Supplementary Information (SI) for Journal of Materials Chemistry A.


**Supporting Information for**

# Atomically Dispersed Copper in $TiO_2$ Supported NiO Nanoparticles Drives High $CH_4$ Productivity, Selectivity, and Stability in $CO_2$ Methanation Via Reversible Oxygen Vacancies Generation

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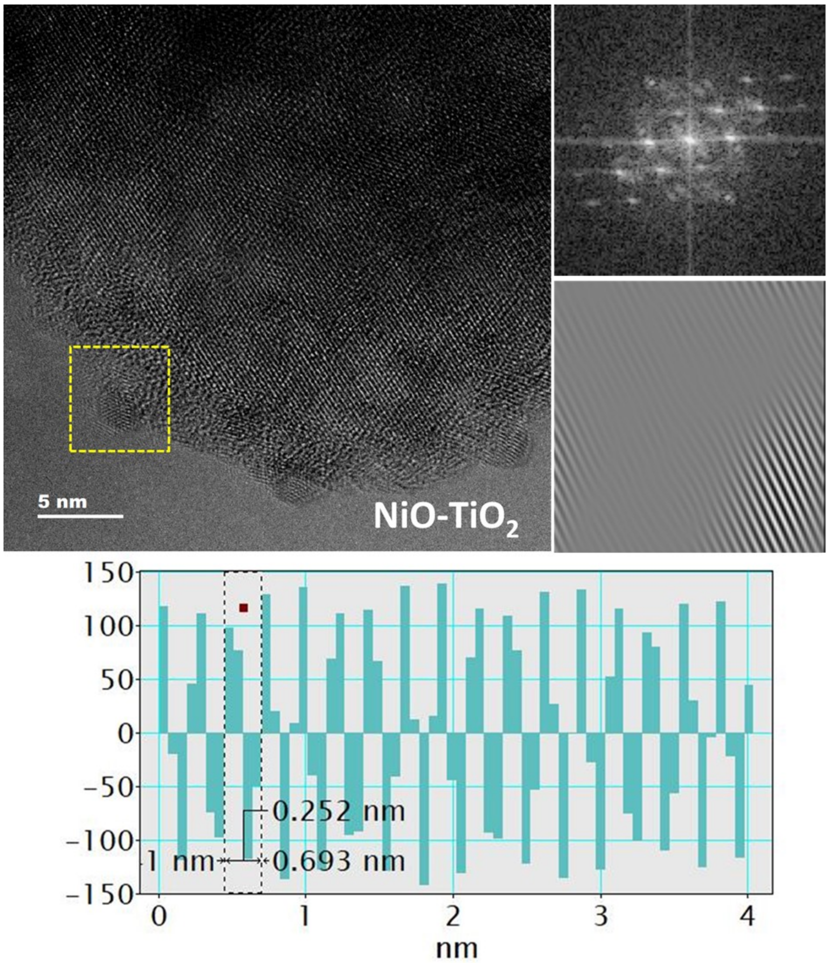



**Figure S1**. The HRTEM image of $NiO-TiO_2$ catalyst.

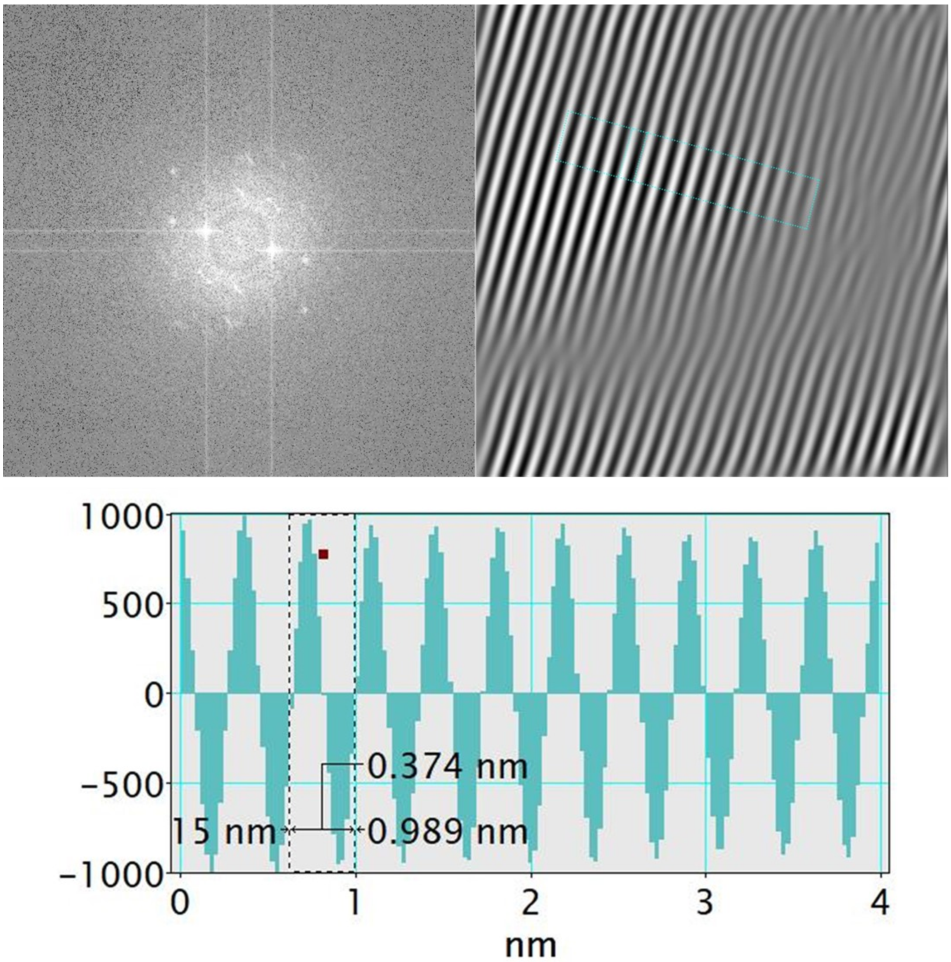



**Figure S2**. The FFT, IFT patterns and corresponding line histograms of NiO-Cu10 catalyst.

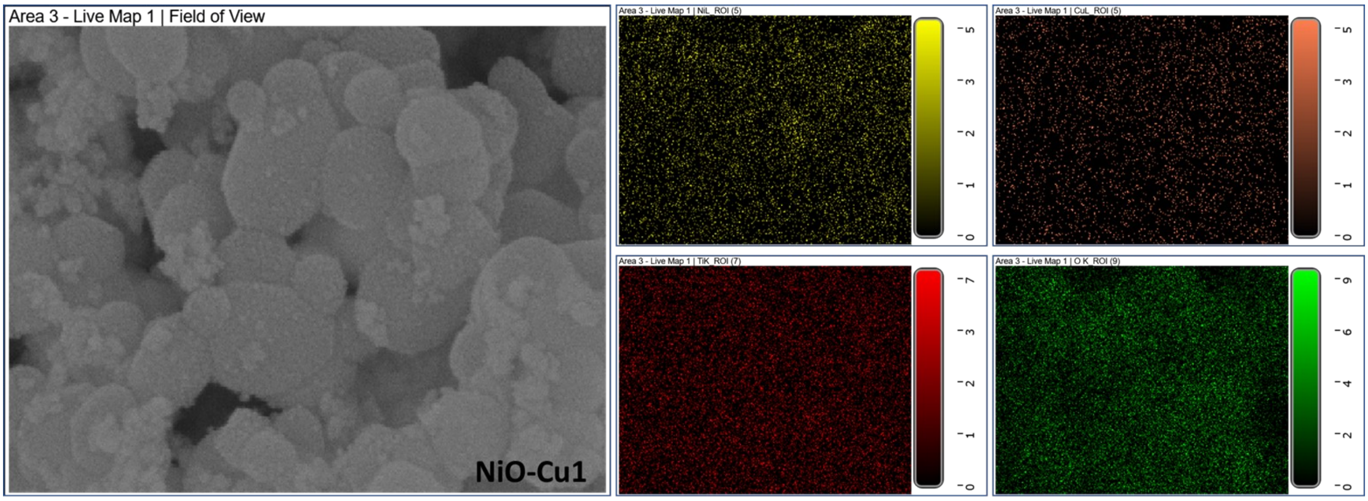
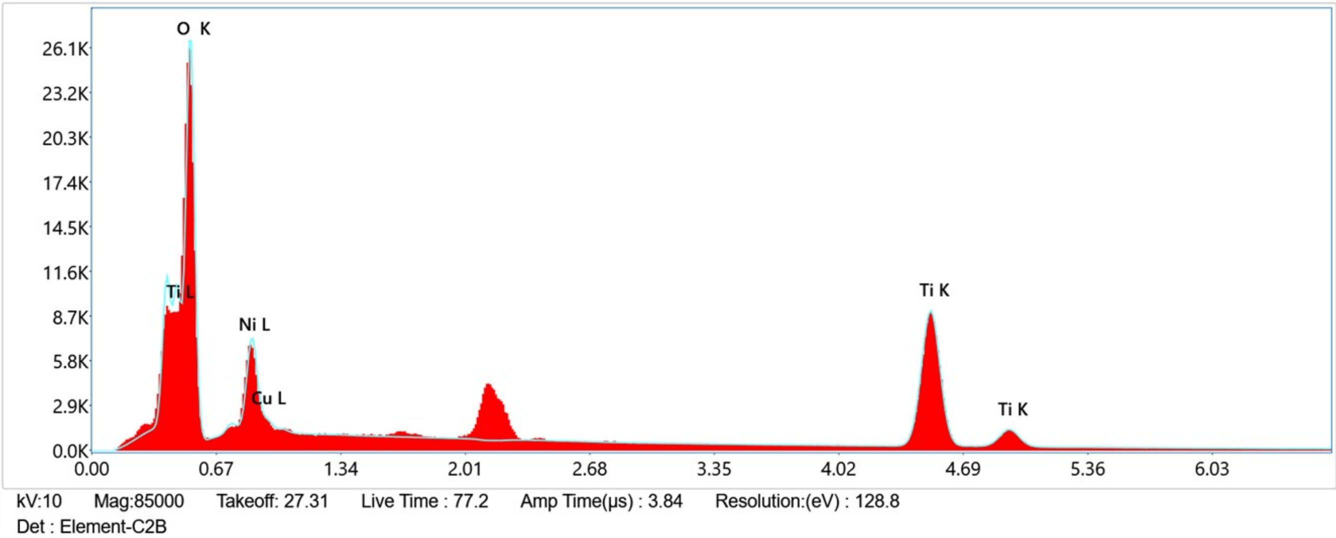



**Figure S3**. FESEM image and corresponding elemental mapping of NiO-Cu1 catalyst.




| **Element** | **Weight %** | **Atomic %** | **Error %** |
|---|---|---|---|
| O K | 44.3 | 71.2 | 10.1 |
| Ti K | 44.9 | 24.1 | 4.0 |
| Ni L | 9.7 | 4.2 | 9.7 |
| Cu L | 1.0 | 0.4 | 16.6 |

**Figure S4**. Energy-dispersive X-ray spectroscopy (EDS) analysis and associated quantitative elemental composition (inset table) of the NiO-Cu1 catalyst.

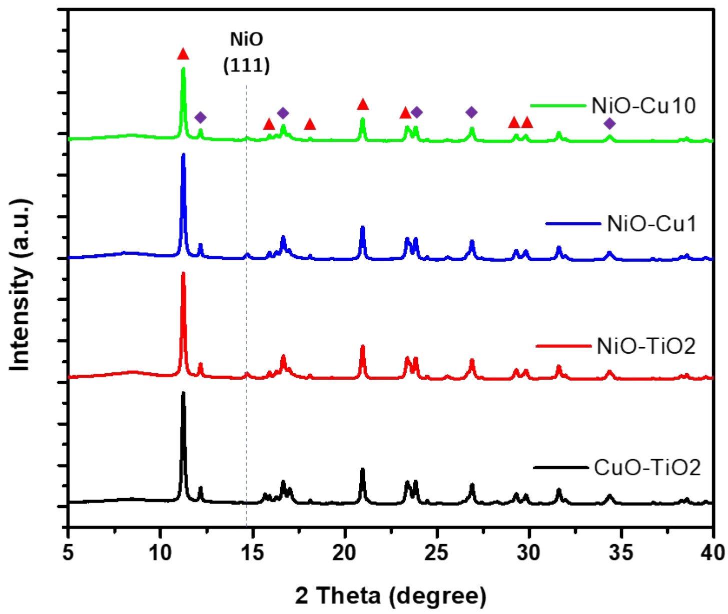



**Figure S5**. The XRD patterns of $CuO-TiO_2$, $NiO-TiO_2$, NiO-Cu1 and NiO-Cu10 catalysts.

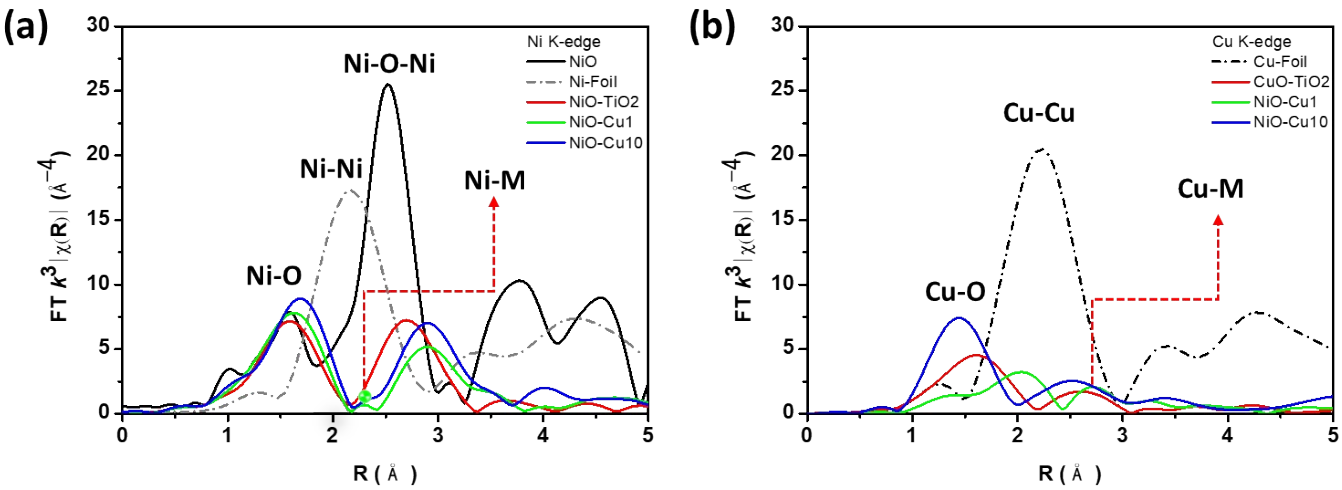



**Figure S6.** FT-EXAFS spectra at the (a) Ni K-edge and (b) Cu K-edge.

**Table S1.** Quantitative results obtained from XAS model fitting at the Ni and Cu K-edges.

| Sample | Ni K-edge | | | Cu K-edge | | |
|---|---|---|---|---|---|---|
| | bond pair | CN | R (Å) | bond pair | CN | R (Å) |
| NiO-Cu1 | Ni-Ni | 0.89 | 2.195 | Cu-Cu | 1.08 | 2.1.96 |
| | Ni-O | 4.45 | 2.047 | Cu-O | 2.43 | 2.009 |
| | Ni-Cu | 0.76 | 2.028 | Cu-Ni | 0.98 | 2.198 |
| NiO-Cu10 | Ni-Ni | N/A | | Cu-Cu | N/A | |
| | Ni-O | 5.58 | Cu-O | Cu-O | 5.27 | 2.014 |
| | Ni-Cu | N/A | | Cu-Ni | N/A | |
| $NiO-TiO_2$ | Ni-Ni | 0.75 | 2.196 | | N/A | |
| | Ni-O | 4.67 | 2.038 | | | |

**Catalytic Activity Measurement**

The catalytic activity of as-prepared catalysts has been measured as per the previously reported method. [22] The following steps have been used to calculate the $CH_4$ production yield:

1. In the first step, the full-scale GC curve has been obtained.
2. Then after, the peak area of $CH_4$ peak has been integrated.
3. The integrated area of $CH_4$ peak (Experimental sample) is divided by the integrated area of $CH_4$ peak (Pure $CH_4$ gas in a 20 sccm flow rate) and times the concentration of $CH_4$ (29.9 ppmv marked on gas bottle). ------ Eq. 1
4. Transform the unit of ppmv to µg: ppmv is divided by the volume (in normal temperature and pressure conditions, i.e. 24.45 litre) and times the molecular weight. ------Eq. 2

$$CH_4\,(\mu g) = CH_4 \div 24.45\,(\text{mole}) \times \text{M.W.}\,\left(\frac{g}{mole}\right)\left(\frac{\mu g}{g}\right) \text{ ------- Eq. 2}$$

6. Transform from µg to µmol: µg is divided by molecular weight. ------Eq. 3
7. Finally, µmol is divided by the weight of catalyst (g). ------Eq. 4
8. Furthermore, the unit $\mu$mol/gm has been changed to $m$mol/gm/h by using the following equation.

$CH_4$ productivity ($m$mol/gm/h) = $CH_4$ production yield ($\mu$mol/gm)*3600/1000.........Eq.5

➔ The $CH_4$ selectivity has been calculated by using the following equation:

$CH_4$ selectivity (%) = $CH_4$ Yield / CO Yield + $CH_4$ Yield * 100

**Table S2**. The benchmark table for the various catalysts for $CO_2$ methanation.

| Catalyst Support | Metal contents | Temperature ($^{o}$C) | Feeding gas | $S_{CH4}$ (%)* | $Yield_{CH4}$ (μmol/g) | References |
|---|---|---|---|---|---|---|
| $TiO_2$ | NiO-Cu1 | 300` | $CO_2$: $H_2$ = 1: 3 | 92.5 | 7916 | This study |
| $TiO_2$ | NiFe | 300` | $CO_2$: $H_2$ = 1: 3 | 92.5 | 6766.2 | Chemical Engineering Journal 493, 152834 |
| $TiO_2$ | Ni-SA+NP | 300` | $CO_2$: $H_2$ = 1: 3 | 90 | 4658 | *ChemCatChem 18 (1), e00938* |
| CNT | NiPd-TMOS ($NiO_TPd$-T) | ~300 | $CO_2$: $H_2$ = 1: 3 | N/A | 1905.1 | *J. Mater. Chem. A*, 2020,8, 12744-12756 |
| $Al_2O_3$ | 0.1% Pd, 10%Ni, 6.1% "$Na_2O$" | 500 | 7.5% $CO_2$, 15% $H_2/N_2$ | N/A | 180.0 | *Green Chemistry*, 2015, 17, 2647-2663. |
| | 0.1% Pt, 10%Ni, 6.1% "$Na_2O$" | | | | 160.0 | |
| | 1% Pt, 10%Ni, 6.1% "$Na_2O$" | | | | 250.0 | |
| | Ru15%CaO | 400 | 1.4% $CO_2$+ 10% $H_2$ | N/A | 414.0 | *Applied Catalysis B-Environmental*, 2019, 256, 11. |
| | 1% Ru, 10% Ni, 6.1% "$Na_2O$" | 320 | 7.5% $CO_2$, 15% $H_2/N_2$ | ~100 | 380.0 | *Green Chemistry*, 2015, 17, 2647-2663. |
| | Ru10%$Na_2CO_3$ | 310 | 1.4% $CO_2$+ 10% $H_2$ | N/A | 383.0 | *Applied Catalysis B-Environmental*, 2019, 256, 11. |
| | 5 wt.% Ni/2 wt.% ceria | 300 | $CO_2$: $H_2$ = 1: 4 | 100 | N/A | *Green Chemistry*, 2015, 17, 2647-2663. |
| | 20 wt.% Ni/H | 300 | | >99 | | |
| $ZrO_2$ | 2CA-Co/$ZrO_2$ | 400 | | 99 | | *Applied Catalysis B-Environmental*, 2019, 254, 531-540. |
| $SiO_2$ | Ni/SiOx-2 | 400 | | 91.4 | | *New Journal of Chemistry*, 2019, 43, 13217-13224. |
| | Ni/$SiO_2$ | 250 | | ~100 | | *Green Chemistry*, 2015, 17, 2647-2663. |
| $CeO_2$ | 10 wt% Ni/$CeO_2$ | 350 | | 100 | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 25Ni-20$CeO_2$ | 300 | | 100 | | *Fuel Processing Technology*, 2019, 193, 114-122. |
| | $NiFe_2O_4$ | 1273 K | 100 ml/min 50% $CO_2$/Ar | | 125.9 | *Applied Surface Science* **2019,** *489*, 693-700 |
| | $LaSrO_3$ | 1273 K | 100 ml/min 50% $CO_2$/Ar | | 124.1 | *Applied Surface Science* **2020,** *509*, 144908 |
| | $La_{0.3}Sr_{0.7}Co_{0.7}Fe_{0.3}O_3$ (LSCF) | 973 K | $H_2O$: $CO_2$ = 1: 1 | | 705 | *International Journal of Hydrogen Energy* **2021,** *46* (48), 24666-24675 |