# Supporting Information

## Alignment of active sites on Ag-Ni catalysts for highly selective $CO_2$ Reduction to CO

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## Figures and Tables

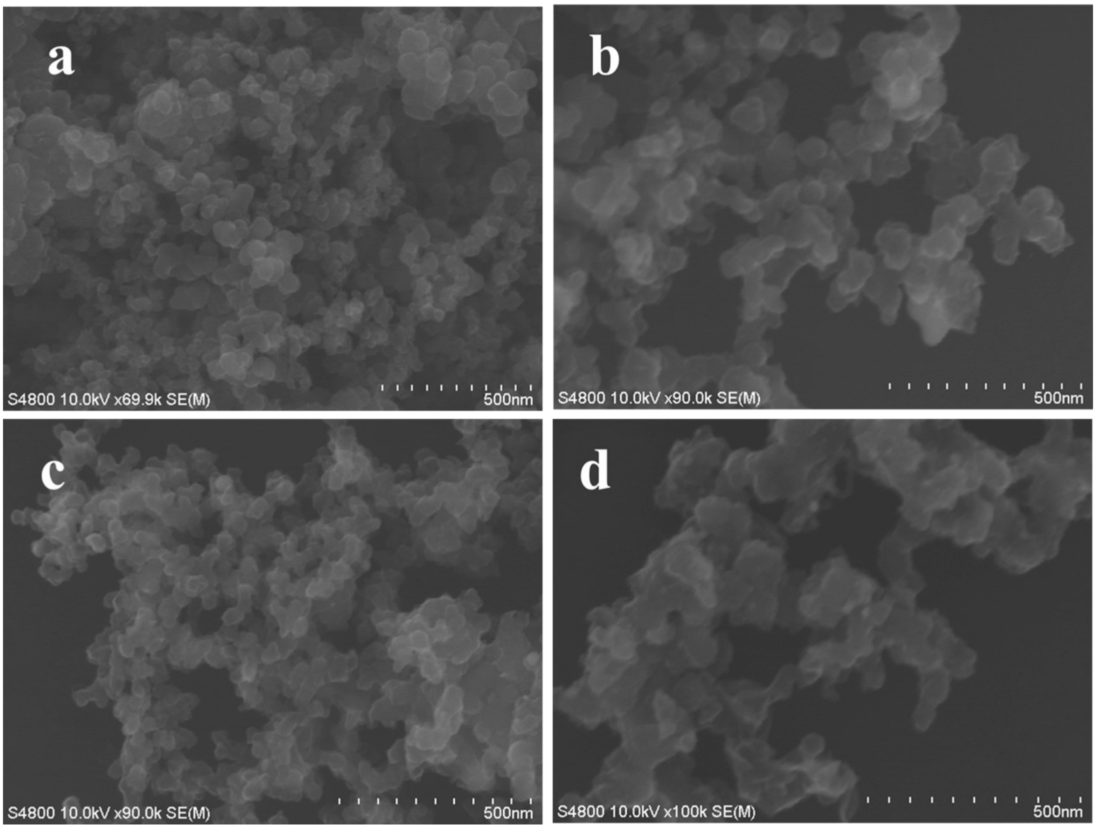


**Figure S1**. SEM images of (a) CB, (b) Ni/CB, (c) Ag/CB and (d) Ag-Ni/CB.

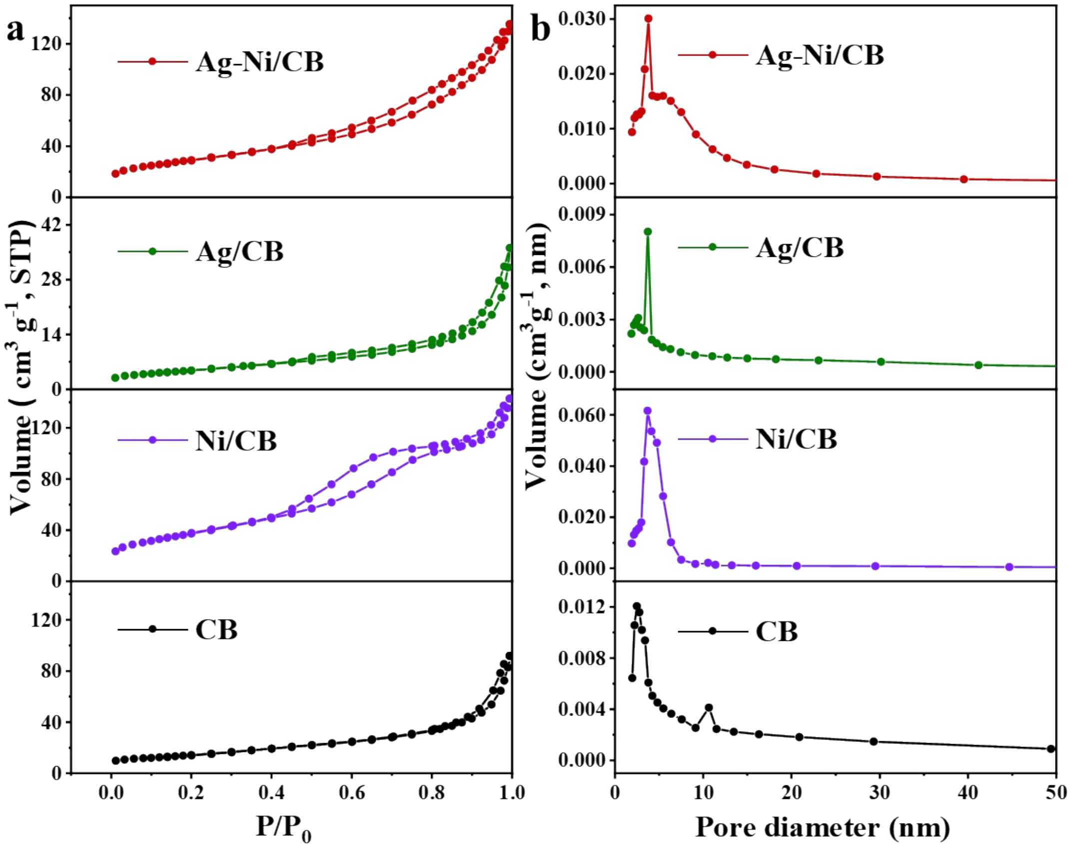


**Figure S2.** (a) $N_2$ adsorption-desorption isotherms and (b) the corresponding pore diameter distribution curves of CB, Ni/CB, Ag/CB and Ag-Ni/CB.

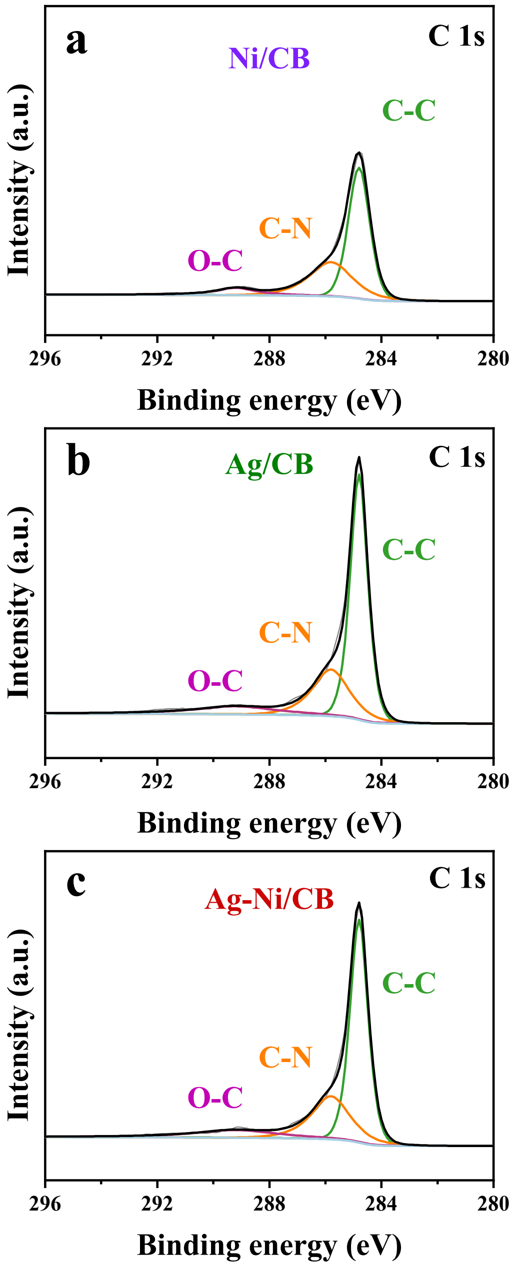


**Figure S3.** High resolution XPS spectra of C 1s for (a) Ni/CB, (b) Ag/CB and (c) Ag-Ni/CB.

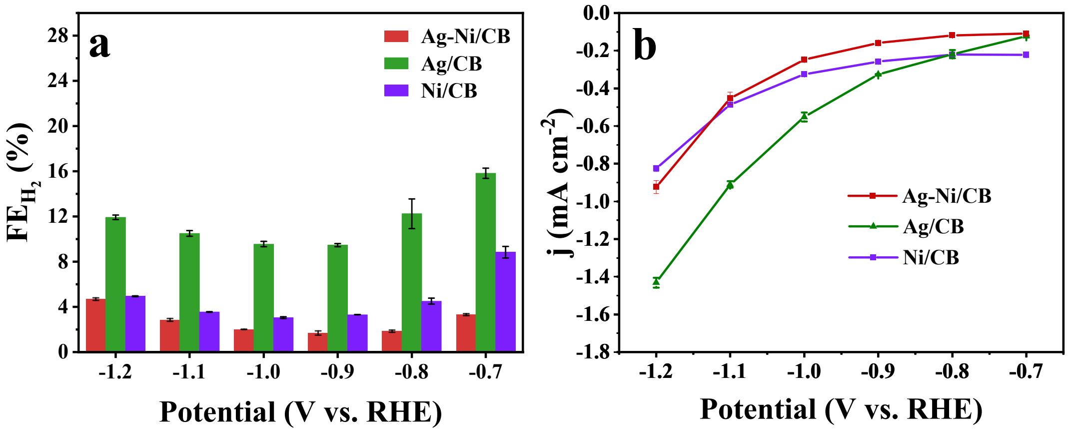


**Figure S4**. (a) Faradaic efficiencies and (b) partial current densities of $H_2$ over the Ni/CB, Ag/CB and Ag-Ni/CB at different applied potentials.

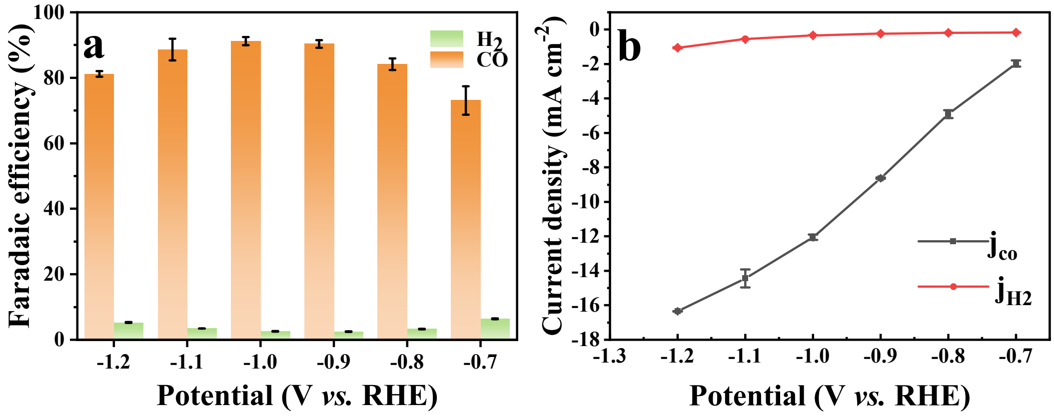


**Figure S5.** (a) Faradaic efficiencies and (b) partial current densities over the Ag-Ni/CB before acid leaching.

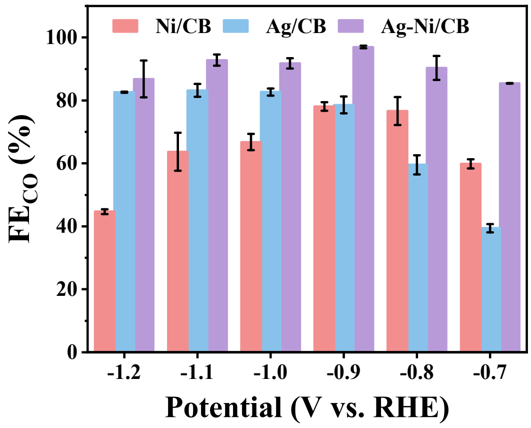


**Figure S6.** Faradaic efficiency of CO over the Ni/CB, Ag/CB and Ag-Ni/CB prepared using 1 M HCl as acid leaching solution.

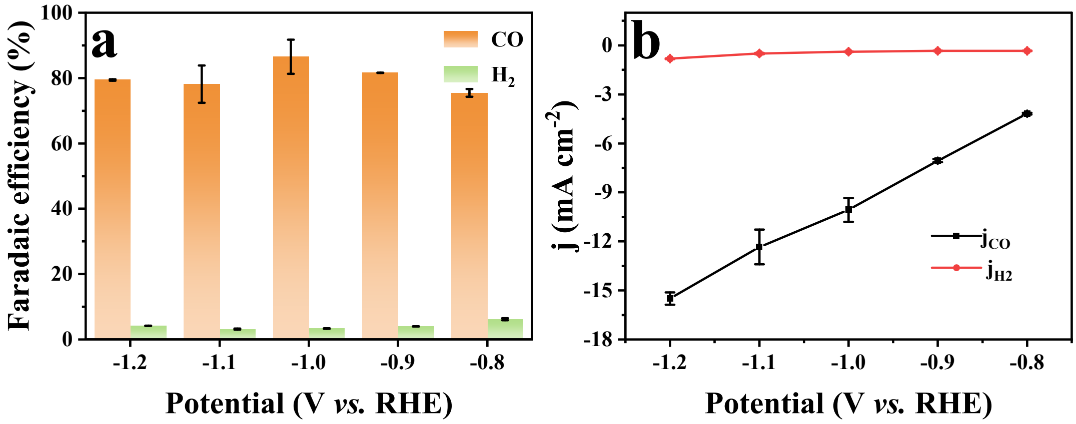


**Figure S7.** (a) Faradaic efficiencies and (b) partial current densities over the Ag-Ni/CB prepared using 1 M $HNO_3$ as acid leaching solution.

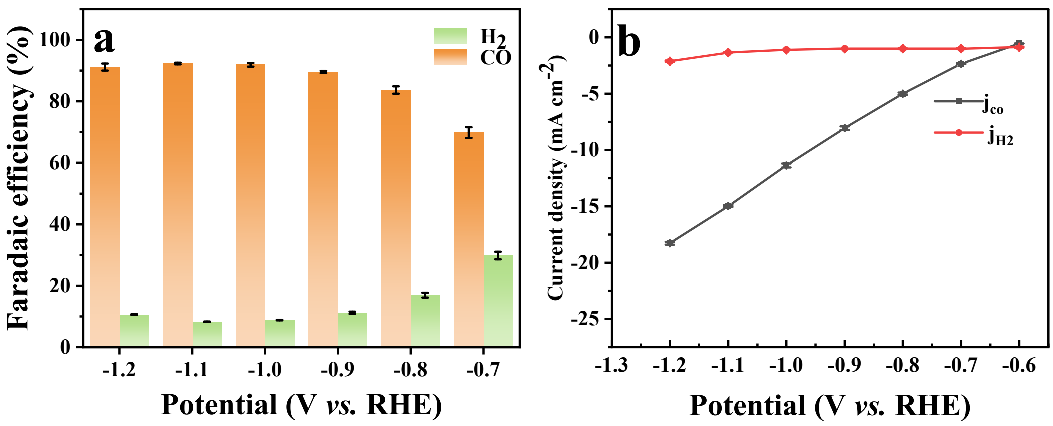


**Figure S8.** (a) Faradaic efficiencies and (b) partial current densities over the physically mixed Ag /CB and Ni/CB.

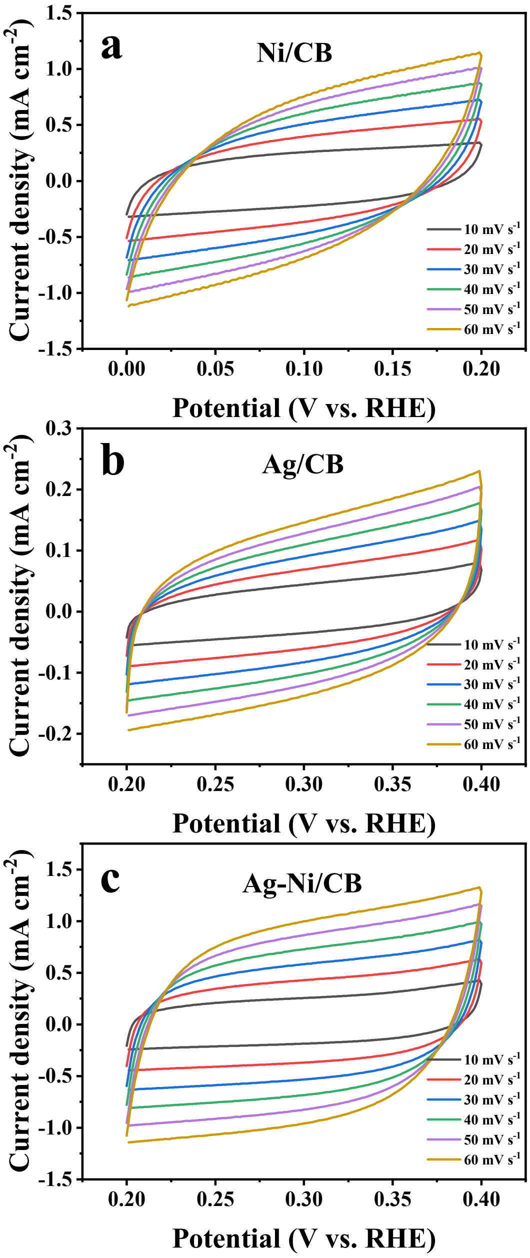


**Figure S9.** CV curves of the Ni/CB, Ag/CB and Ag-Ni/CB at various scan rates.

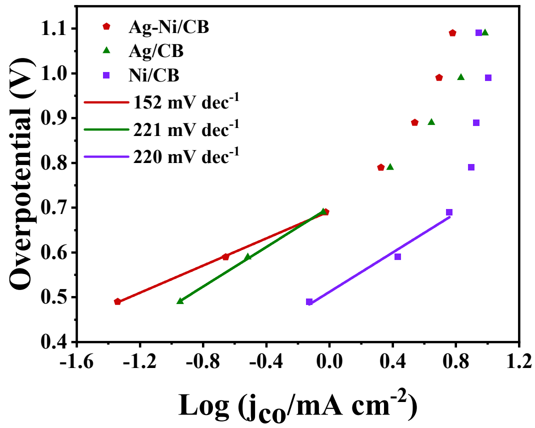


**Figure S10.** Tafel slopes of the Ni/CB, Ag/CB and Ag-Ni/CB catalysts.

**Table S1. ICP-OES results and textural properties of the as-synthesized samples.**

| Sample | Ni (wt%) | Ag (wt%) | BET surface area ($m^2$ $g^{-1}$) | Pore diameter (nm) | Pore volume ($cm^3$ $g^{-1}$) | Particle Size (nm) [a] |
|---|---|---|---|---|---|---|
| CB | -- | -- | 51.5 | 10.0 | 0.14 | -- |
| Ag/CB | -- | 34.8 | 17.6 | 10.7 | 0.06 | 77.0[b] |
| Ni/CB | 13.0 | -- | 133.9 | 5.4 | 0.23 | 19.2[c] |
| Ag-Ni/CB | 4.4 | 4.0 | 103.3 | 7.2 | 0.21 | 54.7[b]<br>14.3[c] |

(a) Calculated from the Scherrer equation. (b) Calculated from the reflection of Ag (111) at about 38°. (c) Calculated from the reflection of Ni (200) at about 51°.

**Table S2. Surface compositions of Ni species on the catalysts according to the XPS results.**

| Samples | $Ni^{2+}$ (%) | $Ni^{0}$ (%) |
|---|---|---|
| Ag-Ni/CB | 82.87 | 17.13 |
| Ni/CB | 84.91 | 15.09 |

**Table S3.** Relative compositions of the different nitrogen species on the surface of samples according to the XPS results.

| Samples | Pyrrolic N (%) | Pyridinic N (%) | Ni-N (%) | Graphitic N (%) |
|---|---|---|---|---|
| Ag-Ni/CB | 11.6 | 16.2 | 45.3 | 26.9 |
| Ag/CB | 13.0 | 52.3 | -- | 34.7 |
| Ni/CB | 9.8 | 27.5 | 42.7 | 20.0 |

**Table S4.** Comparison of $CO_2$RR performances of this work with the previous reported results.

| Catalyst | Electrolyte | Potential (V vs. RHE) | Max FE (%) | Reference |
|---|---|---|---|---|
| Ag-Ni/CB | 0.1 M $KHCO_3$ | -0.8 | 99.3 | This work |
| $Ag_2$-G | 0.5 M $KHCO_3$ | -0.7 | 93.4 | 1 |
| $Ag_{1.01\%}$/CuO | 0.1 M $KHCO_3$ | -0.7 | 91.2 | 2 |
| CuAg/$CeO_2$-6 | 0.1 M $KHCO_3$ | -1.1 | 84 | 3 |
| $In(OH)_3$-Ag/C | 0.1 M $KHCO_3$ | -0.7 | 93 | 4 |
| CuNi-N-CNS | 0.5 M $KHCO_3$ | -0.8 | 90 | 5 |
| Ni,N-C-800 | 0.1 M $KHCO_3$ | -0.86 | 94.8 | 6 |
| $Ni_{0.037}$-NG-H | 0.5 M $KHCO_3$ | -0.8 | 97.3 | 7 |
| Ni@NiNCM | 0.5 M $KHCO_3$ | -0.9 | 97.6 | 8 |
| Ni-SA-BB/C | 0.5 M $KHCO_3$ | -0.9 | 95 | 9 |
| CBNNiGd-700 | 0.5 M $KHCO_3$ | -1.0 | 97 | 10 |
| I-Ni SA/NHCRs | 0.25 M $NaHCO_3$ | -0.80 | 94.91 | 11 |
| $Ni_{NP2}$@$Ni_{SA2}$-NG | 0.25 M $KHCO_3$ | -0.79 | 96.6 | 12 |
| NiSAs@3D-INCT | 0.5 M $KHCO_3$ | -0.86 | 91.4 | 13 |
| CeNClCe$O_2$/Ni/N-C | 0.5 M $KHCO_3$ | -0.8 | 90 | 14 |
| Ni-NCNT-3HS | 0.5 M $KHCO_3$ | -0.7 | 97.4 | 15 |
| Ni-Ag/PC-N | 0.1 M $KHCO_3$ | -0.8 | 99.2 | 16 |
| NiSA/PCFM | 0.5 M $KHCO_3$ | -0.7 | 95 | 17 |

| Catalyst | Electrolyte | Potential (V vs. RHE) | Max FE (%) | Reference |
|---|---|---|---|---|
| Ni-SAC/SNC | 0.5 M $KHCO_3$ | -0.62 | 98 | 18 |
| Ni SAs/OMMNC | 0.5 M $KHCO_3$ | -0.6 | 99 | 19 |
| NiSA–VC/NCNFs | 0.1 M $KHCO_3$ | -0.98 | 99.2 | 20 |

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