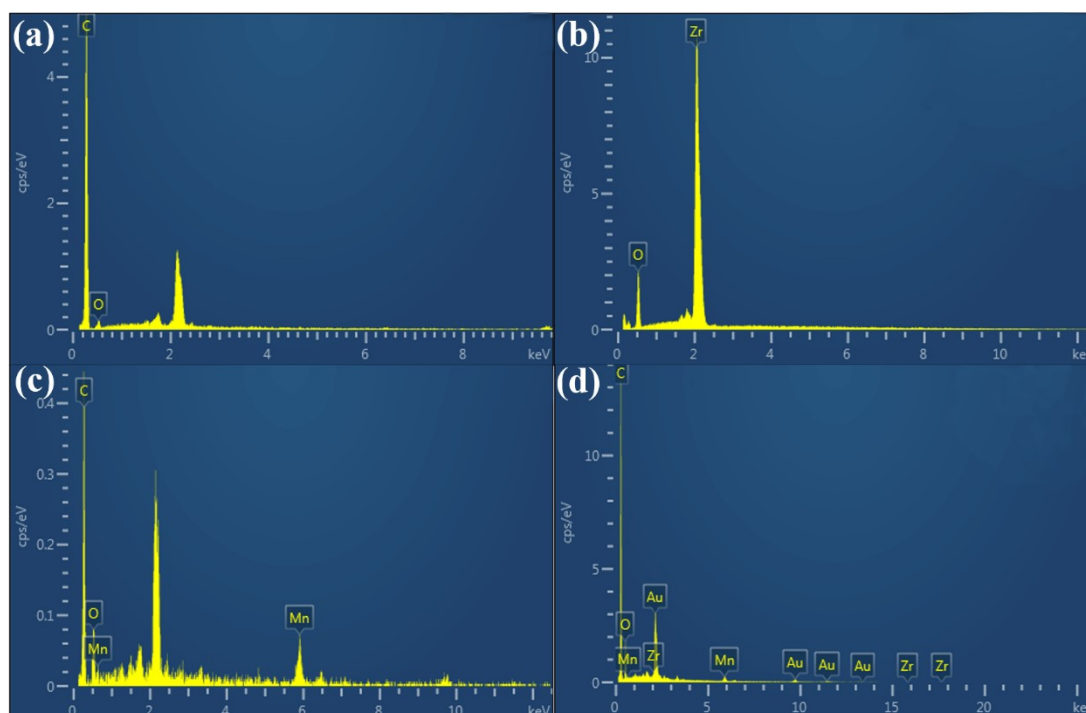E-mail addresses: guihonglan416@sina.com (Guihong Lan).

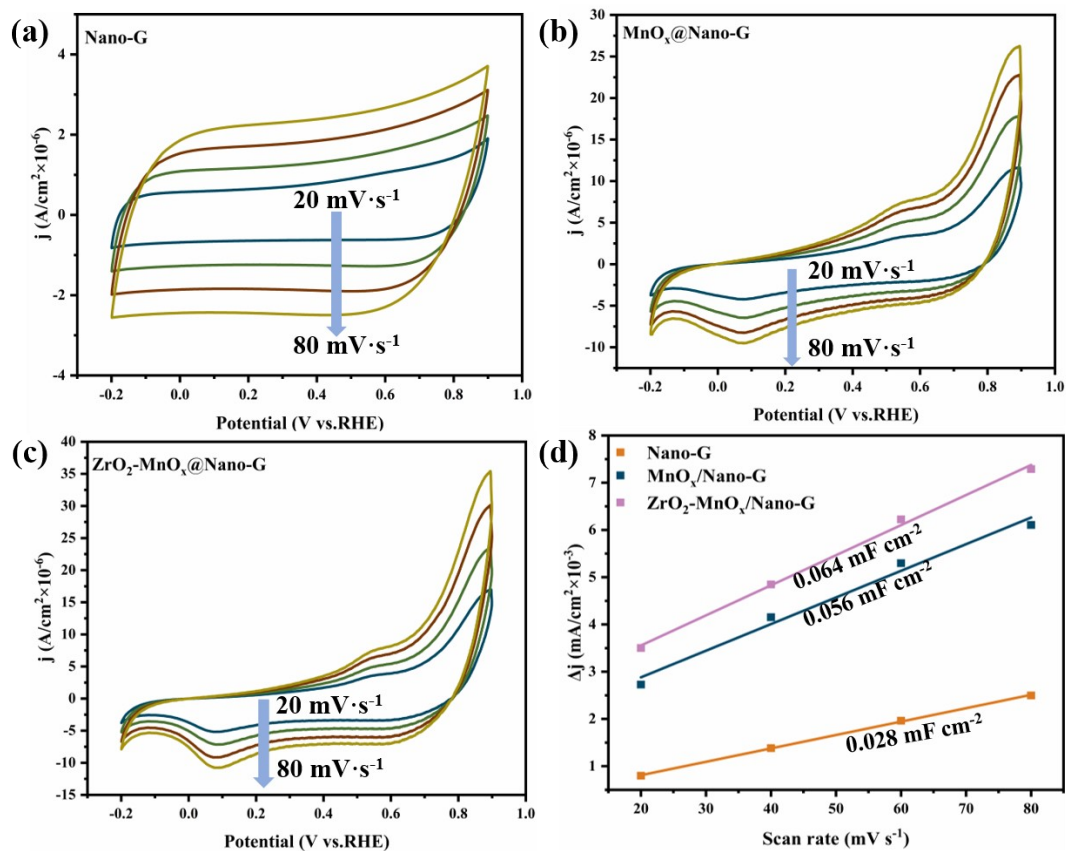**Fig. S1** EDS of (a) Nano-G, (b) ZrO$_2$, (c) MnO$_x$/Nano-G and (d) ZrO$_2$-MnO$_x$/Nano-G composites.

Fig. S2 (a-c) The CV curves of the samples were measured at different scanning speeds and (d) the C$_{dl}$ was evaluated by the changing diagram of the relationship between Δj and scanning speed.
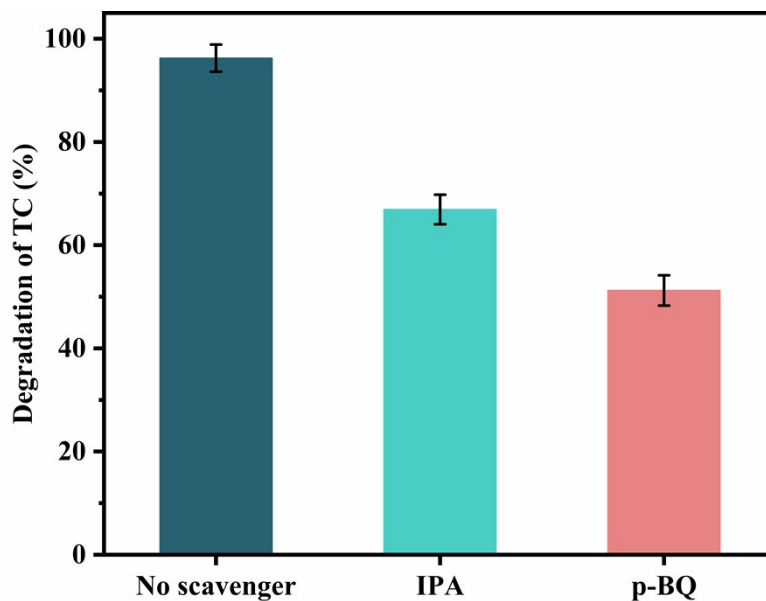

Fig. S3 Quenching study on ZrO$_2$-MnO$_x$/Nano-G electrode for TC degradation. Conditions: TC (20

mg L^{-1}), current density 30 mA cm^{-2}, IPA 10 mmol L^{-1}, P-BQ 0.1 mmol L^{-1}.
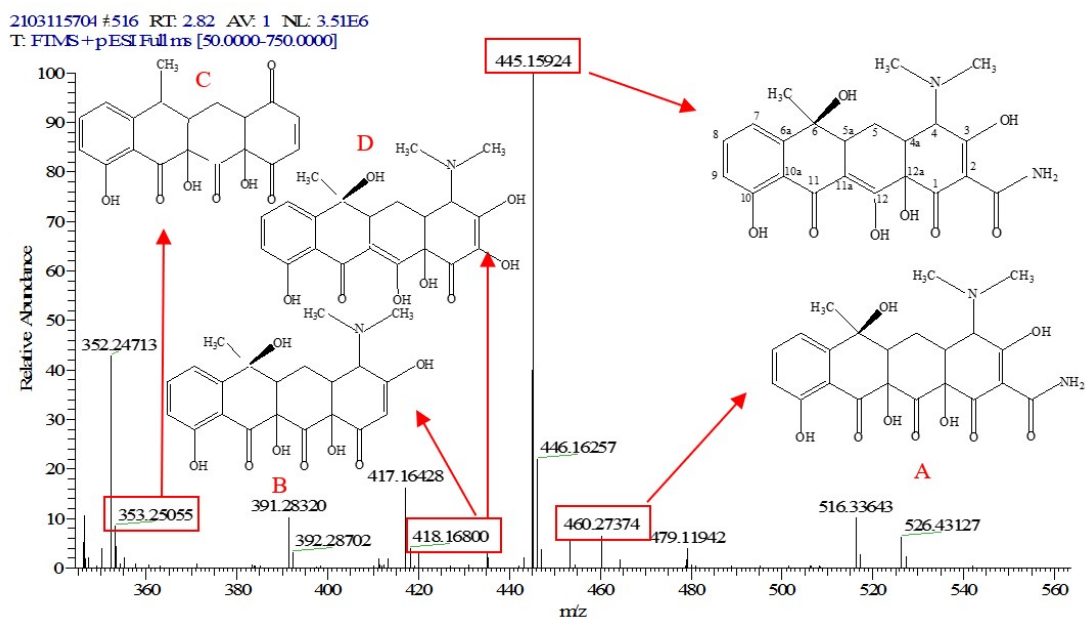

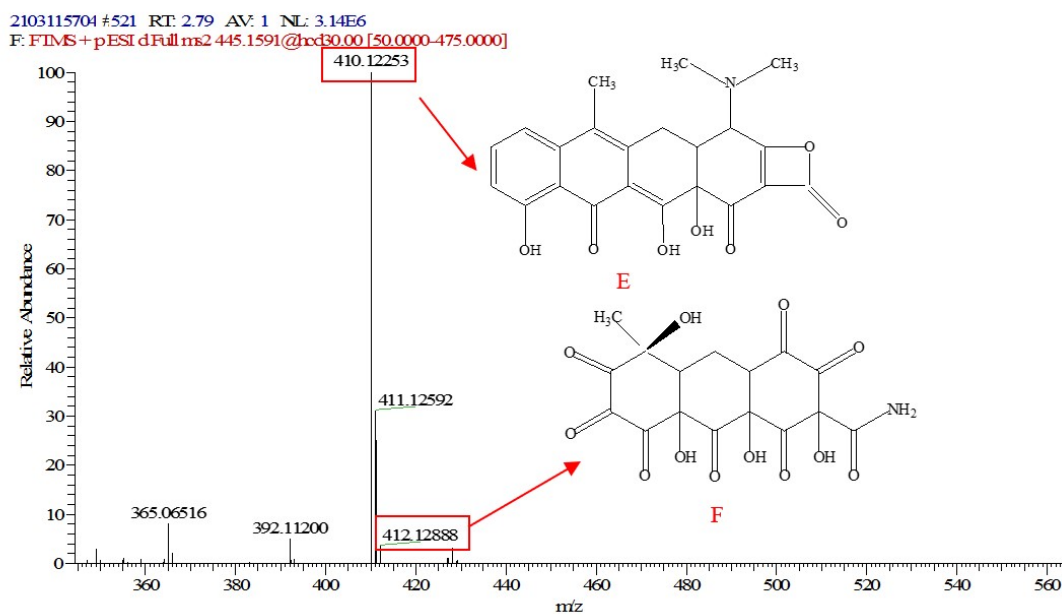**Fig. S4** Mass spectra of TC and intermediates at 2.82 min retention time.

Fig. S5 Mass spectra of TC and intermediates at 2. 79 min retention time.

Fig. S6 Mass spectra of TC and intermediates at 6.83 min retention time.

Fig. S7 Mass spectra of TC and intermediates at 2.0 min retention time.

Table. S1 Element percentage of MnO_x/Nano-G and ZrO_2-MnO_x/Nano-G composites

	Element (wt%)			
	C	O	Mn	Zr
Nano-G	92.22	7.78	-	-
ZrO_2	-	25.97	-	74.03
MnO_x/Nano-G	58.02	15.09	26.9	-
ZrO2-MnOx/Nano-G	61.89	12.34	3.16	0.08

Table. S2 BET surface area and pore volume of Nano-G, MnO_x/Nano-G and ZrO_2-MnO_x/Nano-G composites

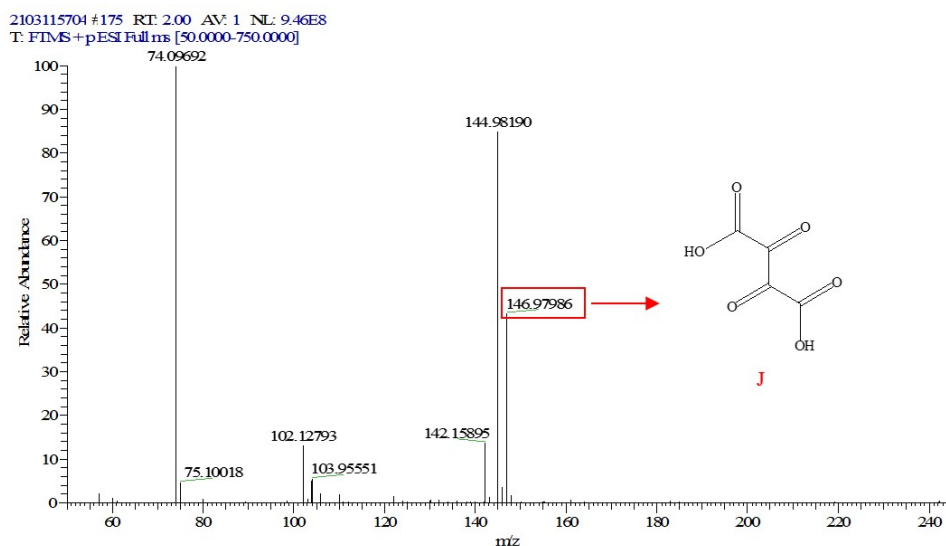| Electrode	BET surface area (m^2/g)	Pore volume (cm^3/g)
Nano-G	4.78	0.024
MnO_x/Nano-G	6.24	0.030
ZrO_2-MnO_x/Nano-G	6.85	0.048

Table. S3 Reported literature about the treatment of TC

Materials	Technologies	Concentration	Degradation rate	References
$MnFe_2O_4$/CNT	Electrocatalysis	40 mg/L	87.7% within 2h	[1]
SnO_2-Sb/ACFs	Electrocatalysis	20 mg/L	100 % within 2 h	[2]
Bi-Sn-Sb/γ-Al_2O_3	Electrocatalysis	100 mg/L	85.9% within 3 h	[3]
Bi_2O_3 film	Photoelectrocatalysis	10 mg/L	70.0% within 5 h	[4]
Ag@Bi_2WO_6/$FeWO_4$ nanosheet	Peroxymonosulfate activation	10 mg/L	96%within 60 min	[5]
ZrO_2-MnO_x/Nano-G	Electrocatalysis	20 mg/L	93% within 120 min	This work

Table. S4 Frontier electron densities on atoms and Hirshfeld charge of the TC molecule

Atom	Fukui (-)	Fukui (+)	Fukui (0)	CDD	Hirshfeld charge
C (1)	0.004	0.023	0.014	0.019	-0.0322
C (2)	0.005	0.014	0.009	0.009	-0.0676
C (3)	0.004	0.016	0.01	0.012	0.0727
C (4)	0.003	0.009	0.006	0.006	-0.0435
C (5)	0.002	0.012	0.007	0.01	-0.0013
C (6)	0.005	0.013	0.009	0.008	-0.0633
C (7)	0.001	0.002	0.002	0.001	0.0899
C (8)	0.004	0.004	0.004	0	-0.0185

C (9)	0.006	0.02	0.013	0.014	-0.049
C (10)	0.005	0.039	0.022	0.034	0.1013
C (11)	0.004	0.005	0.005	0.001	-0.0594
C (12)	0.011	0.003	0.007	-0.008	-0.0217
C (13)	0.001	0.014	0.007	0.013	0.0723
C (14)	0.002	0.026	0.014	0.024	0.0828
C (15)	0.022	0.008	0.015	-0.014	0.0272
C (16)	0.014	0.076	0.045	0.062	0.1153
C (17)	0.025	0.033	0.029	0.008	-0.0491
C (18)	0.017	0.092	0.055	0.075	0.1182
C (19)	0.001	0.003	0.002	0.002	-0.1023
O (20)	0.002	0.005	0.003	0.003	-0.2331
O (21)	0.007	0.02	0.014	0.013	-0.2207
O (22)	0.008	0.044	0.026	0.036	-0.2526
O (23)	0.009	0.031	0.02	0.022	-0.1878
O (24)	0.036	0.105	0.07	0.069	-0.2334
C (25)	0.005	0.004	0.005	-0.001	0.1397
O (26)	0.017	0.024	0.02	0.007	-0.3666
O (27)	0.025	0.06	0.042	0.035	-0.1284
N (28)	0.009	0.011	0.01	0.002	-0.1184
N (29)	0.208	0.016	0.112	-0.192	-0.0769
O (30)	0.007	0.027	0.017	0.02	-0.2062
C (31)	0.051	0.007	0.029	-0.044	-0.0531
C (32)	0.049	0.005	0.027	-0.044	-0.0726

Reference

1 H. Zhang, X. Tong and H. Xiao, et al., Promoting the performance of electrooxidation-PMS system for degradation of tetracycline by introduction of $MnFe_2O_4$/CNT as a third-electrode, *Sep. Purif. Technol.*, 2022, **294**, 121171.

2 C. Shi, S. Yu and C. Li, Fabrication of aligned carbon nanofiber doped with SnO_2-Sb for efficient electrochemical removal of tetracycline, *Chem. Eng. J.*, **441**, 136052.

3 W. Sun, Y. Sun and K. J. Shah, et al., Electrocatalytic oxidation of tetracycline by Bi-Sn-Sb/γ-Al_2O_3 three-dimensional particle electrode, *J. Hazard. Mater.*, **370**, 24-32.

4 T. Chen, Q. Hao and W. Yang, et al., A honeycomb multilevel structure Bi_2O_3 with highly efficient catalytic activity driven by bias voltage and oxygen defect, *Appl. Catal., B*, **237**, 442-448.

5 Zhuang Xie, Guoqing Xiao and Xiang Zeng, et al., Ion-exchange synthesis Ag@Bi_2WO_6/$FeWO_4$ nanosheet with white-LED-light-driven for efficient activation of peroxymonosulfate: Synthesis, characterization, and mechanism, *Sep. Purif. Technol*, **315**, 123481.