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

Creating electron-rich region on ultrafine Bi_2O_3 nanoparticles to boost the electrochemical carbon dioxide reduction to formate

Jiayu Zhan,[a] Lu-Hua Zhang,*[a] Xueli Wang,[a] Yuqi Hu,[a] Yi Jiang,*[b] and Fengshou Yu*[a]

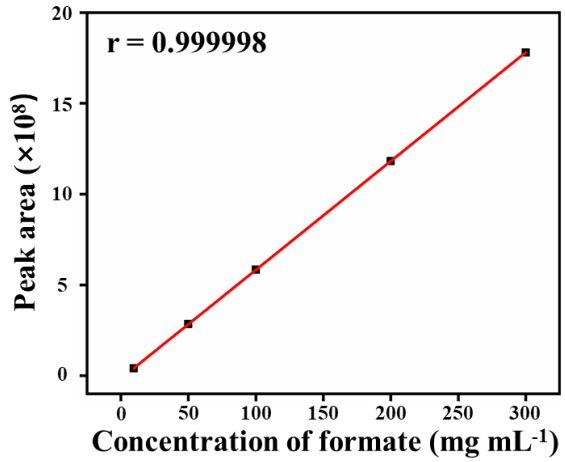

Figure S1. Linear relationship between the formate concentration and peak area

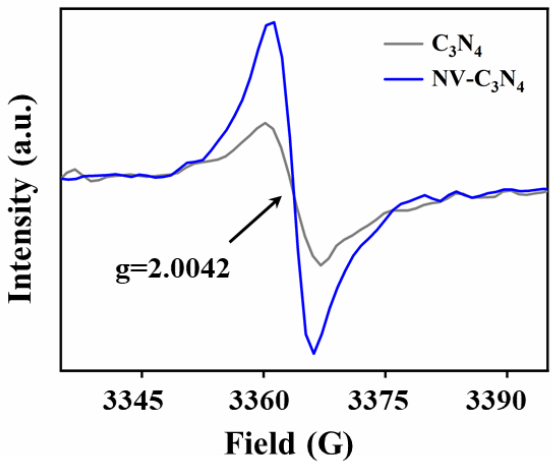

Figure S2. Solid EPR spectra of NV-C_3N_4 and C_3N_4

The paramagnetic absorption signal at g=2.0042 corresponds to the unpaired electrons captured by the NVs.

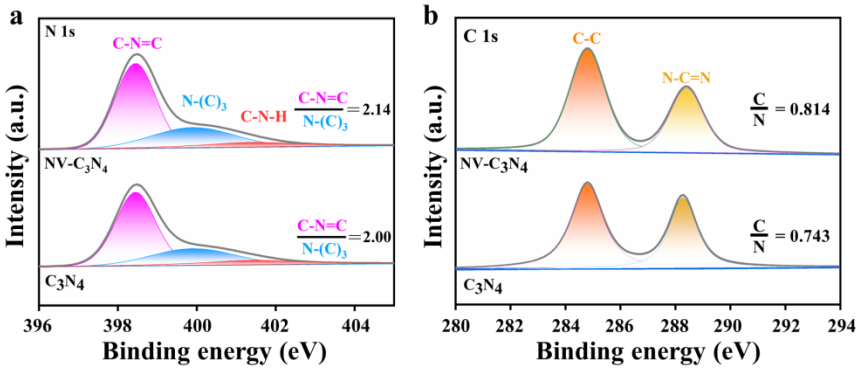

Figure S3. (a) N 1s spectra of NV-C_3N_4 and C_3N_4; (b) C 1s spectra of NV-C_3N_4 and C_3N_4

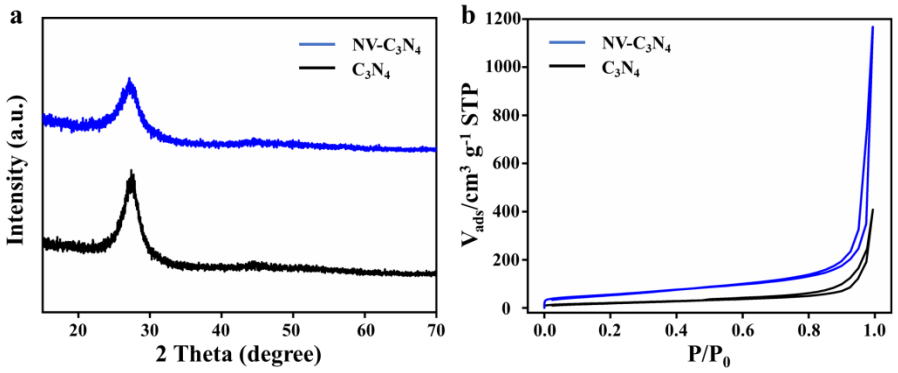

Figure S4. (a) XRD patterns and (b) N_2 adsorption isotherms for NV-C_3N_4 and C_3N_4.

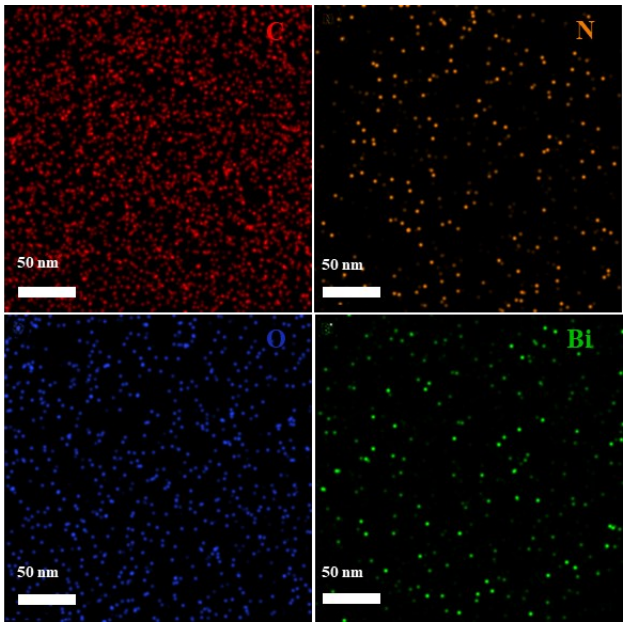

Figure S5. element mapping of Bi_2O_3/NV-C_3N_4.

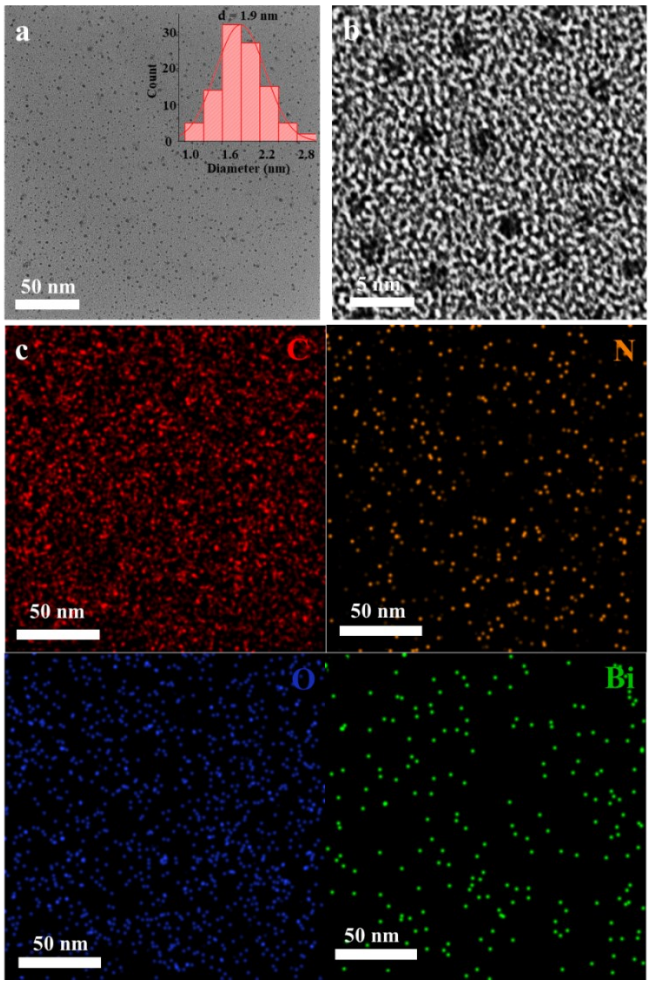

Figure S6. TEM images (a-b) and element mapping (c) of Bi_2O_3/C_3N_4

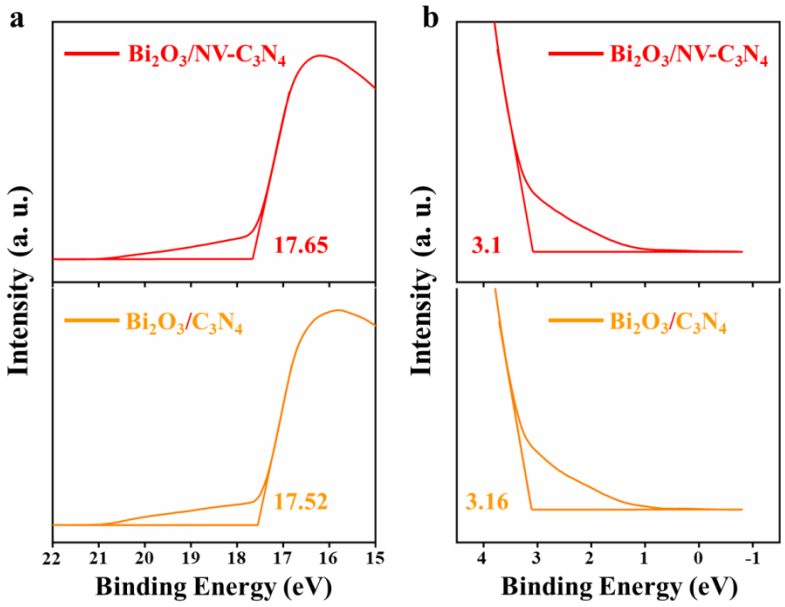

Figure S7. (a) Secondary electron cut-off energy ($E_{cut\text{-}off}$) for Bi_2O_3/NV-C_3N_4 and Bi_2O_3/C_3N_4 catalysts; (b) Onset(E_i) energy regions of Bi_2O_3/NV-C_3N_4 and Bi_2O_3/C_3N_4 samples. The work function calculated as the following equation, $\Phi = 21.22\ eV - (E_{cut\text{-}off} - E_i)$, is 6.67 eV and 6.86 eV for Bi_2O_3/NV-C_3N_4 and Bi_2O_3/C_3N_4 samples

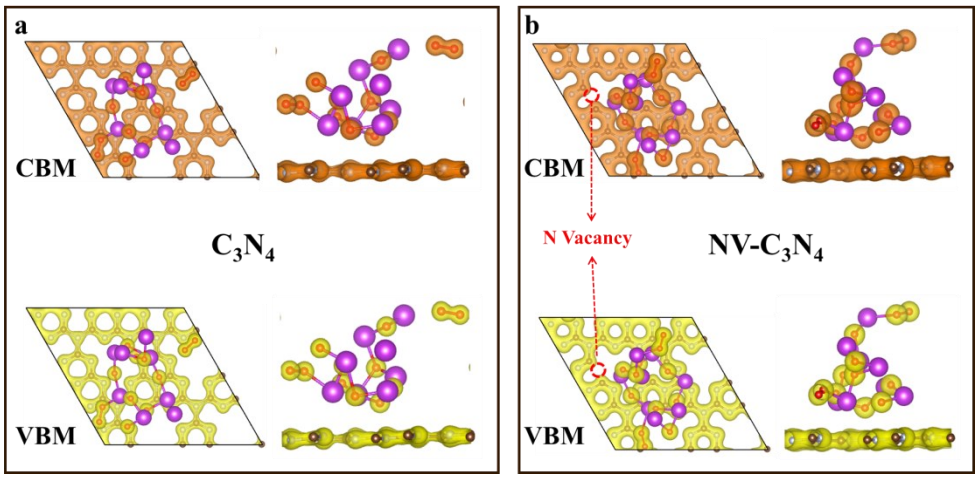

Figure S8. The DFT calculations of the electronic structure of (a) Bi_2O_3/C_3N_4 and (b) Bi_2O_3/NV-C_3N_4 with corresponding charge distribution of VBM (valence band maximum) and CBM (conduction band minimum).

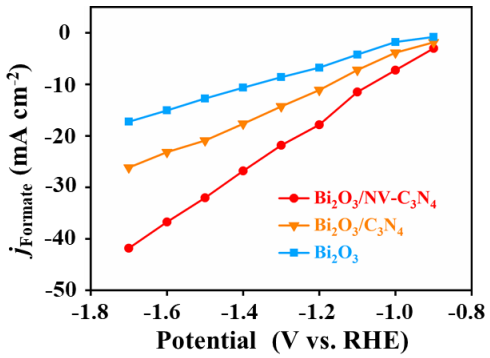

Figure S9. Partial current density of formate.

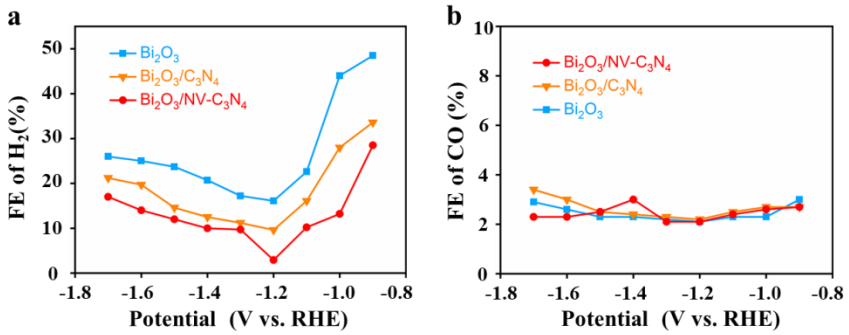

Figure S10. Bi_2O_3, Bi_2O_3/C_3N_4 and Bi_2O_3/NV-C_3N_4 (a) FE of H_2; (b) FE of CO.

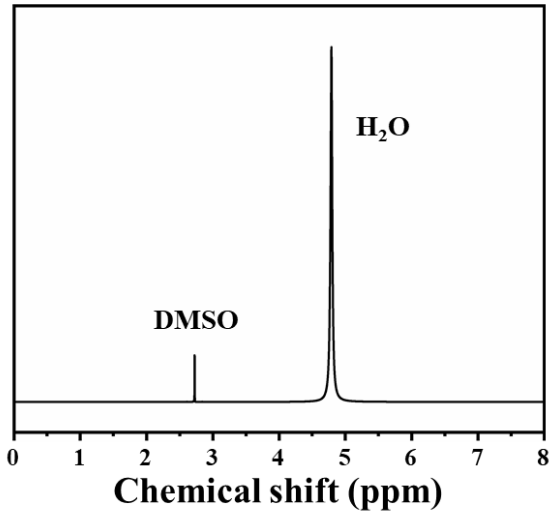

Figure S11. ^{1}H-NMR spectra of the liquid products from the CO_2RR

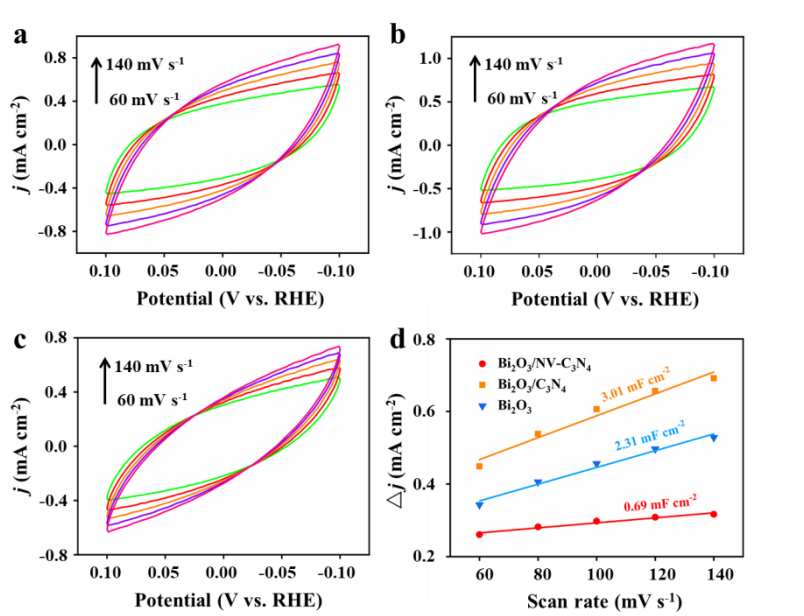

Figure S12. Cyclic voltammograms at the range of -0.10 to 0.10 V vs. RHE with different scan rates (60, 80, 100, 120 and 140 mV s^{-1}) (a) Bi_2O_3; (b) Bi_2O_3/C_3N_4; (c) Bi_2O_3/NV-C_3N_4; (d) Charging current density differences plotted against scan rates.

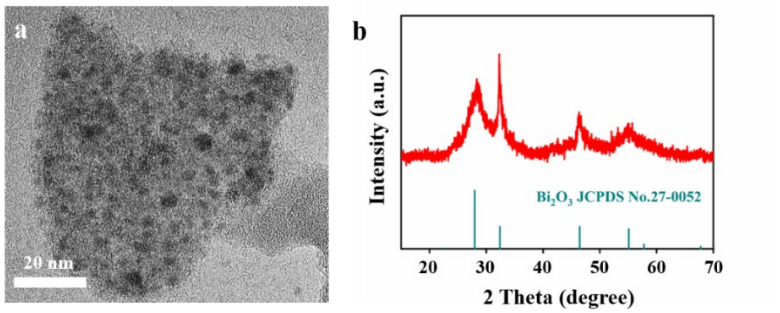

Figure S13. Bi_2O_3/NV-C_3N_4 (a) TEM after electrolysis; (b) XRD pattern after electrolysis.

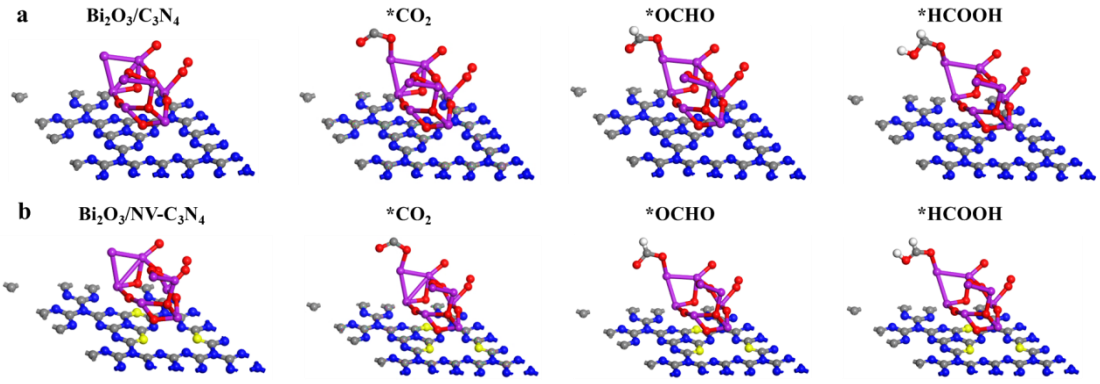

Figure S14. Optimized geometric structure models of three intermediate *CO_2, *OCHO and *HCOOH adsorbed on (a) Bi_2O_3/C_3N_4, (b) Bi_2O_3/NV-C_3N_4 surfaces; the purple, gray, red, and white spheres represent Bi, C, O, and H atoms, respectively; Especially, the yellow spheres in Bi_2O_3/NV-C_3N_4 represent the removed N atoms.

Table S1. Atomic percentage of different samples

Samples	Bi 4f at %	O 1s at %	C 1s at %	N 1s at %
C_3N_4	---	---	42.62	57.38
NV-C_3N_4	---	---	44.90	55.10
Bi_2O_3	18.79	52.47	28.74	---
Bi_2O_3/C_3N_4	17.03	44.22	25.92	12.83
Bi_2O_3/NV-C_3N_4	13.22	34.46	30.84	21.49

Table S2. Electrochemical CO_2 reduction performance of different Bi-based catalysts.

Catalysts	Maximum $FE_{Formate}$ (%)	Potential range of $FE_{Formate}$>80%	Stability time (h)	Reference
Bi_2O_3/NV-C_3N_4	95	700	24	This work
Bi/rGO	98	400	12	[1]
Bi@NPC	92	400	24	[2]
Bi (PC-6c)	100	400	10	[3]

Bi(B)-2	95	600	12	[4]
Bi nanosheets	86	200	10	[5]
Bi nanotubes	97	600	10	[6]
Bi-001	95.9	200	16	[7]
Bi NP@MWCNTs	95.2	100	10	[8]

References

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