Supporting information for

A Synergetic cocatalyst for conversion of carbon dioxide, sunlight and water into methanol

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This Supplementary Information file includes:

Figures S1 to S16 and Table S1 to Table S8:



Supplementary Figure 1 | XRD spectrum of InGaN/GaN nanowire samples. Local XRD spectrum of InGaN/GaN nanowire (a). Loaded co-catalysts nanoparticles are near undetectable for XRD measurement (b). Here we observed the Cu(111) peak as **Fig. 2c** shown.



Supplementary Figure 2 | **Cu metal LMM Auger absorption peak (918.7 eV).** Usually, Cu 2p XPS spectrum could not clearly tell the copper element is in its metal state or oxide state. But the Cu LMM Augur absorption peak proves the metal copper here.



Supplementary Figure 3 | Photoluminescence spectrum of as grown InGaN/GaN nanowire array.



Supplementary Figure 4 | **Time evolution of methanol and oxygen generation in a closed reaction chamber.** The reduction of generation rate is likely due to enhanced backward reaction. The reaction chamber is filled with CO₂ and deionized water with RhCr₂O₃Cu loaded InGaN/GaN wafer and is illuminated with a Xenon lamp equipped with an AM1.5G filter together with a 400 nm long pass filter.



Supplementary Figure 5 | GC-MS spectrum of ${}^{16}O_2$. O₂ generated from CO₂ reduction reaction with CO₂, deionized water, Rh/Cr₂O₃/Cu loaded InGaN/GaN wafer. The sample is illuminated with a Xenon lamp equipped with an AM1.5G filter together with a 400 nm long pass filter.



Supplementary Figure 6 | HADDF and EDS mapping of InGaN nanowires loaded with Cu and Cr_2O_3 (co-deposited) (a). No large particles can be observed on nanowires surface. EDS spectrum of InGaN nanowires loaded with Cu and Cr_2O_3 (co-deposited) (b). The chromium signals are fairly weaker than Cu signals.



Supplementary Figure 7 | EDS and HADDF of Cu@InGaN. Here we only applied copper precursor in the photo deposition. From EDS mapping and HAADF image, 10 nm level large particles were clearly dispersed on nanowire surface.



Supplementary Figure 8 | **GC 2010-Plus FID readout spectrum.** Methanol produced by Rh/Cu/Cr₂O₃@GaInN was marked as red line, standard methanol was marked as blue line and comparison group without catalysts was marked as black line.



Supplementary Figure 9 | SEM image of Rh/Cu/Cr₂O₃@InGaN/GaN nanowires sample after 12 circles. Top view (a) and 45°-tilted view (b).



Supplementary Figure 10 | **EDS mapping and HADDF of an Rh/Cu/Cr₂O₃@InGaN/GaN.** This figure shown that after one cycle reaction, the coated cocatalysts were well preserved, while for Rh/Cu/Cr₂O₃@InGaN/GaN after 12 cycles (**Fig. 4c**), most of the cocatalysts were removed.



Supplementary Figure 11 | Interaction energies between (a) Rh(111) and (b) Cu(111) and GaN(100) surfaces in the unit of eV/surface Rh(Cu) atom. Grey, blue, light blue and green balls represent Rh, Cu, N, and Ga atoms.



Supplementary Figure 12 | Growth Mechanism and calculated reaction free energies of CrOOH layers on M(111) Surfaces (M = Rh and Cu) in eV per CrOOH unit. Grey, brown, red, and white balls represent metal (Rh or Cu), Cr, O, and H atoms.



Supplementary Figure 13 | Layered CrOOH structure for efficient proton transfer. *a*) Layered structure of CrOOH determined by neutron diffraction with half occupancy of protons between different layers; *b*) DFT optimized layered structures of CrOOH on the Born-Oppenheimer potential energy surface; *c*) Potential energy curve of proton transfer between different CrOOH layers and the energy levels and wavefunctions of the first two vibrational states. r_{OH} is defined in Fig. S3*b*. The vibrational wave functions clearly indicated delocalized protons between nearby



Supplementary Figure 14 | Free energy profiles of CO_2 reduction of different reaction pathways in gas phase at 298.15 K. The pathway shown in black is the thermodynamically most favorable pathway. However, the pathway involves $*OCH_2O*$ is only slightly higher in free energy than that involves HCOOH* in gas phase. The relative free energy changes are calculated using CO_2 , H_2 , and the Cu(111) surface as the zero reference.



Supplementary Figure 15 | Free energy profiles of CO₂ reduction in gas phase and aqueous solution at 298.15 K. The relative free energy changes are calculated using CO₂, H₂, and the Cu(111) surface as the zero reference.



Supplementary Figure 16 | Free energy profile of CO₂ reduction by surface hydrogen atom using CO₂, the Cu(111) surface, and the Rh–H at the Rh(111)/CrOOH(001) interface with 3 layers of CrOOH as the zero-reference. The relative free energy between Rh–H at the

Rh(111)/CrOOH(001) interface with 3 layers of CrOOH with respect to $H_2(g)$ is +0.35 eV. The active *in situ* surface H atoms at the Rh(111)/CrOOH(001) interface provide thermodynamic driving force of the CO₂ reduction toward CH₃OH.

| lattice constants | <i>a</i> (Å) | <i>c</i> (Å) |
|----------------------------|--------------|--------------|
| exptl. ^{<i>a</i>} | 3.19 | 5.19 |
| PBE | 3.21 | 5.24 |
| PBE-D3 | 3.20 | 5.21 |

Table S1. Experimental and DFT optimized lattice constants of GaN.

^{*a*} Experimental lattice constants of GaN were taken from Ref. 1.

| Table S2. Experimenta | and DFT optimized lat | tice constants of Rh and Cu in Å. |
|-----------------------|-----------------------|-----------------------------------|
|-----------------------|-----------------------|-----------------------------------|

| | Cu | Rh |
|---------------------|------|------|
| exptl. ^a | 3.60 | 3.79 |
| PBE | 3.63 | 3.85 |
| PBE-D3 | 3.57 | 3.81 |

^{*a*} Experimental lattice constants of Cu and Rh were taken from Ref. 2.

Table S3. Experimental and DFT optimized lattice constants and key bond lengths of CrOOH

in Å.

| properties ^a | а | С | d _{Cr-O1} | d _{Cr-O2} | do-o' |
|-------------------------|------|-------|--------------------|--------------------|-------|
| exptl. ^b | 2.98 | 13.37 | 1.99 | 1.99 | 2.46 |
| PBE | 3.02 | 13.42 | 1.98 | 2.03 | 2.49 |
| PBE-D3 | 3.00 | 13.31 | 1.98 | 2.02 | 2.45 |
| $PBE+U(D3)^{c}$ | 3.03 | 13.30 | 2.01 | 2.03 | 2.42 |

^{*a*} O1 and O2 denote the O and OH in the same layer. $d_{O-O'}$ denotes the distance between O

atoms between two layers.

^{*b*} Experimental geometry taken from Ref. ³ Christensen, et al. J. Solid State Chem. 1977, 21, 325-329.

^{*c*} The U-J value was chosen to be 4 eV for calculation of CrOOH, as in Refs. 4 and 5.

Table S4. Mismatching of lattice constants between the GaN(10–10)/M(111) interface (M = Cu and Rh)^{*a*}

| | GaN(10-10) | Rh(111) | Cu(111) |
|-----------------------------------|------------|---------|---------|
| | | Expt. | |
| <i>a</i> (Å) | 3.19 | 4.65 | 4.40 |
| <i>b</i> (Å) | 5.19 | 2.68 | 2.52 |
| <i>a'</i> (Å) ^{<i>b</i>} | 9.57 | 9.29 | 8.81 |
| <i>b'</i> (Å) ^{<i>b</i>} | 5.19 | 5.36 | 5.05 |
| mismatch in a | | 3.0 | 8.6 |
| mismatch in b | | -3.2 | 2.8 |
| | | Calc. | |
| <i>a</i> (Å) | 3.20 | 4.67 | 4.37 |
| <i>b</i> (Å) | 5.21 | 2.70 | 2.52 |
| <i>a'</i> (Å) ^{<i>b</i>} | 9.59 | 9.34 | 8.74 |
| <i>b'</i> (Å) ^{<i>b</i>} | 5.21 | 5.39 | 5.05 |
| mismatch in <i>a</i> | | 2.7 | 9.7 |
| mismatch in b | | -3.3 | 3.2 |

^a Mismatching of lattice constants was calculated according to

Mismatching =
$$\frac{a_{core} - a_{shell}}{a_{shell}} \times 100\%$$
,

where a_{core} and a_{shell} are the lattice constants of the core and shell, respectively. By this definition, a negative mismatching indicates the compression of the shell lattice. We calculated the matching of lattice constants with both the experimental and DFT optimized lattice constants.

^{*b*} The *a*' and *b*' lattice vectors of GaN(10-10) supercell are $3 \times a$ and $1 \times b$, while those of M(111) supercell are $2 \times a$ and $2 \times b$.

Table S5. Mismatching of lattice constants (%) between the M(111) and CrOOH (001) (M = Cu and Rh) and Rh(111)/Cu(111) core-shell interfaces ^{*a*}

| | Cu(111)/CrOOH(001) | Rh(111)/CrOOH(001) | Rh(111)/Cu(111) |
|----------------|--------------------|--------------------|-----------------|
| Expt. Lattices | -14.6 | -10.0 | 5.5 |
| Calc. Lattices | -16.7 | -11.0 | 6.8 |

^a Mismatching of lattice constants was calculated according to

$$\text{Mismatching} = \frac{a_{core} - a_{shell}}{a_{shell}} \times 100\%,$$

where a_{core} and a_{shell} are the lattice constants of the core and shell, respectively. By this definition, a negative mismatching indicates the compression of the shell lattice. We calculated the matching of lattice constants with both the experimental and DFT optimized lattice constants.

Table S6. Calculated hydrogen adsorption energies and free energies on Cu(111), Rh(111), andRh(111)/CrOOH(001) interface.

| | high coverage ($\theta = 1$) | | low coverage ($\theta = 1/12$) | |
|--------------------|--------------------------------|----------------|----------------------------------|----------------|
| | $\Delta E(eV)$ | $\Delta G(eV)$ | $\Delta E(eV)$ | $\Delta G(eV)$ |
| Cu(111) | -0.29 | -0.07 | -0.34 | -0.14 |
| Rh(111) | -0.51 | -0.32 | -0.64 | -0.45 |
| Rh(111)/CrOOH(001) | | | | |
| (1-layer CrOOH) | -0.14 | 0.06 | | |
| Rh(111)/CrOOH(001) | | | | |
| (2-layer CrOOH) | 0.08 | 0.30 | | |
| Rh(111)/CrOOH(001) | | | | |
| (3-layer CrOOH) | 0.14 | 0.35 | 0.17 | 0.42 |

Table S7. Charges of intermediates in the CO₂ reduction based on Bader charge analysis.

| intermediates | Charges on adsorbates (e) |
|-------------------------|---------------------------|
| *H | -0.30 |
| *OOCH | -0.63 |
| *HOOCH | 0.00 |
| *HOCH ₂ O* | -0.60 |
| *OH + *OCH ₃ | -1.14 |
| *OCH ₃ | -0.56 |
| *HOCH3 | 0.00 |
| *OCH ₂ O* | -1.14 |
| *OCH ₂ * | -0.51 |

Table S8. Calculated electronic energies, thermal correction to free energies at 298.15 K and

| | E(eV) | G - E (eV) | $\Delta G_{ m solv} ({ m eV})$ |
|-----------------------|---------|------------|--------------------------------|
| * | -240.13 | 0.00 | 0.06 |
| *Н | -243.85 | 0.17 | 0.06 |
| *OOCH | -267.30 | 0.51 | -0.05 |
| *HOOCH | -270.21 | 0.75 | -0.47 |
| *HOCH ₂ O* | -274.22 | 1.13 | -0.11 |
| *OH + *OCH3 | -278.23 | 1.31 | -0.12 |
| *OCH ₃ | -267.32 | 1.03 | 0.02 |
| *HOCH3 | -270.92 | 1.28 | -0.11 |
| *OCH ₂ O* | -270.27 | 0.84 | -0.01 |
| *OCH ₂ * | -262.77 | 0.69 | 0.00 |

solvation free energies of intermediates of CO₂ reduction.

Reference

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