**Supplementary Information**

# $Cu_3P$@CoO Core-shell Heterostructure with Synergistic Effect for Highly Efficient Hydrogen Evolution

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**Details of DFT calculations**

The DFT calculations are carried out by the Vienna ab-initio simulation package software (VASP)[1-3]. The projector augmented wave method (PAW)[4] with Perdew, Burke, and Ernzerhof functional (PBE)[5] is used. The energy cutoff is set at 500 eV. (5×5×5), (3×3×3), (3×3×1), (3×3×1), (1×1×1) k-point mesh are used for bulk CoO, bulk $Cu_3P$, CoO (111) surface, $Cu_3P$ (300) surface, and $Cu_3P$@CoO, respectively. The convergence tolerance is set at $10^{-4}$ eV. For the systems containing Co, spin-polarization is considered. The bulk and surface models of CoO are both regarded as antiferromagnetism.

**Model structures**

The CoO (111) and $Cu_3P$ (300) slabs with vacuum width of 15 Å are built from bulk CoO (space group Fm-3m) and bulk $Cu_3P$ (space group $P6_3cm$) with (3×3) and (1×1) surface periodicity, respectively. $Cu_3P$@CoO is built with (5×3) CoO (111) surface and (2×2) $Cu_3P$ (300) surface. The lattice mis-match is less than 5.5%.

**HER mechanism**

The HER steps in alkaline solutions could be written as:

$$H_2O + * + e^- \rightarrow H* + OH^- \quad (1)$$

$$H_2O + e^- + H* \rightarrow H_2 + OH^- \text{ or } H* + H* \rightarrow H_2 \quad (2)$$

The Gibbs free energies are calculated as follows:

$$G = E_{DFT} + E_{ZPE} - TS \quad (3)$$

where $E_{DFT}$ is the energy obtained by DFT calculations, $E_{ZPE}$ is the zero-point energy (ZPE) correction, T is 298.15 K, and S is the entropy. The free energy of liquid $H_2O$ at 298.15 K equals to that of gas $H_2O$ at 0.035 bar.

Vibrational frequency of $H^+$ and $OH^-$ obtained by DFT is used to evaluate the ZPE and entropy change, and the latter one could be calculated as follows:

$$S(T) = \sum_{i=1}^{3N} \left[ -Rln\left(1 - e^{-\frac{h\nu_i}{k_B T}}\right) + \frac{N_A h\nu_i \; e^{-\frac{h\nu_i}{k_B T}}}{T \; 1 - e^{-\frac{h\nu_i}{k_B T}}} \right] \quad (4)$$

Four states in the HER process are mainly considered, *i.e.*, initial state, activated $H_2O$ state, adsorbed H state, and final state. The Gibbs free energy of each state is calculated as follows:

$$G_0 = G_* + G_{H_2O} \quad (5)$$

$$G_1 = G_{H_2O*} \quad (6)$$

$$G_2 = G_{H*} + G_{OH^-} \quad (7)$$

$$G_3 = G_* + G_{OH^-} + \frac{1}{2}G_{H_2} \quad (8)$$

The change of Gibbs free energy for each intermediate is as follows:

$$\Delta G_{H_2O*} = G_1 - G_0 \quad (9)$$

$$\Delta G_{H*} = G_2 - G_3 \quad (10)$$

DFT simulated energies, ZPE and entropy corrections, and free energies of $H_2$ (g), $H_2O$ (l), H*, and $H_2O$*, as well as the Gibbs free energy in each step of HER are provided in Table S1 and S2, respectively.

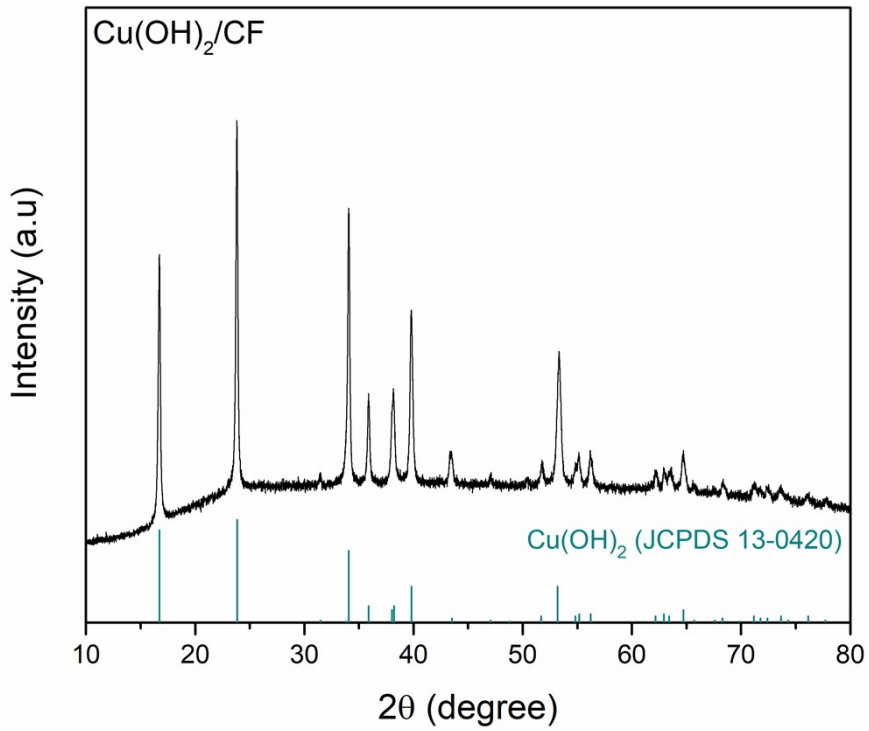


Fig. S1. XRD pattern of $Cu(OH)_2$/CF.

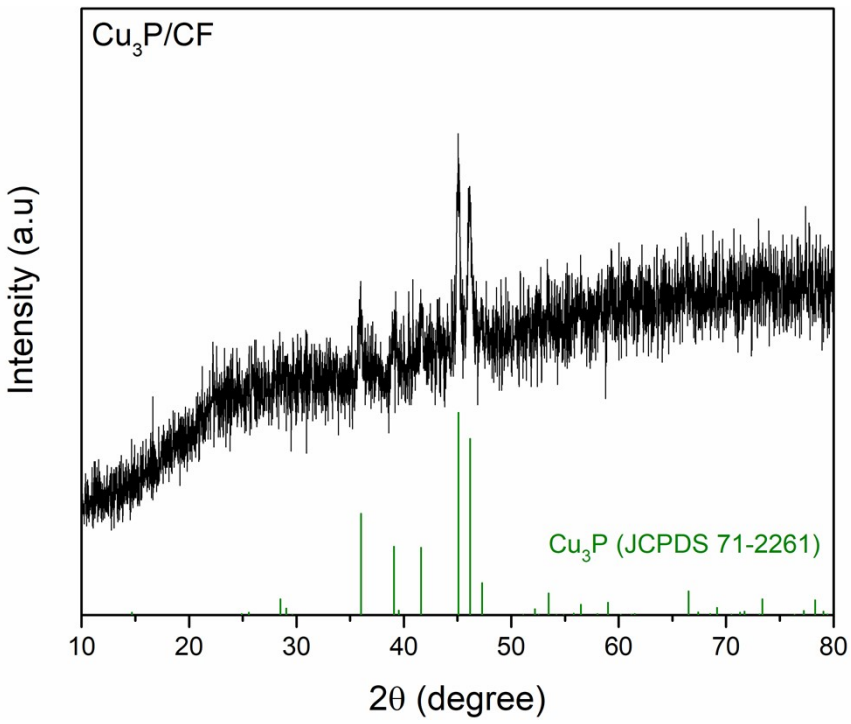


Fig. S2. XRD pattern of $Cu_3P$/CF.

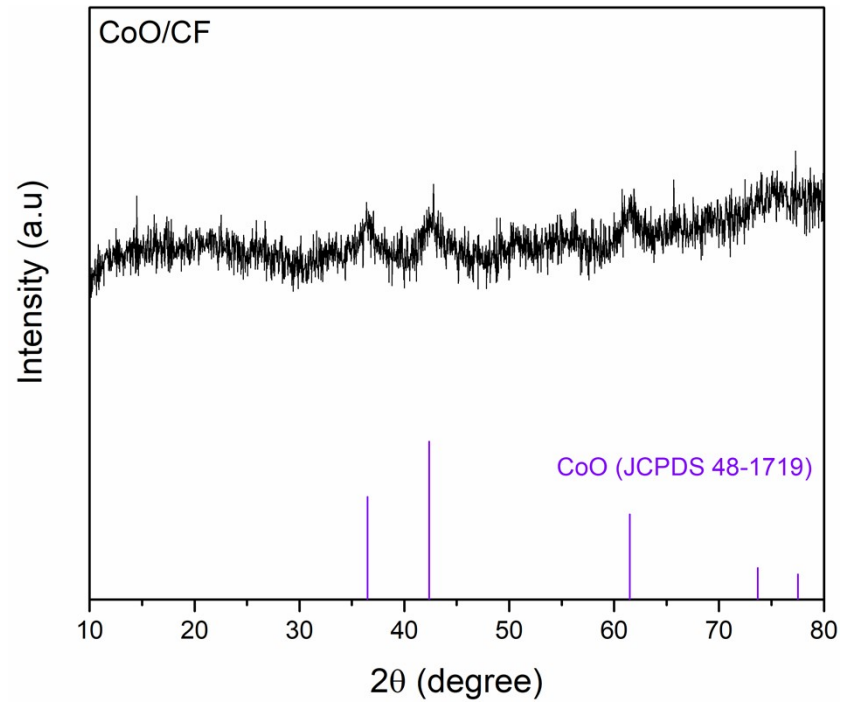


Fig. S3. XRD pattern of CoO/CF.

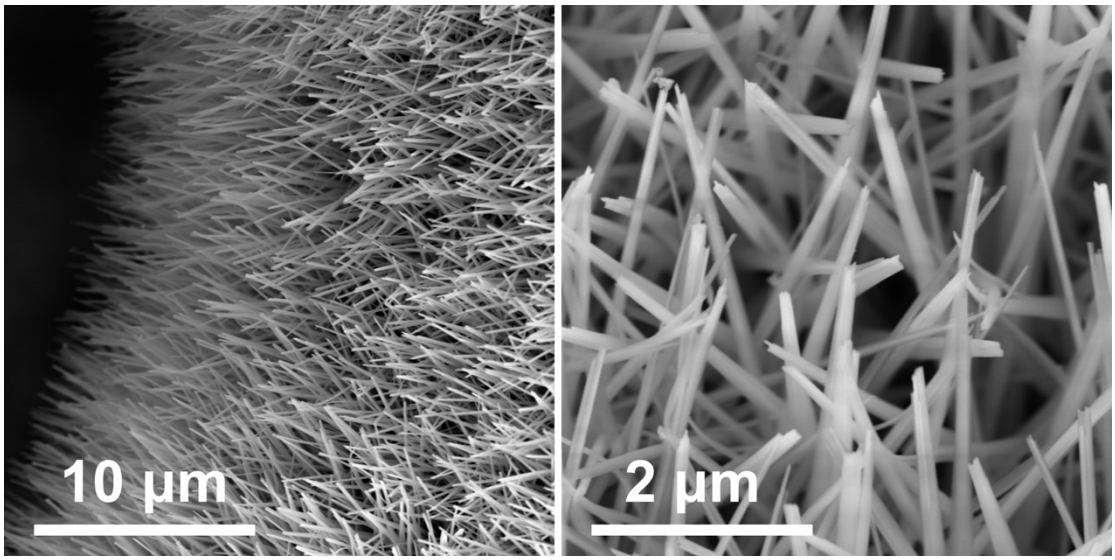


Fig. S4. SEM images of $Cu(OH)_2$/CF.

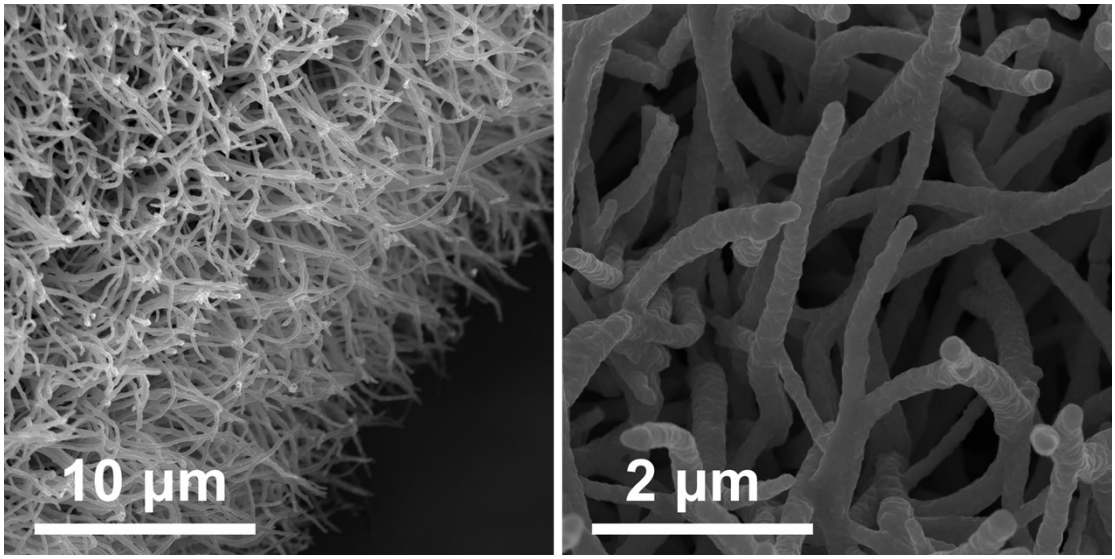


Fig. S5. SEM images of $Cu_3P$/CF.

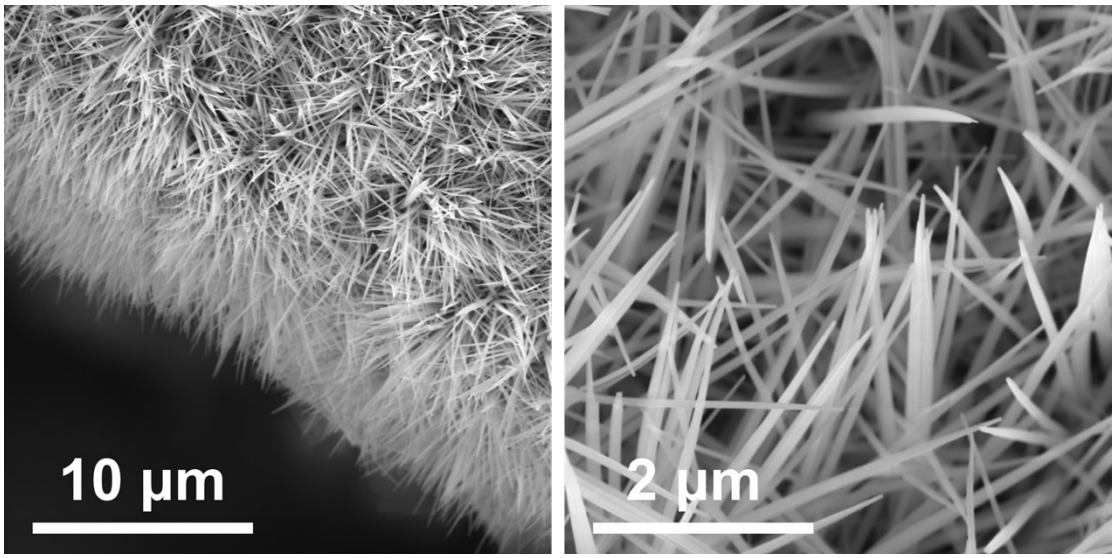


Fig. S6. SEM images of CoO/CF.

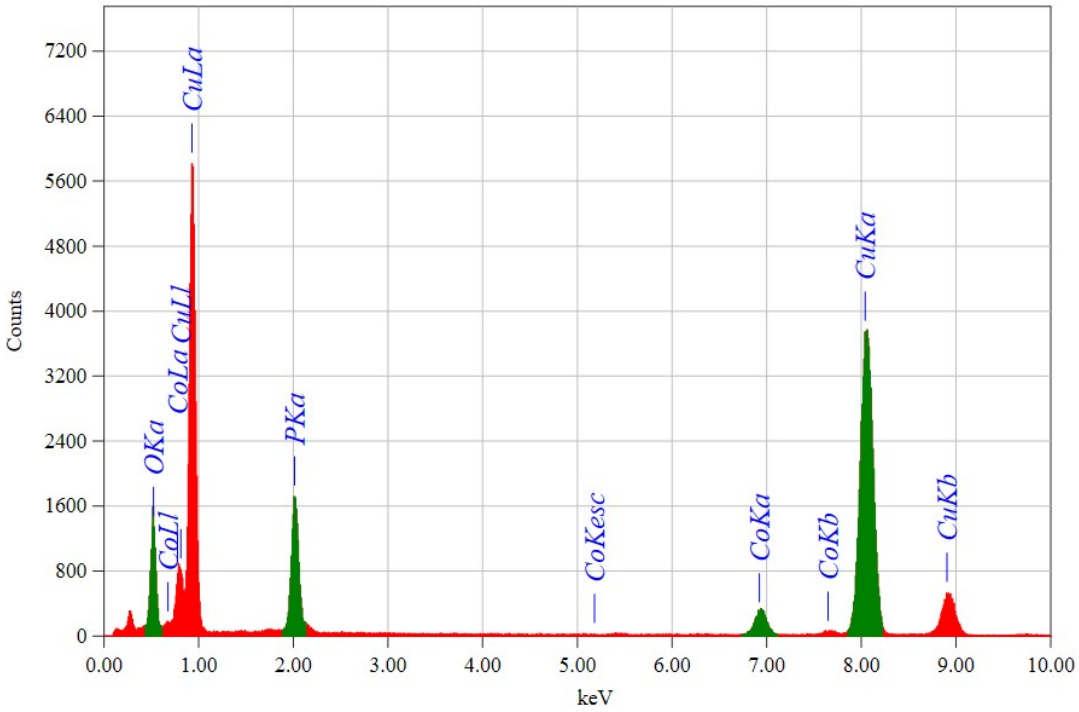


Fig. S7. EDX spectroscopy of $Cu_3P$@CoO-4.

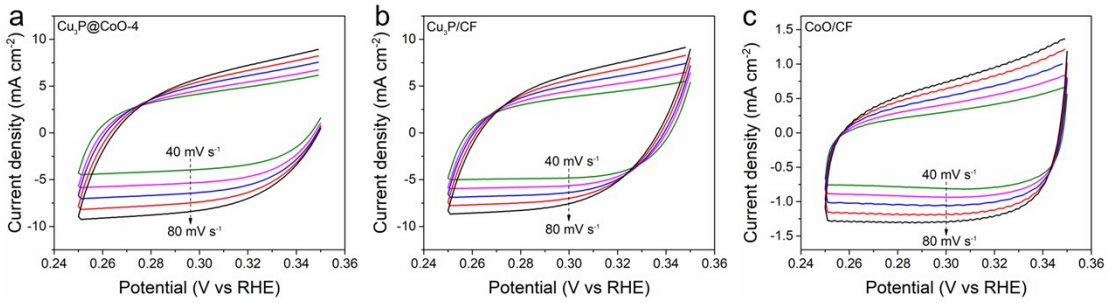


Fig. S8. CV curves for estimation of $C_{dl}$.

Table S1. DFT simulated energies, ZPE and entropy corrections, and free energies of $H_2$ (g), $H_2O$ (l), H*, and $H_2O$*.

| | $E_{DFT}$ (eV) | ZPE-TS (eV) | G (eV) |
|---|---|---|---|
| $H_2O$ (l) | -14.232 | -0.101 | -14.334 |
| $H_2$ (g) | -6.773 | -0.135 | -6.908 |
| CoO (111) | | | |
| H* | -278.087 | 0.308 | -277.779 |
| $H_2O$* | -289.526 | 0.422 | -289.104 |
| $Cu_3P$ (300) | | | |
| H* | -146.423 | 0.172 | -146.251 |
| $H_2O$* | -156.617 | 0.468 | -156.149 |
| $Cu_3P$@CoO | | | |

| | | | |
|---|---|---|---|
| H* | -1151.475 | 0.322 | -1151.153 |
| $H_2O$* | -1162.578 | 0.389 | -1162.189 |

Table S2. The Gibbs free energy in each step of HER.

| | $G_0$ (eV) | $G_1$ (eV) | $G_2$ (eV) | $G_3$ (eV) |
|---|---|---|---|---|
| CoO (111) | -288.252 | -289.104 | -288.659 | -288.252 |
| $Cu_3P$ (300) | -156.826 | -156.149 | -157.131 | -156.826 |
| $Cu_3P$@CoO | -1161.837 | -1162.189 | -1162.033 | -1161.837 |

## References


1. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169.
2. G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15-50.
3. G. Kresse and J. Hafner, *Physical Review B*, 1993, **47**, 558.
4. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758.
5. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865.