Supporting Information (SI)

Synergy of a Metallic NiCo Dimer Anchored on a C_2N−Graphene Matrix Promotes the Electrochemical CO_2 Reduction Reaction

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Number of tables : 2

S1. Computational Details

Gibbs free energy of reaction for CO_2 RR elementary steps involving ($H^+ + e^-$) pair transfer was calculated using computational hydrogen electrode (CHE) model by Nørskov et al.[1], defined as $\Delta G_n(U) = \Delta G_n (U=0) + neU$, where n is the number of ($H^+ + e^-$) pairs transferred in CO_2 RR, e is the unit charge and U is the electrode potential versus the reversible hydrogen electrode (RHE). At U=0 V, $\Delta G_n = \Delta E_n - T\Delta S + \Delta ZPE + \Delta E_{sol} + \Delta G_{pH}$, where ΔE_n is DFT-calculated reaction energy in vacuum, $T\Delta S$ is the entropy contributions to the reaction at T=298K, ΔZPE is zero-point energy (ZPE) correction based on the calculated vibrational frequencies, ΔE_{sol} represents the correction of H_2O solvation effect at the water-solid interface, and ΔG_{pH} represents the correction of the free energy due to the variations in H^+ concentration, defined as $G_{pH} = -kT \ln[H^+] = kT \ln 10 \times pH$, and the value of pH was set to 0 for strong acidic medium in this work and therefore, the calculated limiting potentials (U_L) were referenced to the RHE. Implicit model was used for treating H_2O solvation effect, where ΔE_{sol} was accounted for depending on OH-containing species and their binding situations[2]: *R-OH bound to M directly/indirectly through hydroxyl is stabilized by approximately 0.5eV/0.25eV, respectively, and those containing no hydroxyl (e.g., *CO, *CHO, *CH_2O, *CH_3O, CH_x) were stabilized approximately by 0.1eV. The free energy of gaseous molecules (CO_2, CO, H_2, CH_2O, and CH_4) was calculated under the standard pressure of 1 bar, while the free energy of liquid-phase molecules (H_2O, HCOOH, and CH_3OH) was calculated as an ideal gas using their corresponding vapor fugacity (f) at μ(liguid)= μ(vapor)[2], and accordingly, a correction of chemical potential (μ) for liguid products $\Delta\mu = RT*\ln(f)$ is added as -0.09eV, -0.22eV, and -0.07eV for H_2O(l), HCOOH(l), and CH_3OH(l), respectively. The limiting potential (U_L) is obtained from the maximum free energy change (ΔG_{max}) among all elementary steps along the lowest-energy pathway by using the relation of $U_L = -\Delta G_{max}/e$.

S2. Zero-point Energy (ZPE) and Entropy Corrections (TS)

The entropies of the gaseous molecules were taken from the NIST Chemistry WebBook[3] and the zero-point energy (ZPE) was calculated according to:

$$E_{ZPE} = \sum_{i=1}^{3N} \frac{h\nu_i}{2}$$

The entropy change for adsorbed intermediates was calculated within the harmonic approximation:

$$\Delta S_{ads}(0 \rightarrow T, P^0) = S_{vib} = \sum_{i=1}^{3N} \left[\frac{N_A h\nu_i}{T(e^{h\nu_i/k_B T} - 1)} - R\ln(1 - e^{-h\nu_i/k_B T}) \right]$$

Where ν_i is DFT-calculated normal-mode frequency for species of *3N* degree of freedom (*N*=number of atoms) adsorbed on M@Cu(211) SACs, N_A is the Avogadro's constant(6.022×10^{23} mol^{-1}), *h* is the Planck's constant (6.626×10^{-34}J s), and k_B is the Boltzmann constant (1.38×10^{-23} JK^{-1}), *R* is the ideal gas constant (8.314 J K^{-1} mol^{-1}), and *T* is the system temperature, and T=298.15K in this work.

Table S1. Binding energy (BE, in eV) of Ni_2, Co_2 and NiCo dimers on *p*(2 × 2) C_2N graphene in (**I**) asymmetric and (**II**) symmetric bonding configuration (a) one pair of dimer (b) four pairs of dimers.

(a)

Configuration	Ni_2*	Co_2*	(NiCo)**
(**I**)	-8.55	-8.33	-8.47
(**II**)	-8.20	-8.06	-8.27

*$BE = E_{M_2@C_2N} - E_{C_2N} - 2*E_M$

**$BE = E_{NiCo@C_2N} - E_{C_2N} - E_{Ni} - E_{Co}$

(b)

Configuration	$4Ni_2$*	$4Co_2$*	4(NiCo)**	$2Co_2+2Ni_2$***
(**I**)	-8.96	-8.63	-8.98	-8.90
(**II**)	-8.29	-8.20	-8.36	-8.19

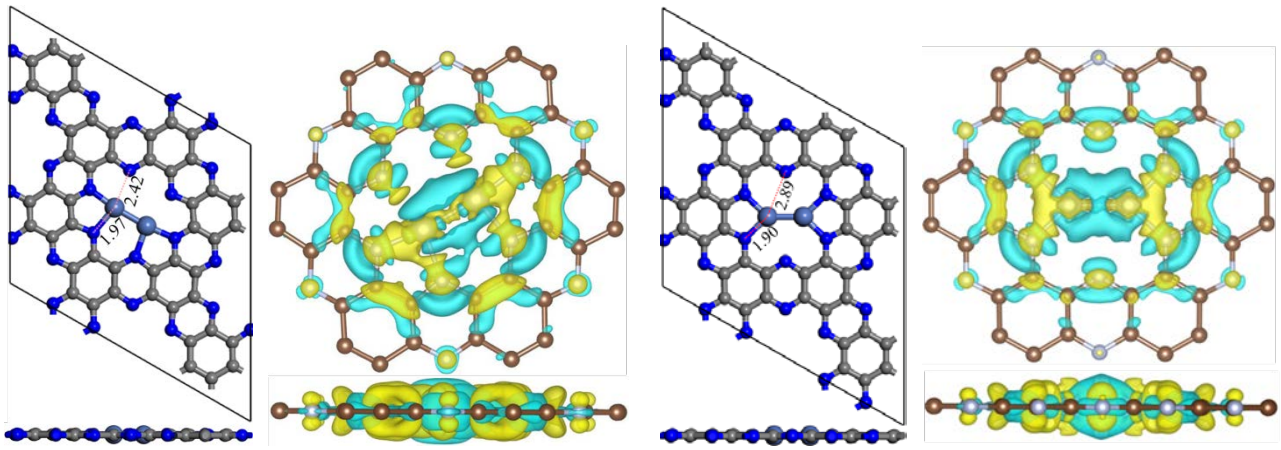
*$BE = [E_{4M_2@C_2N} - E_{C_2N} - 8*E_M]/4$

**$BE = [E_{4(NiCo)@C_2N} - E_{C_2N} - 4*E_{Ni} - 4*E_{Co}]/4$

***$BE = [E_{[2Co_2+2Ni_2]@C_2N} - E_{C_2N} - 4*E_{Ni} - 4*E_{Co}]/4$

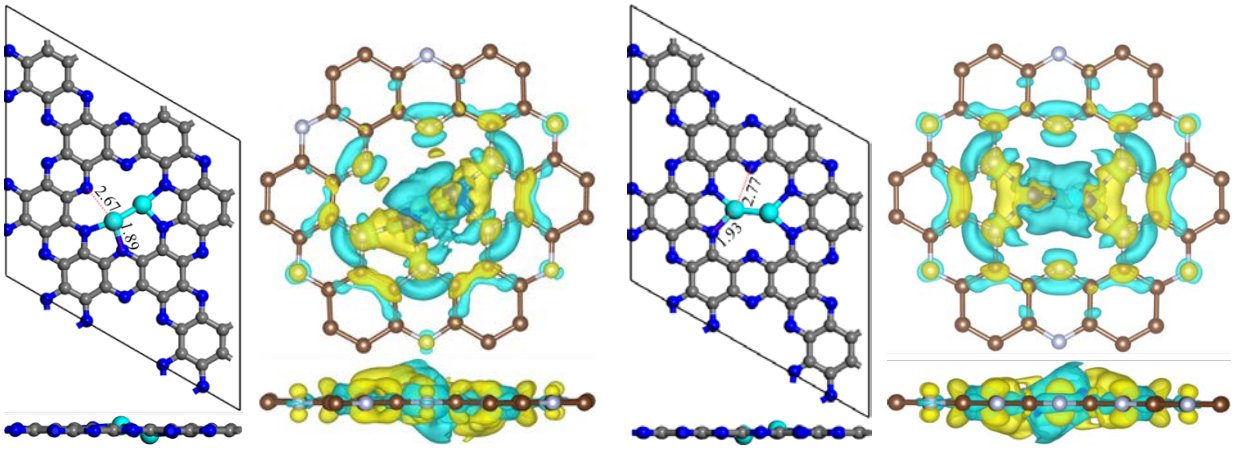
Table S2. Binding energy (in eV) of $*CO_2$, *CO, *HCOOH, $*CH_2O$, and $*CH_3OH$ on $Ni_2@C_2N$, $Co_2@C_2N$ and $NiCo@C_2N$ calculated using their corresponding gas-phase energy as the reference.

Metal	$*CO_2$	*CO	*HCOOH	$*CH_2O$	$*CH_3OH$
Ni_2	-0.29	-2.38	-0.44	-1.41	-0.30
Co_2	-0.84	-2.92	-0.89	-1.75	-0.56
NiCo	-0.51	-2.57	-0.68	-1.43	-0.39



I-0.00eV **II**- 0.35eV

(a) $Ni_2@C_2N$



I-0.00eV **II**-0.27eV

(b) $Co_2@C_2N$

Figure S1. Optimized structure and isosurface of charge density difference ($\Delta\rho$) for (a)$Ni_2@C_2N$ and (b) $Co_2@C_2N$ which have two distinct M-M arrangements with pyridinic N atoms (**I** and **II**). Both top and side views are displayed. Yellow: charge accumulation; Cyan: charge depletion. Isosurface level=0.004 e/Bohr^3. $\Delta\rho = \rho_{(slab+ads)} - \rho_{(slab)} - \rho_{(ads)}$.

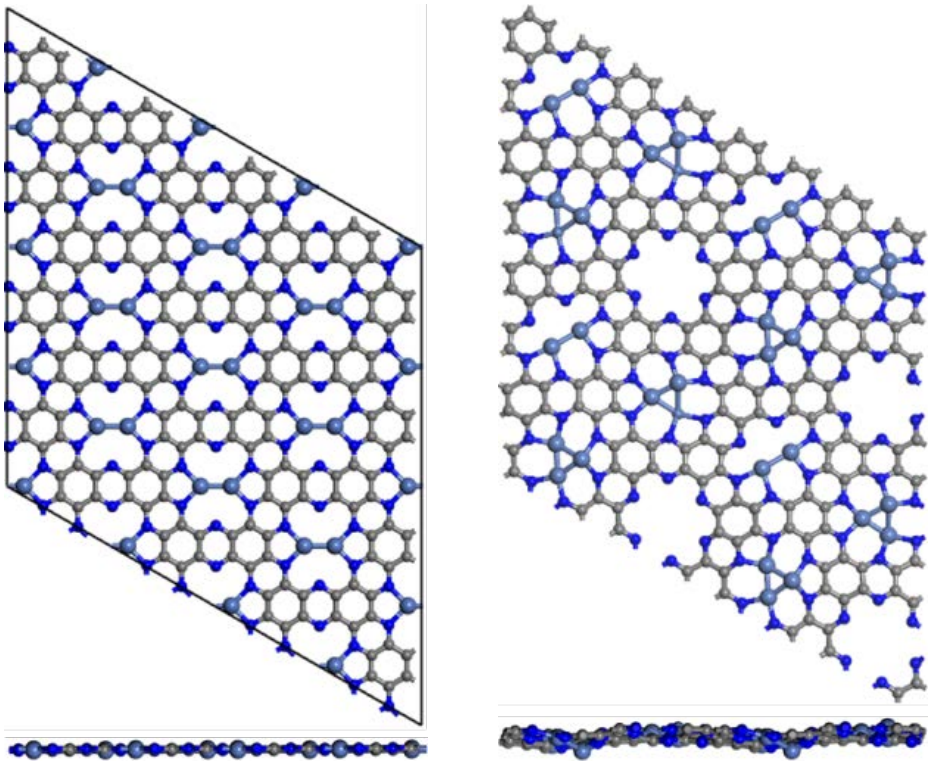


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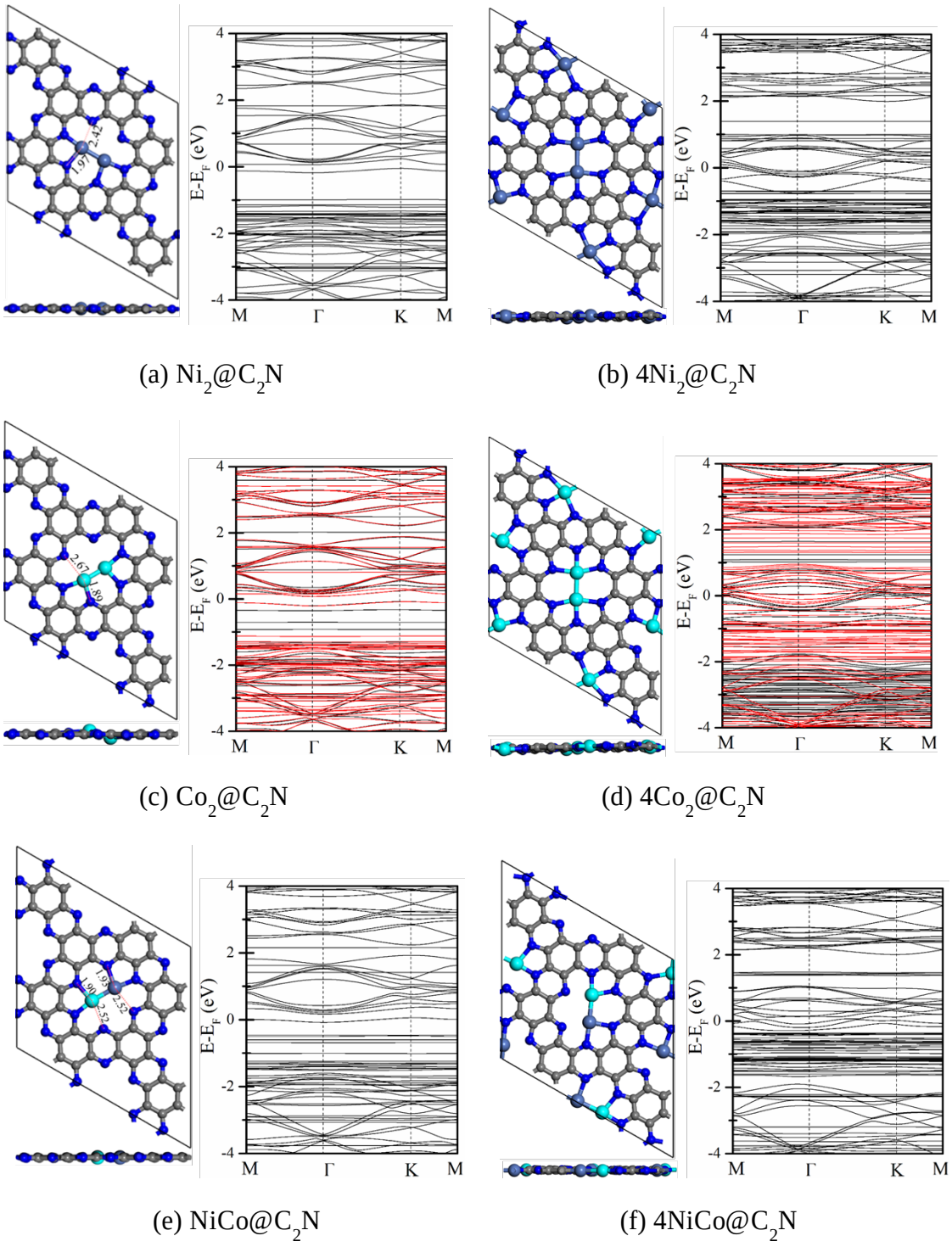
Figure S2. The snapshot of geometric structure of *p*(4 × 4) $Ni_2@C_2N$ during AIMD simulations at 500 K.

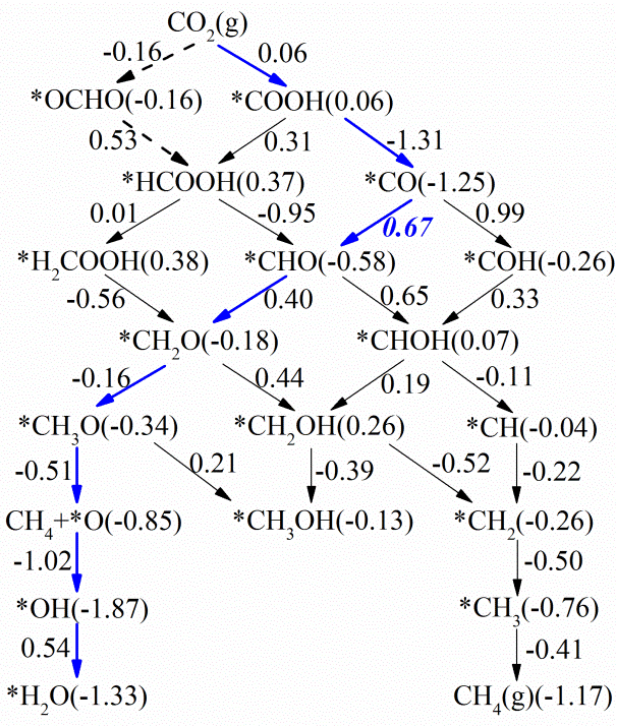


(a) $Ni_2@C_2N$ (b) $4Ni_2@C_2N$

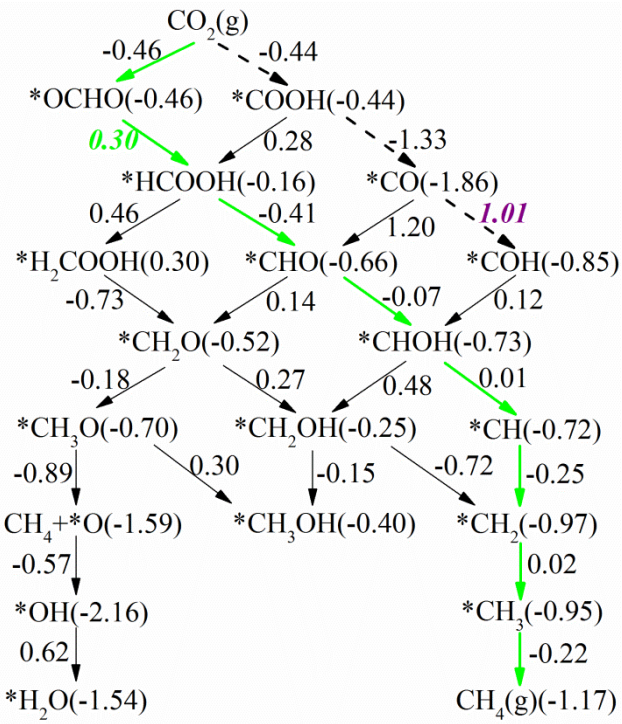
(c) $Co_2@C_2N$ (d) $4Co_2@C_2N$

(e) $NiCo@C_2N$ (f) $4NiCo@C_2N$

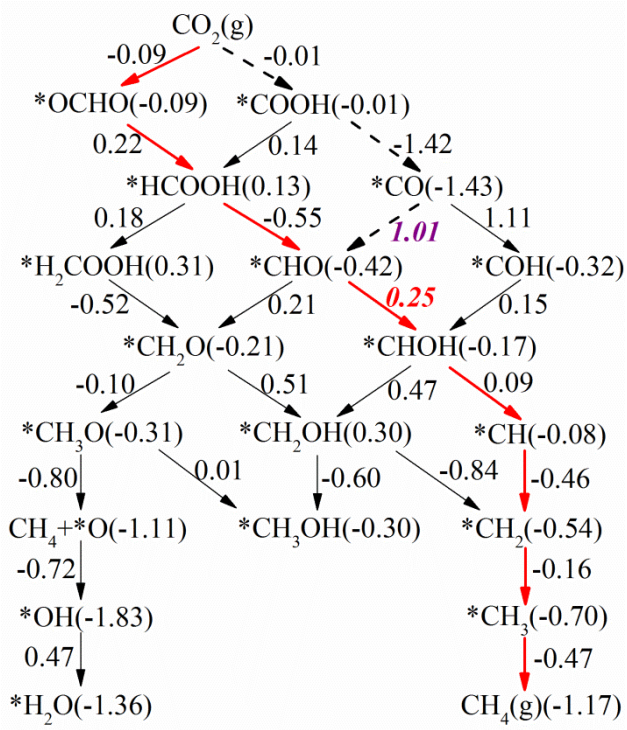
Figure S3. GGA+U calculated electronic band structure along side with geometric structure. (a) $Ni_2@C_2N$, (b) $4Ni_2@C_2N$, (c) $Co_2@C_2N$, (d) $4Co_2@C_2N$, (e) $NiCo@C_2N$, (f) $4NiCo@C_2N$. Black: spin-up electrons; Red: spin-down electrons. Here, (a) and (b) contain zero magnetic moment, (e) and (f) contain nearly zero magnetic moment.



(a)



(b)



(c)

Figure S4. Complete CO_2 RR pathways via *OCHO and *COOH intermediates towards CH_4 and CH_3OH formation on (a)$Ni_2@C_2N$, (b)$Co_2@C_2N$ and (c)$NiCo@C_2N$. The numbers besides arrow and in parenthesis represent Gibbs free energy change and position (in eV), respectively. The numbers in colored italics represent the likely free energy barriers.

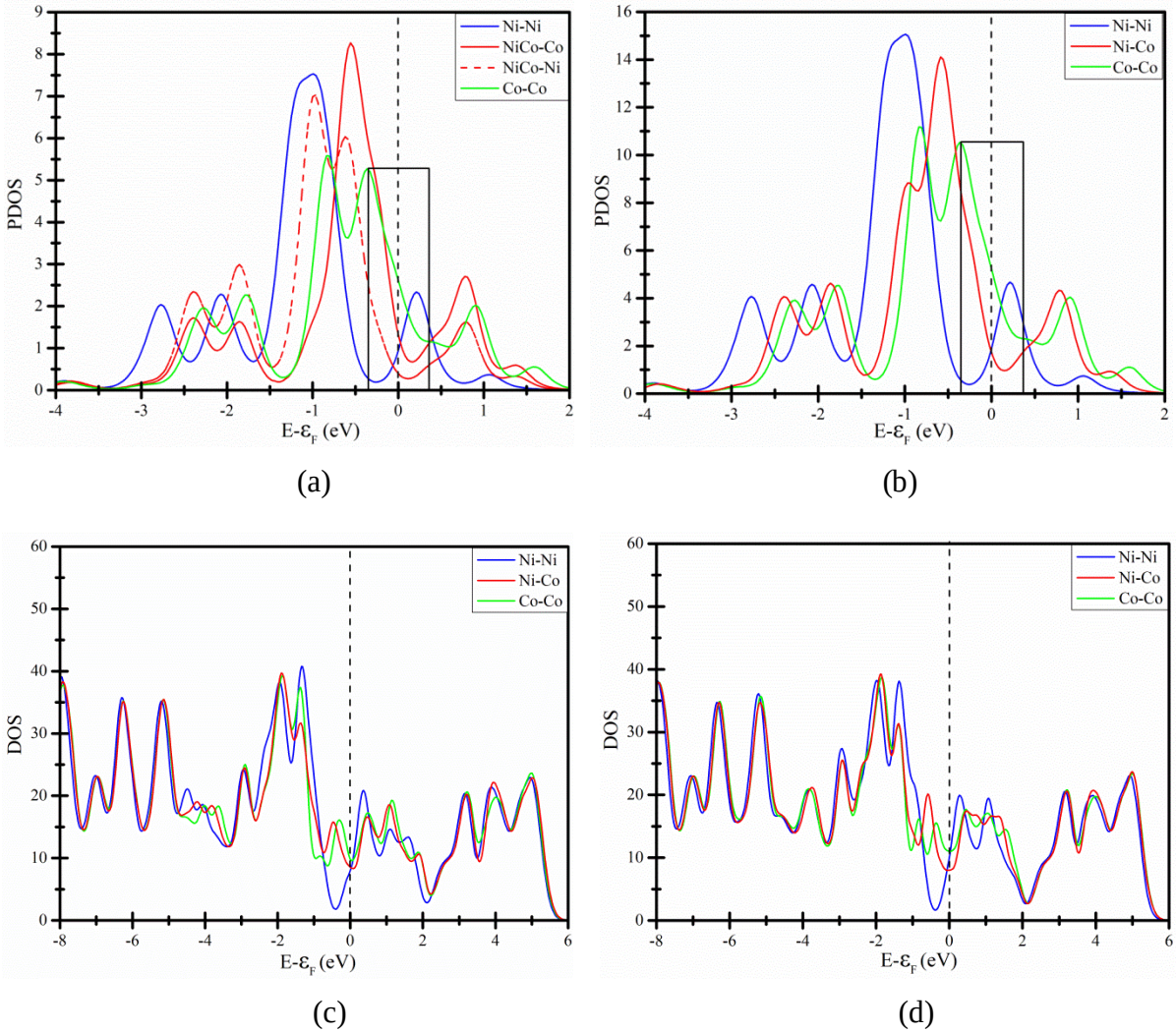


Figure S5. Partial density of states (PDOS) of *3d*-orbitals of Ni_2, Co_2 and NiCo@C_2N (**II**): (a) monomer (b) dimer. Total density of states (TDOS) of Ni_2, Co_2 and NiCo@C_2N: (c) Asymmetric **I** configurations (c) Symmetric **II** configurations. The Fermi level is set to zero in black dashed line.

References

1. Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H., Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004,** *108*, 17886-17892.
2. Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K., How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels. *Energy Environ. Sci.* **2010,** *3*, 1311-1315.
3. https://webbook.nist.gov/chemistry/.