Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Enhancement of formic acid formation by nitrogen-doped graphene oxide nanosheets decorated with Sn nanoparticles in electrochemical CO_2 reduction

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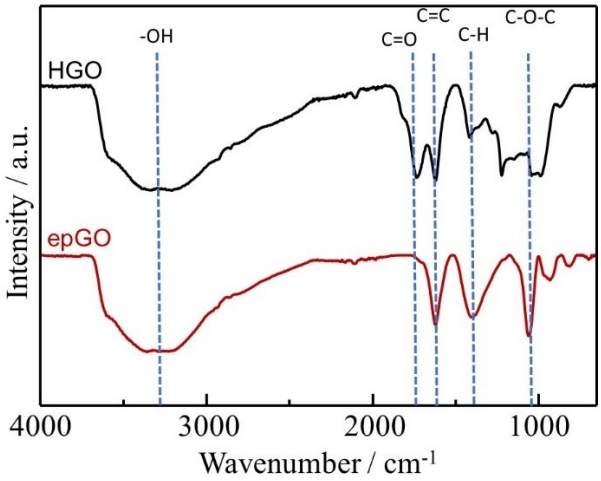

Figure S1: FT-IR spectra of HGO and epGO.

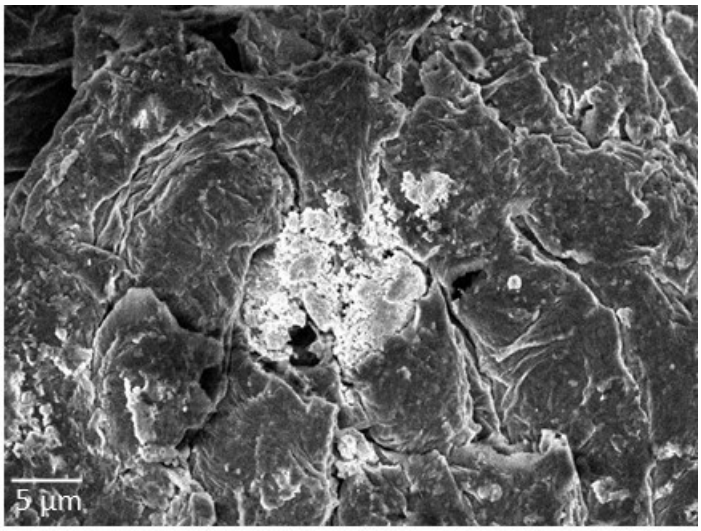

Figure S2: Aggregation of Sn on graphene after thermal annealing.

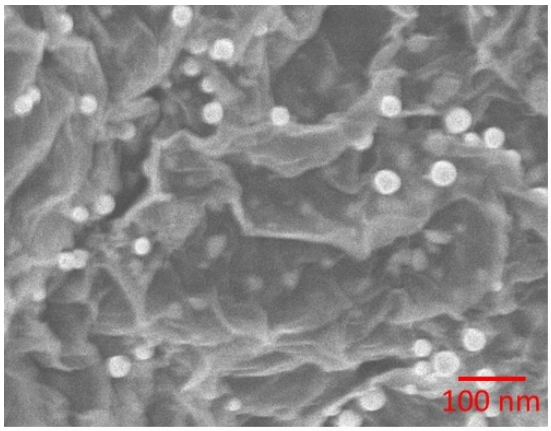

Figure S3: A representative TEM image of Sn on graphene oxide (Sn/rHGO). Hydrothermally prepared SnO_2 was used as the precursor.

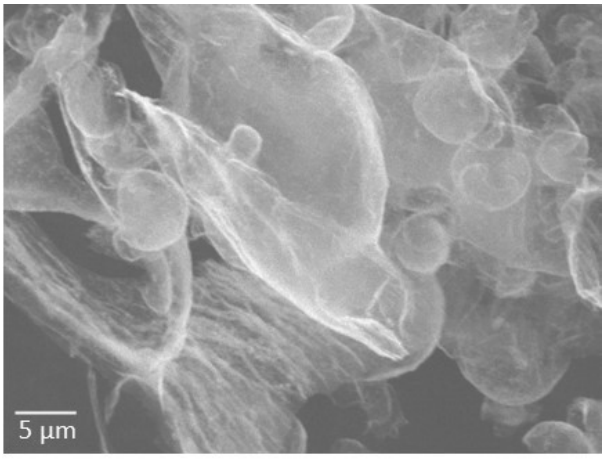

Figure S4: A representative TEM image of Sn on graphene oxide (Sn/rHGO). Commercial SnO_2 was used as the precursor.

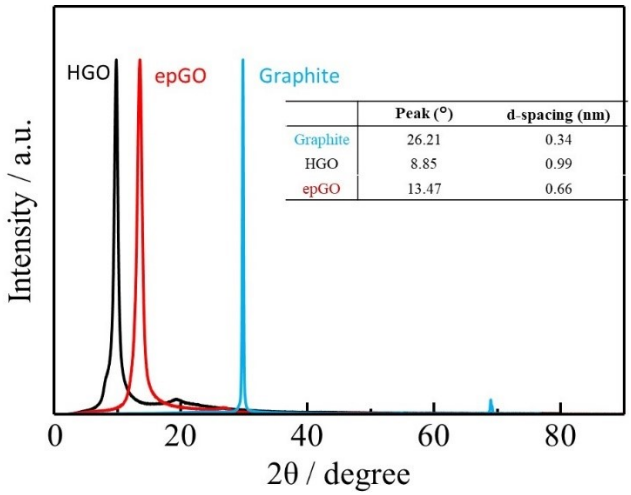

Figure S5: XRD patterns of GO synthesized by the Hummers' method (HGO), epoxy-controlled GO (epGO), and starting precursor, graphite.

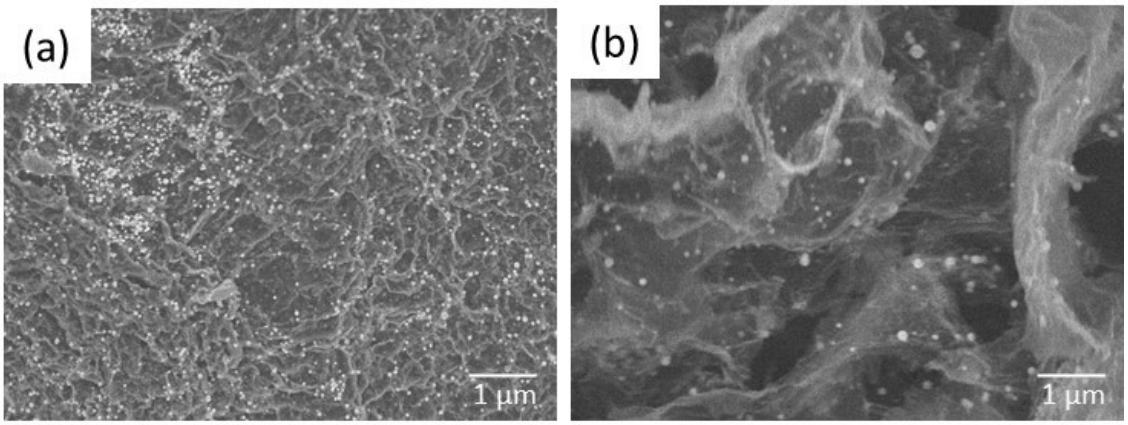

Figure S6: SEM images of (a) Sn/NrHGO and Sn/NrepGO.

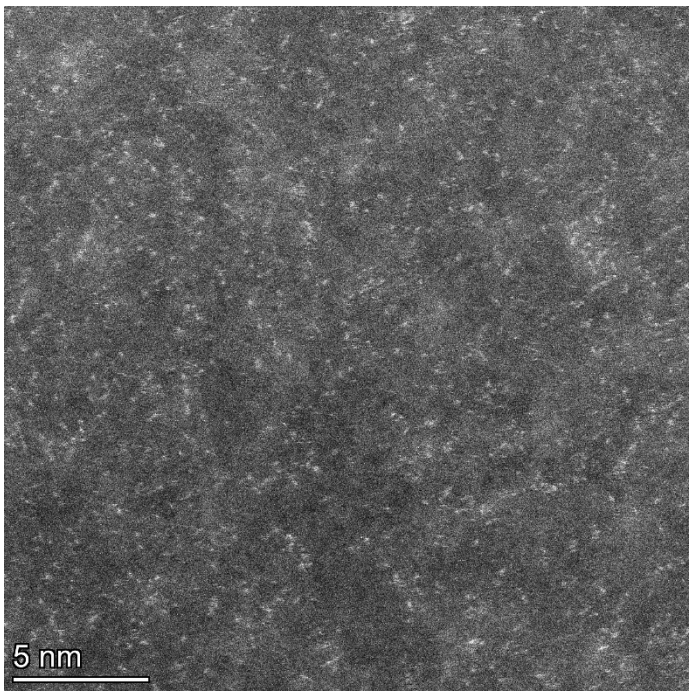

Figure S7: HRTEM image of Sn/NrepGO. The high-density bright dots correspond to atomic Sn, which are homogeneously distributed across the entire graphene framework.

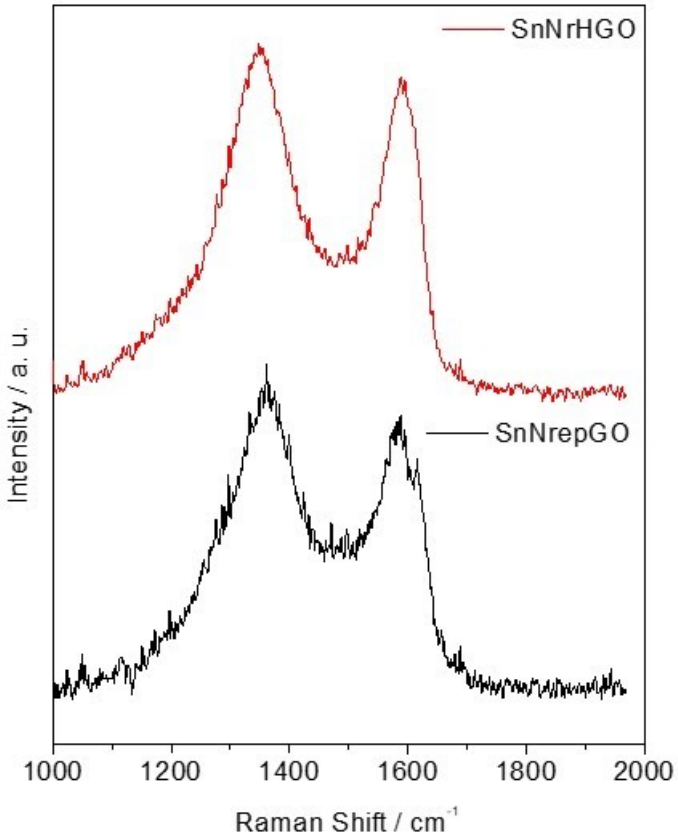

Figure S8: Raman spectra of Sn/NrHGO and Sn/NrepGO.

Table S1: Raman spectrum of graphene oxide and composites. The unit of the spectra is cm^{-1}

Entry		I_D/I_G
1	Graphene oxide	1.00
2	repGO	1.13
3	rHGO	1.14
4	Sn/NrepGO	1.10
5	Sn/NrHGO	1.11

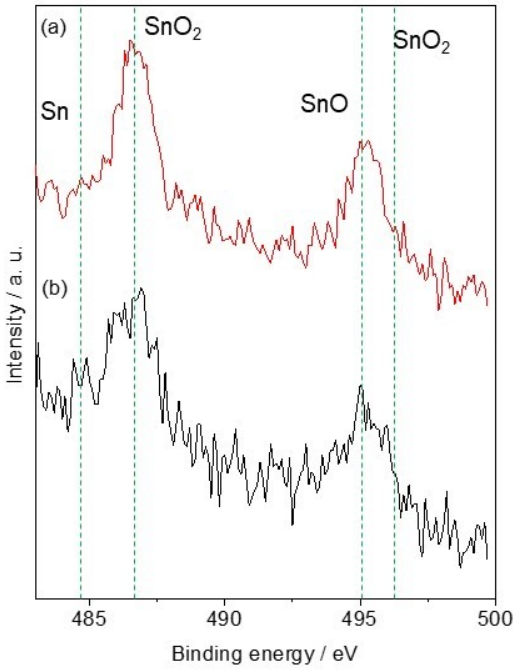

Figure S9: Sn 3d XPS deconvoluted spectra of (a) Sn/NrepGO and (b) Sn/NrHGO.

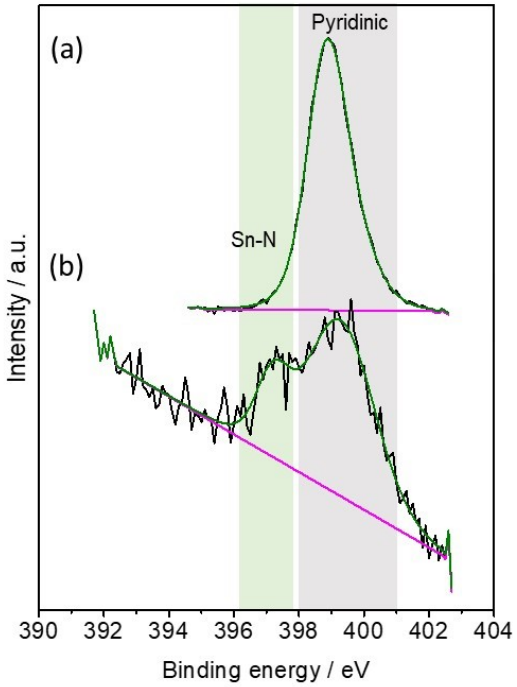

Figure S10: N 1s XPS deconvoluted spectra of (a) Sn/NrepGO and (b) Sn/NrHGO.

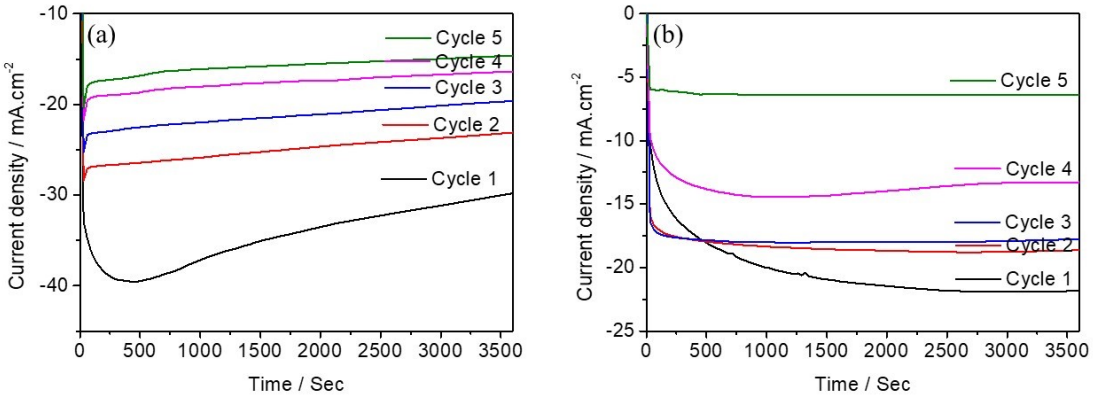

Figure S11. Cycle durability of the (a) Sn/NrepGO, (b) Sn/NrHGO electrodes at -1.6 V vs Ag/AgCl (1M KOH under CO_2 flow).

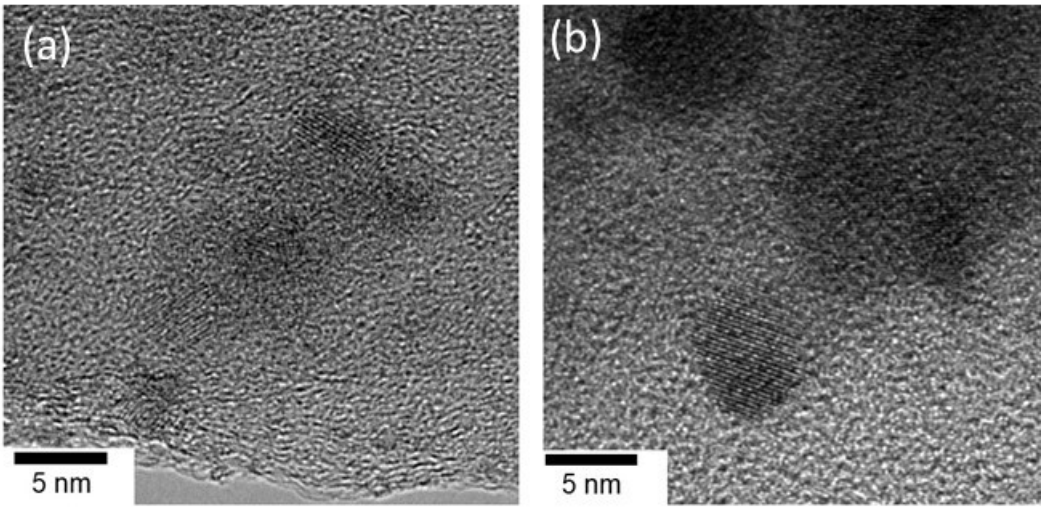

Figure S12. STEM images of the Sn/NrHGO electrode (a) before and (b) after the electrochemical test. The images obtained after a 1 h CA test showed that the Sn particles almost retained their original shape and sizes.

Table S2. Comparison of the performance of Sn/NrepGO with the reported catalysts.

Catalyst	electrolyte	Sn quantity (mg/cm^2)	Applied voltage (vs. RHE)	FE for formic acid	Ref.
Sn/NrepGO	1 M KOH	0.34	-0.57	75	This work
Sn NP/C-GDE	0.5 M $KHCO_3$	0.75	-1.5	70	[1]
CuSn	0.5 M $KHCO_3$	N/A	-1.3	57	[2]
SnO_2/carbon black	0.1 M $NaHCO_3$	0.212	-1.8	86	[3]
Sn/rGO_800	0.1 M $KHCO_3$	0.510	-0.82	98	[4]

(1) A. Del Castillo, M. Alvarez-Guerra, J. Solla-Gullón, A. Sáez, V. Montiel and A. Irabien, *J. CO_2 Util.*, 2017, **18**, 222–228.
(2) M. Watanabe, M. Shibata, A. Kato, M. Azuma and T. Sakata, *J. Electrochem. Soc.*, 1991, **138**, 3382.
(3) S. Zhang, P. Kang and T. J. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 1734–1737.
(4) T. Tsujiguchi, Y. Kawabe, S. Jeong, T. Ohto, S. Kukunuri, H. Kuramochi, Y. Takahashi, T. Nishiuchi, H. Masuda, M. Wakisaka, K. Hu, G. Elumalai, J. Fujita and Y. Ito, *ACS Catal.*, 2021, **11**, 3310–3318.