# Two Birds with One Stone: High Catalytic Areas and Abundant Nitrogen Sites Inspired by Fluorine doping contributing to $CO_2RR$ Activity and Selectivity

Hongyu Chen,[a,b] Yi Zhang,[b] Tianfang Yang,[c] Yizhu Shang,[b] Qiuying Zhu,[b] Shoufu Cao,[b] Xiaojing Lin,[b] Siyuan Liu,[b] Shuxian Wei,[a] Baojun Wei,*[a] Zhaojie Wang,*[b] Xiaoqing Lu*[b]

[a]College of Science, China University of Petroleum, No.66 Changjiang West road, Huangdao District, Qingdao, Shandong 266580, P. R. China

[b]School of Materials Science and Engineering, China University of Petroleum, No.66 Changjiang West road, Huangdao District, Qingdao, Shandong 266580, P. R. China

[c]College of Arts and Science, China University of Petroleum-Beijing at Karamay, No. 355 Anding Road, Karamay District, Karamy, Xinjiang 834000, P.R. China

Corresponding Author:

*E-mail: weibj@upc. edu.cn, wangzhaojie@upc.edu.cn, luxq@upc.edu.cn

**Keywords:** Diverse heteroatoms, PVDF, Nitrogen fixator, $CO_2$ Electroreduction, CO

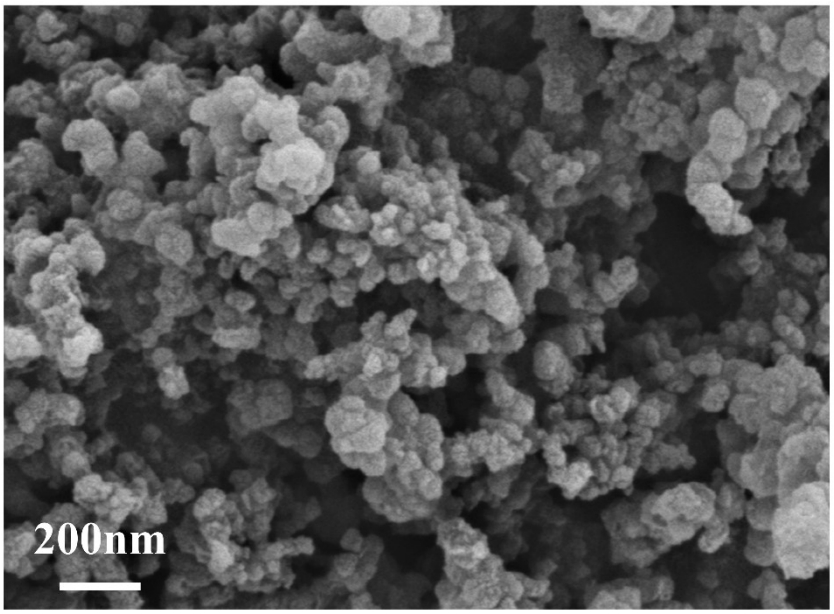


**Fig. S1.** SEM image of CB.

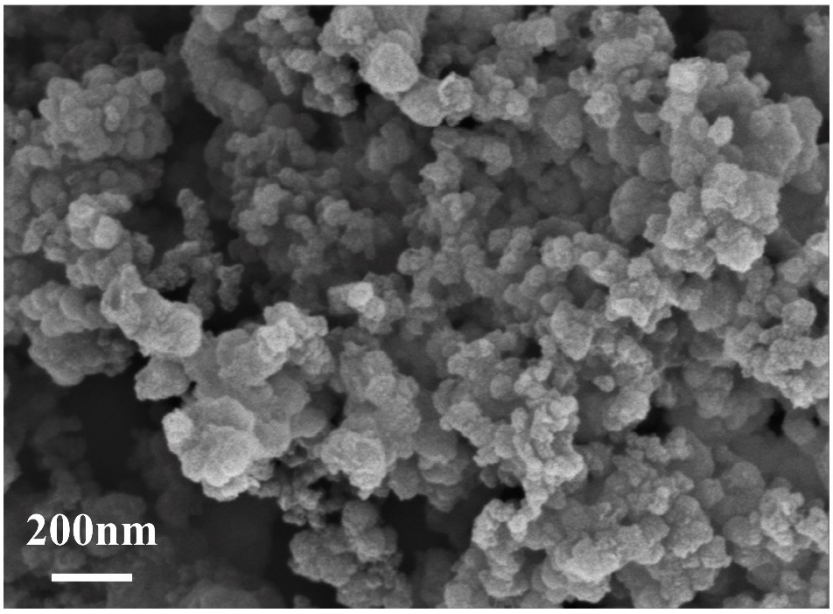


**Fig. S2.** SEM image of N-CB.

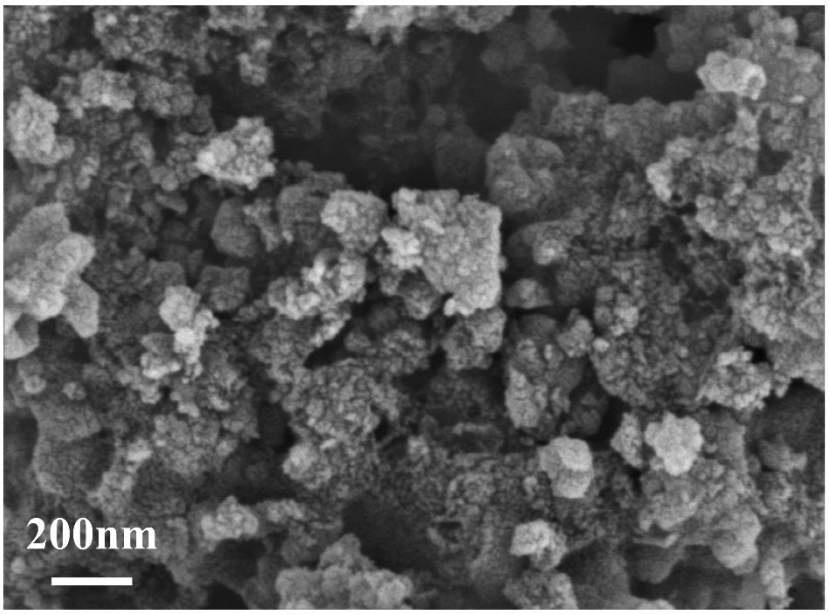


**Fig. S3.** SEM image of F-CB.

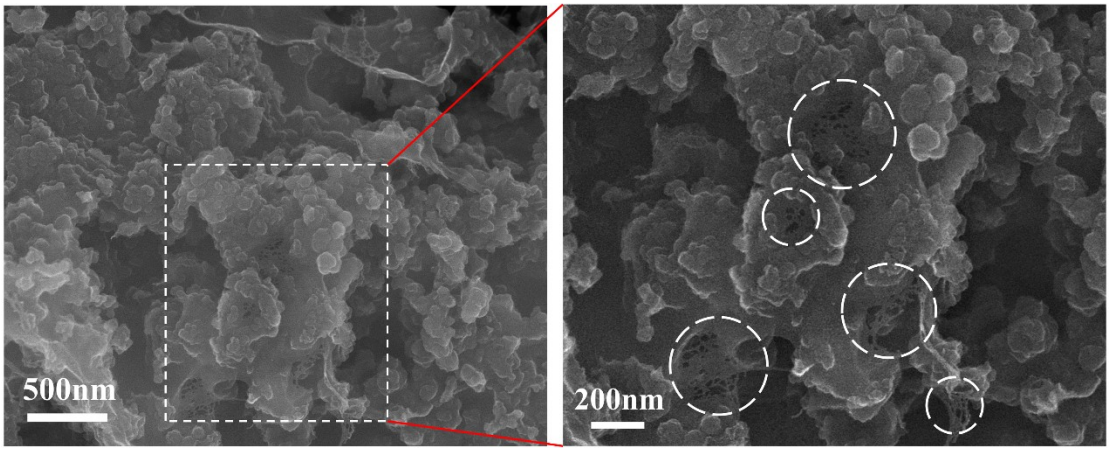


**Fig. S4.** SEM images of N,F-CB.

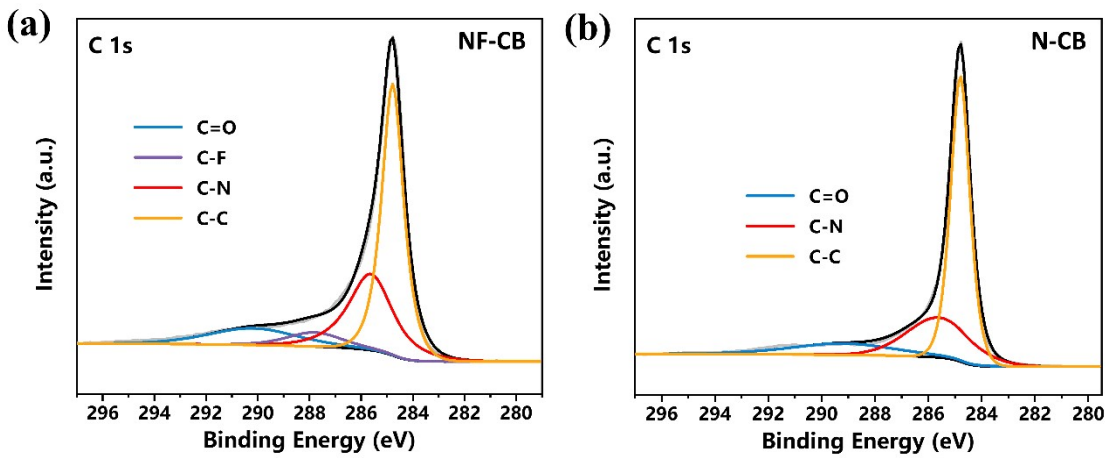


**Fig. S5.** High-resolution XPS spectra of C 1s of (a) N,F-CB and (b) N-CB.

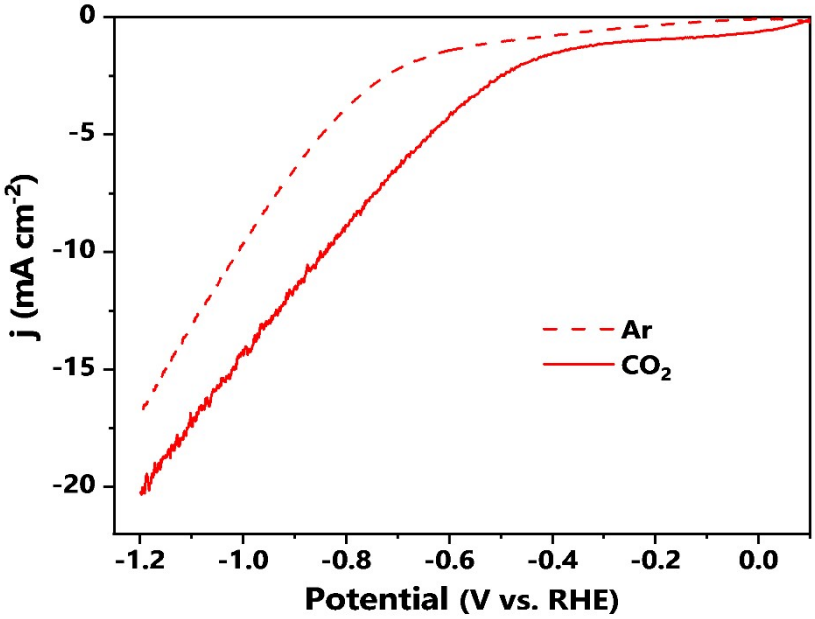


**Fig. S6.** LSV curves of N,F-CB in $CO_2$- or Ar-saturated 0.1 M $KHCO_3$ solutions.

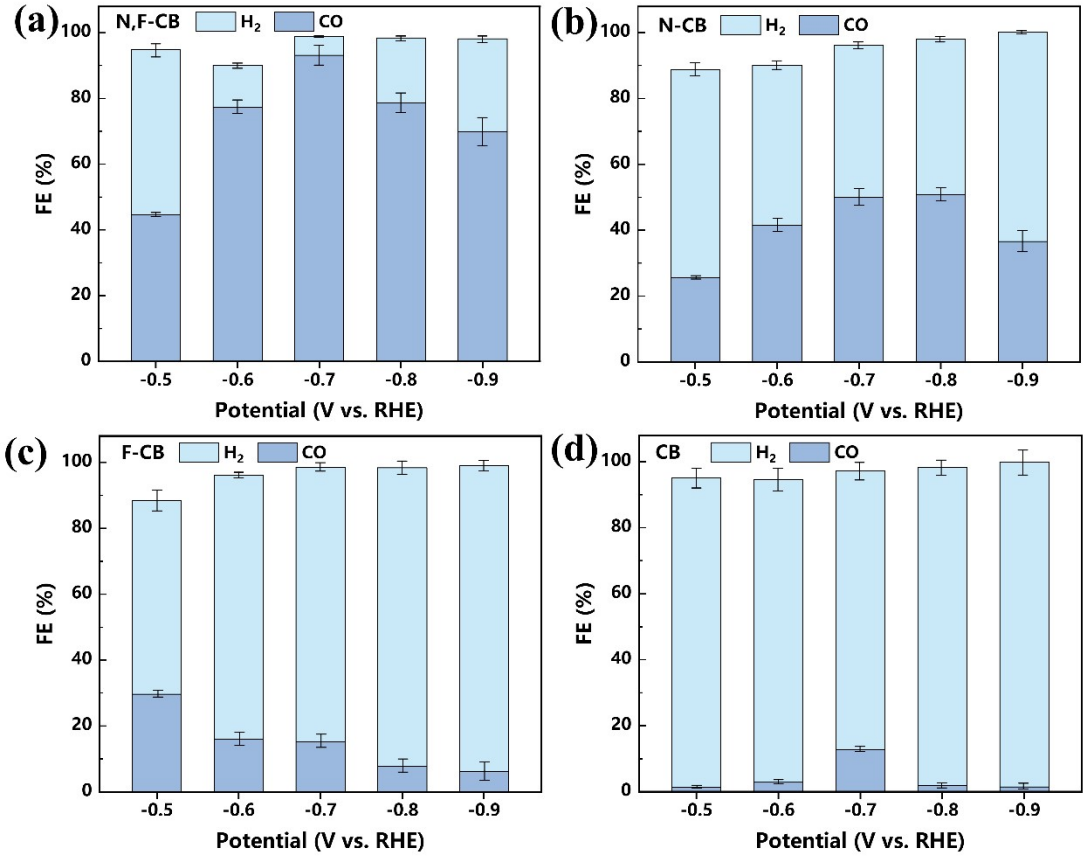


**Fig. S7.** Faradaic efficiencies of products for the (a) N,F-CB, (b) N-CB, (c) F-CB, (d) CB.

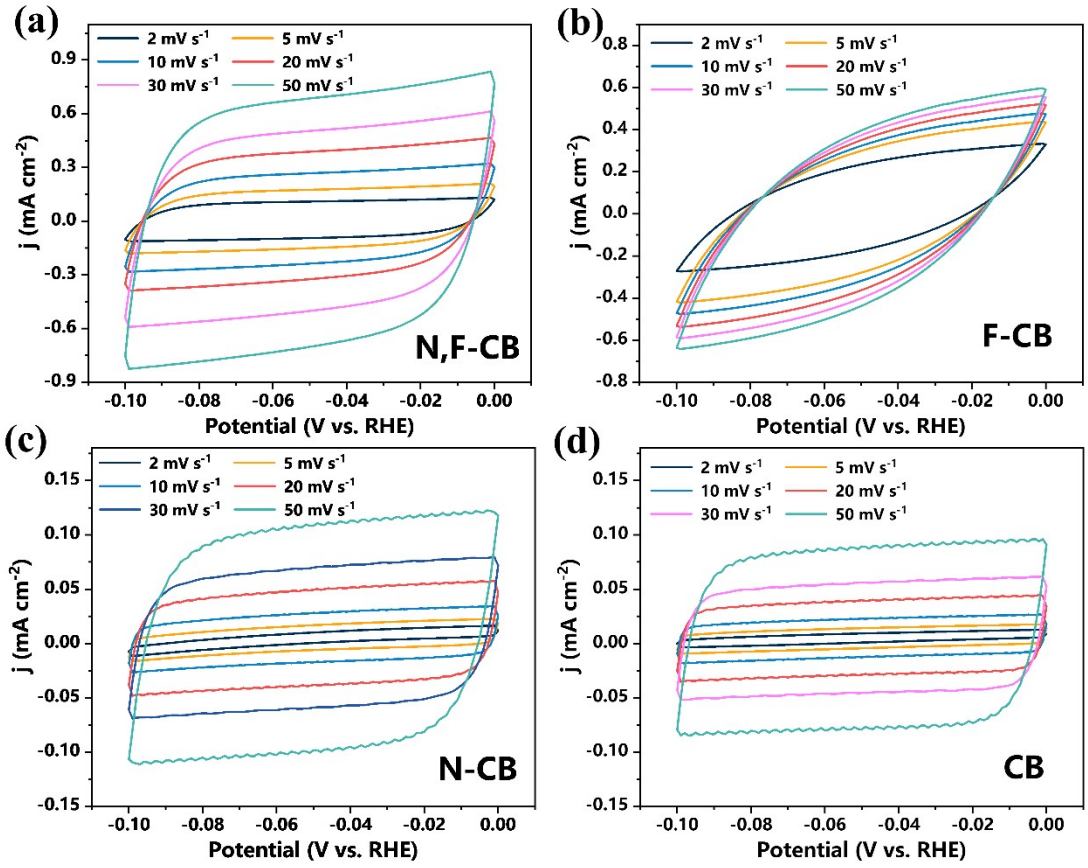


**Fig. S8.** The CV curves of (a) N,F-CB, (b) F-CB, (c) N-CB, and (d) CB measured in 0.1 M $KHCO_3$ solutions saturated with $CO_2$ at different scan rate from 2 to 50 mV $s^{-1}$ in the potential ranges of 0 V ~ -0.10 V vs. RHE.

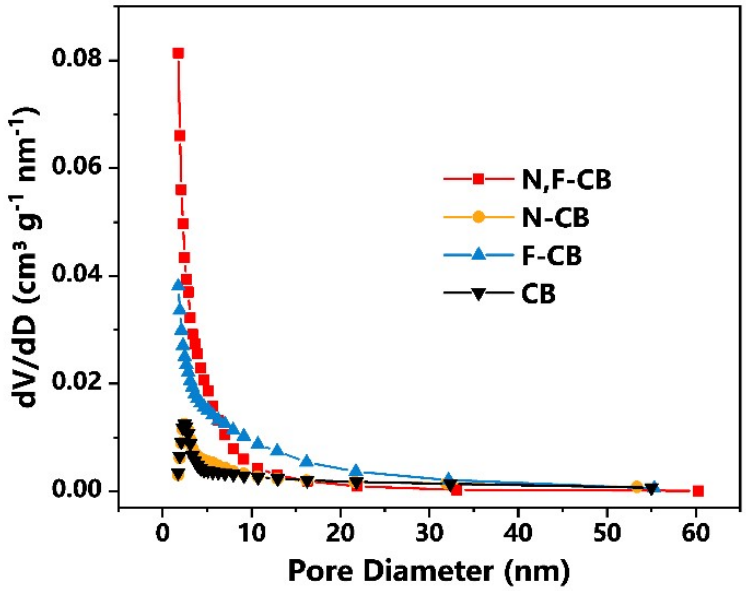


**Fig. S9.** The pore size distribution curves of N,F-CB, N-CB, F-CB, and CB.

**Table S1.** The N contents of catalysts summary from XPS analysis.

| | **N-CB** | **N,F-CB** |
|---|---|---|
| **N (at. %) of XPS** | 0.52 | 3.27 |
| Pyridinic N | 34.37% | 32.52% |
| Graphitic N | 38.57% | 39.34% |
| Pyrrolic N | 21.69% | 15.60% |
| Oxidized N | 5.37% | 12.54% |

**Table S2.** Summary of the reported nitrogen doped carbon electrocatalysts in $CO_2RR$.

| Electrocatalyst | Electrolyte ($KHCO_3$) | Potentials (V vs. RHE) | $FE_{CO}$ (%) | $j_{CO}$ (mA $cm^{-2}$) | Ref. |
|---|---|---|---|---|---|
| N,F-CB | 0.1 M | -0.7 | 93 | 4.6 | This work |
| Au-N-C | 0.1 M | -0.5 | 80 | 6 | S1 |
| NC($NH_3$) | 0.1 M | -0.5 | 83 | ~ | S2 |
| NS-CNSs-1000 | 0.5 M | -0.55 | 85.4 | 2.5 | S3 |
| MNC-D | 0.1 M | -0.58 | 92 | 6.8 | S4 |
| A-350-1000 | 0.1 M | -0.68 | 89 | 0.8 | S5 |
| NRMC-1000 | 0.1 M | -0.7 | 80 | 2.9 | S6 |
| NCNT-$NH_3$ | 0.5 M $NaHCO_3$ | -0.8 | 96.5 | ~13 | S7 |
| NCNTs | 0.1 M | -0.8 | 80 | -0.8 | S8 |
| N-graphenes | 0.5 M | -0.84 | 73 (Formate) | 7.0 | S9 |
| NCNT-3-700 | 0.5 M $NaHCO_3$ | -0.9 | 90 | 5.0 | S10 |
| NC-900 | 0.1 M | -0.93 | 78 | 0.8 | S11 |
| NCNTs-ACN-850 | 0.1 M | -1.05 | 80 | ~ | S12 |
| g-$C_3N_4$/ MWCNTs | 0.1 M | -0.75 | 60 | 0.55 | S13 |
| BAX-M-950 | 0.1 M | -0.66 | 40 | 1.5 | S14 |

**Table S3.** The double layer capacitance of different catalysts and the corresponding normalized roughness factor.

| Catalysts | $C_{dl}$ (mF $cm^{-2}$) | $R_f$ |
|---|---|---|
| CB | 1.68 | 1 |
| N-CB | 2.05 | 1.22 |
| F-CB | 5.22 | 3.11 |
| N,F-CB | 11.56 | 6.88 |

**References**

S1 A. S. Varela, N. R. Sahraie, J. Steinberg, W. Ju, H. S. Oh and P. Strasser, *Angew. Chem. Int. Ed.*, 2015, **54,** 10758-10762.

S2 W. O. Silva, G. C. Silva, R. F. Webster, T. M. Benedetti, R. D. Tilley and E. A. Ticianelli, *ChemElectroChem*, 2019, **6,** 4626-4636.

S3 G. Wang, M. Liu, J. Jia, H. Xu, B. Zhao, K. Lai, C. Tu and Z. Wen, *ChemCatChem*, 2020, **12,** 2203-2208.

S4 M. Kuang, A. Guan, Z. Gu, P. Han, L. Qian and G. Zheng, *Nano Research*, 2019, **12,** 2324-2329.

S5 M. Chen, S. Wang, H. Zhang, P. Zhang, Z. Tian, M. Lu, X. Xie, L. Huang and W. Huang, *Nano Research*, 2020, **13,** 729-735.

S6 R. Daiyan, X. Tan, R. Chen, W. H. Saputera, H. A. Tahini, E. Lovell, Y. H. Ng, S. C. Smith, L. Dai, X. Lu and R. Amal, *ACS Energy Lett.*, 2018, **3,** 2292-2298.

S7 C. Ma, P. Hou, X. Wang, Z. Wang, W. Li and P. Kang, *Appl. Catal. B-Environ.*, 2019, **250,** 347-354.

S8 J. Wu, R. M. Yadav, M. Liu, P. P. Sharma, C. S. Tiwary, L. Ma, X. Zou, X. Zhou, B. I. Yakobson, J. Lou and P. M. Ajayan, *ACS Nano*, 2015, **9,** 5364-5371.

S9 H. Wang, Y. Chen, X. Hou, C. Ma and T. Tan, *Green Chem.*, 2016, **18,** 3250.

S10 J. Xu, Y. Kan, R. Huang, B. Zhang, B. Wang, K. H. Wu, Y. Lin, X. Sun, Q. Li, G. Centi and D. Su, *ChemSusChem*, 2016, **9,** 1085-1089.

S11 R. Wang, X. Sun, S. Ould-Chikh, D. Osadchii, F. Bai, F. Kapteijn and J. Gascon, *ACS Appl. Mater. Interfaces*, 2018, **10,** 14751-14758.

S12 P. P. Sharma, J. Wu, R. M. Yadav, M. Liu, C. J. Wright, C. S. Tiwary, B. I. Yakobson, J. Lou, P. M. Ajayan and X. Zhou, *Angew. Chem. Int. Ed.*, 2015, **54,** 13701-13705.

S13 X. Lu, T. H. Tan, Y. H. Ng and R. Amal, *Chem. Eur. J.*, 2016, **22,** 11991-11996.

S14 W. Li, B. Herkt, M. Seredych and T. J. Bandosz, *Appl. Catal. B-Environ.*, 2017, **207,** 195-206.