

# Cu<sub>3</sub>N Nanocubes for Selective Electrochemical Reduction of CO<sub>2</sub> to Ethylene

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## **Experimental Procedures**

### **Chemicals and materials.**

The nanoparticle synthesis was carried out using standard airless procedures and commercially available reagents. All reagents were used as received. Oleylamine (OAm, >70 %), 1-octadecene (ODE, technical grade, 90%), 1-octadecylamine (ODA, 97%), squalene (96 %), trioctylphosphine (TOP, 97 %), potassium bicarbonate ( $\geq 99.99\%$  trace metals basis, 99.7- 100.5% dry basis), copper(I) chloride ( $\geq 99.99\%$ ) were from Sigma-Aldrich. Cupper(II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 99.5 %) were from Strem Chemicals. Hexane (98.5%), isopropanol (100 %) and ethanol (100%) were purchased from Fisher Scientific. Platinum wire (0.5 mm diameter, Premion®, 99.997%), Toray Carbon Paper (TGP-H-60) was from Alfa Aesar. Polyvinylidene

fluoride (PVDF) was from MTI corporation. These chemicals were used without further purification. The deionized water was obtained from a Millipore Autopure System.

**Synthesis of 25 nm Cu<sub>3</sub>N NCs.** Under a gentle flow of Ar, 100 mg Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 2.5 g of octadecylamine and 2.5 mL of oleylamine were mixed in a flask and the mixture was heated to 150°C and kept at this temperature for an hour (note that we tested different combinations of octadecylamine/oleylamine and found 2.5 g/2.5 mL (about 1/0.8 mass ratio) combination worked best for the synthesis.). The resultant light green solution was heated to 240°C and kept at this temperature for 30 min before it was cooled to room temperature. The reaction solution was then mixed with 240 mL isopropanol and centrifuged at 8500 rpm for 8 min to separate the solid product. The product was dispersed in 20 mL hexane and precipitated by adding 240 mL ethanol followed by centrifugation at 8500 rpm for 8 min. The process was repeated once and the product, 25 nm Cu<sub>3</sub>N NCs were dispersed in hexane for further use.

**Synthesis of 20 nm Cu<sub>3</sub>N NCs.** The process was same as what was described in the synthesis of 25 nm NCs except that the reaction temperature was kept at 250°C.

**Synthesis of 10 nm Cu<sub>3</sub>N NCs.** The process was same as what was described in the synthesis of 25 nm NCs except that the reaction temperature was kept at 260°C.

**Synthesis of 20 nm Cu<sub>3</sub>N NPs.** The process was same as what was described in the synthesis of 25 nm NCs except that the reaction temperature was kept at 230°C.

**Synthesis of 29 nm Cu NCs.** Under an inert ( $N_2$  or Ar) atmosphere, 100 mg CuCl, 200 mg octadecylamine and 2.5 mL squalene were mixed in a flask and heated to 200°C for 30 min to obtain a solution. In another flask, 19 mL oleylamine and 1 mL trioctylphosphine were mixed and heated to 320°C under an inert atmosphere, and the CuCl solution (~2.5 mL) added quickly to the 320°C solution and the mixed solution was kept at 320°C for 2 min before it was cooled to room temperature. The product was precipitated by adding 120 mL isopropanol and centrifuging at 8500 rpm for 8 min. The product was dispersed in 10 mL hexane and precipitated by adding 120 mL ethanol followed by centrifugation. The process was repeated one more time to obtain the NC product, which was dispersed in hexane for further use.

**Catalyst Preparation.** 20 mg NCs were deposited onto 20 mg Ketjen Carbon (C) (EC300J) by sonicating the mixture of NC dispersion in 40 mL hexane, giving C-NC. The C-NC catalyst was separated from hexane by centrifugation 8500 rpm for 10 min. Then the C-NC was suspended in 60 mL n-butylamine and stirred for three days under  $N_2$  atmosphere and ambient temperature (to remove the surfactant). The mixture was separated by centrifugation (8500 rpm, 10 min) and washed with ethanol and dried under  $N_2$ .

**Electrode Preparation.** 40 mg of the dried catalyst powder was ground with 4 mg polyvinylidene fluoride (PVDF) (industrial adhesive) with a few drops of 1-methyl-2-pyrrolidone (MP) (solvent) to produce catalyst paste that was painted directly onto a 1.0 cm x 2.0 cm carbon paper (Toray TGP-H-060). The catalyst-decorated carbon paper was dried in a vacuum-oven overnight and served as a working electrode.

Electrochemical CO<sub>2</sub>RR Test. EC-Lab VSP Ultimate electrochemical workstation was used to conduct CO<sub>2</sub> reduction experiments in aqueous 0.1 M KHCO<sub>3</sub> (pH = 6.8 when saturated with CO<sub>2</sub>, pH = 8.3 when saturated with Ar). A platinum wire was used as counter electrode. All potentials were measured against an Ag/AgCl reference electrode (4.0 M KCl, Pine instrument) and were converted to those against a reversible hydrogen electrode (RHE). The experiments were performed in a gas-tight cell with two-compartments separated by an anion exchange membrane (Nafion® 212). Each compartment contained 20 mL electrolyte with approximately 5 mL headspace.

**Product Analysis.** Before the experiment, the electrolyte in the cathode compartment was saturated with CO<sub>2</sub> by bubbling CO<sub>2</sub> gas for at least 30 min and was stirred at 900 rpm. CO<sub>2</sub> gas was delivered at an average rate of 30 mL/min (at room temperature and ambient pressure) and routed directly into the gas sampling loop of a gas chromatograph (Agilent 7890A). The gas phase composition was analysed by GC every 30 min. The GC analysis was set up to split the gas sample into two aliquots whereof one aliquot was routed through a packed MoleSieve 5A column and a packed HP-PLOT Q column before passing a thermal conductivity detector (TCD) for CO quantification. Argon (Corp Brother, 99.9999%) and Helium (Corp Brother, 99.9999%) were employed as carrier or make-up gases respectively. The second aliquot was routed through a packed HP-PLOT Q + PT column equipped with a flame ionization detector (FID) for analysing C1 to C3 hydrocarbons. The GC was calibrated using commercially available calibration standards from JJS Technical Services. <sup>1</sup>H NMR was employed at the end of experiments to characterize liquid products. To be specific, 700 μL aliquot of the electrolyte was mixed with 35 μL dimethyl

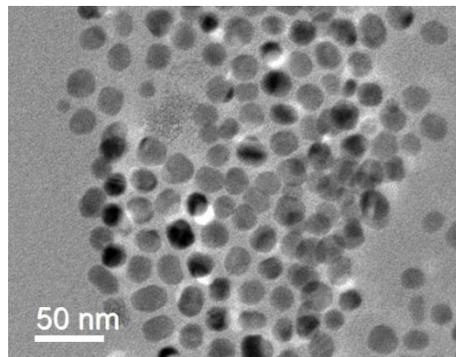
sulfoxide (DMSO) standard solution (20 mM DMSO in D<sub>2</sub>O). <sup>1</sup>H NMR spectra were recorded on Bruker DRX 400 Avance and 600 Avance MHz spectrometers.

**Catalyst Characterization.** Samples for transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analyses were prepared by depositing a single drop of diluted NP dispersion/suspension on amorphous-carbon-coated copper grids. Images were acquired on a JEOL 2100 TEM (200 kV). Scanning transmission electron microscopy (STEM) analyses were carried out on a Hitachi HD2700C (200 kV) with a probe aberration corrector. The electron energy loss spectroscopy (EELS) line-scan was obtained on a high-resolution Gatan-Enfina ER with a probe size of 1.3 Å. X-ray powder diffraction (XRD) was collected on a Bruker AXS D8-Advanced diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). X-ray photoelectron spectroscopy (XPS) was performed on an ESCA 210 and MICROLAB 310D spectrometer using an Mg K $\alpha$  source.

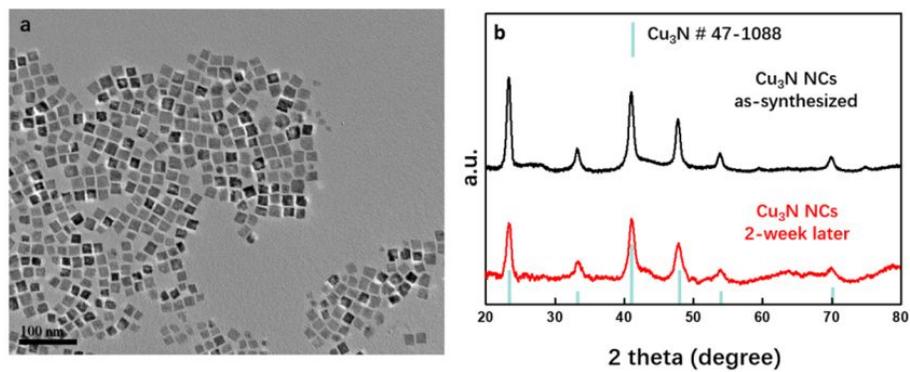
**DFT Calculations.** DFT calculations were performed using the Vienna ab initio Simulation Package (VASP)<sup>1</sup> with the projector-augmented wave pseudopotentials.<sup>2</sup> The exchange-correlation interaction was described by the revised Perdew-Burke-Ernzerhof (RPBE) functional.<sup>3</sup> The plane-wave energy cutoff was 400 eV and the Brillouin-zone was sampled with a  $4 \times 4 \times 1$  k-mesh according to the Monkhorst-Pack scheme.<sup>4</sup> All atomic structures were optimized until the forces were less than  $0.03 \text{ eV } \text{Å}^{-1}$ . Transition state searches were performed using the Climbing-Image-Nudged Elastic Band (CI-NEB) method.<sup>5</sup> The electrolyte was incorporated implicitly during the calculation of the relative energy diagram with the Poisson-Boltzmann model

implemented in VASPsol.<sup>6-7</sup> The relative permittivity of the media was chosen as  $\epsilon_r = 78.4$  (corresponding to that of water) and the concentration of the electrolyte was set to 0.1 M (equivalent to a Debye length of 9.61 Å). The Cu (100) and anti- $\text{ReO}_3$  perovskite type  $\text{Cu}_3\text{N}$  (100) surfaces were modeled by four-atomic-layer slab models. The atoms in the top two layers were fully relaxed, while in the bottom two layers were fixed in the equilibrium positions. The adjacent slabs were separated by a 15 Å vacuum in the normal direction of the surface.

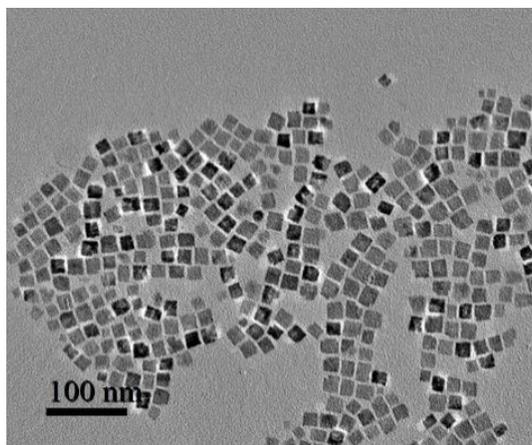
## 2. Supplementary Figures



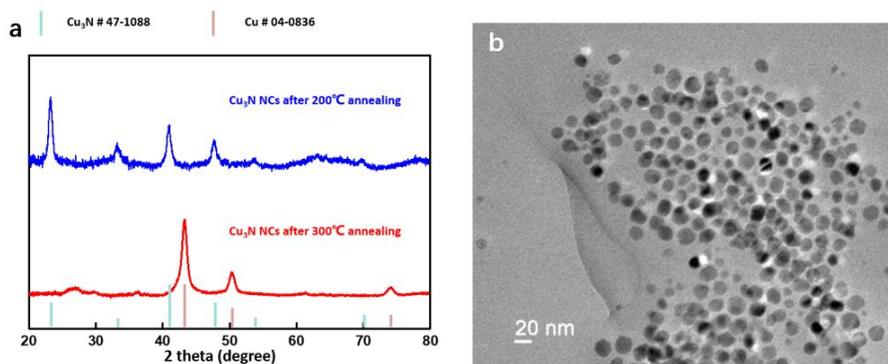
**Figure S1.** TEM image of 20 nm  $\text{Cu}_3\text{N}$  NPs.



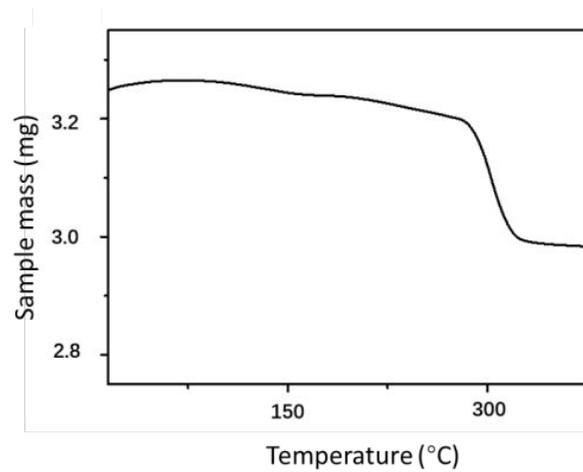
**Figure S2.** (a) TEM image of 25 nm  $\text{Cu}_3\text{N}$  NCs after their hexane dispersion exposure to air for two-weeks. (b) XRD patterns of as-synthesized  $\text{Cu}_3\text{N}$  NCs (black line) and those after two-week exposure to air (red line).



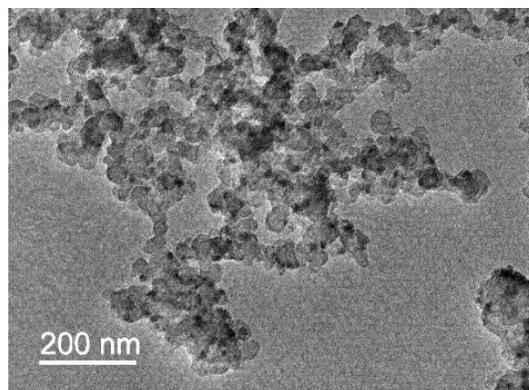
**Figure S3.** TEM image of 25 nm  $\text{Cu}_3\text{N}$  NCs after annealing at 200°C under Ar for 2 h.



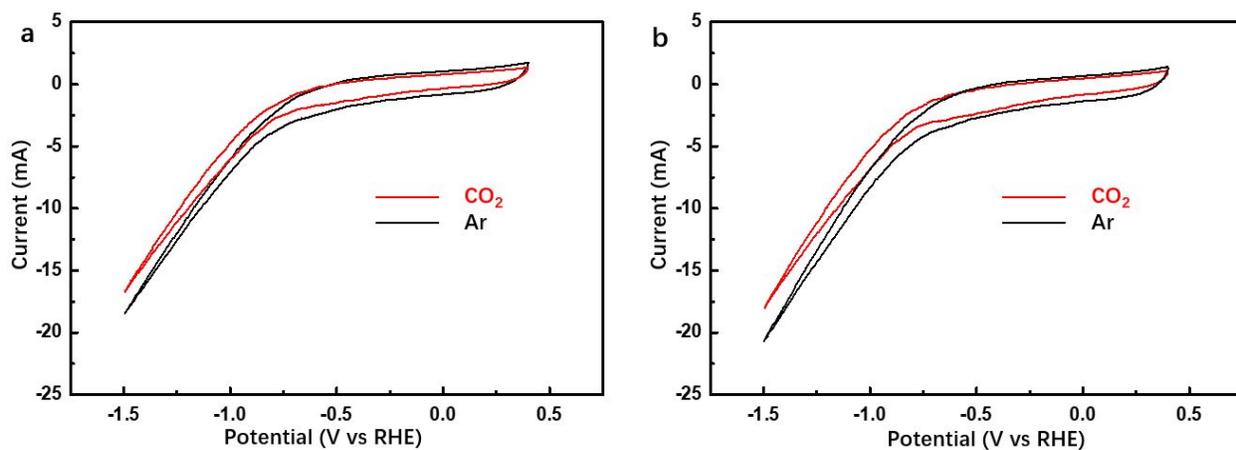
**Figure S4.** a, XRD patterns of  $\text{Cu}_3\text{N}$  NCs after 200°C (blue line) and 300°C (red line) annealing in Ar for 2 h. b, TEM image of 25 nm  $\text{Cu}_3\text{N}$  NCs after 300°C annealing in Ar for 2 h.



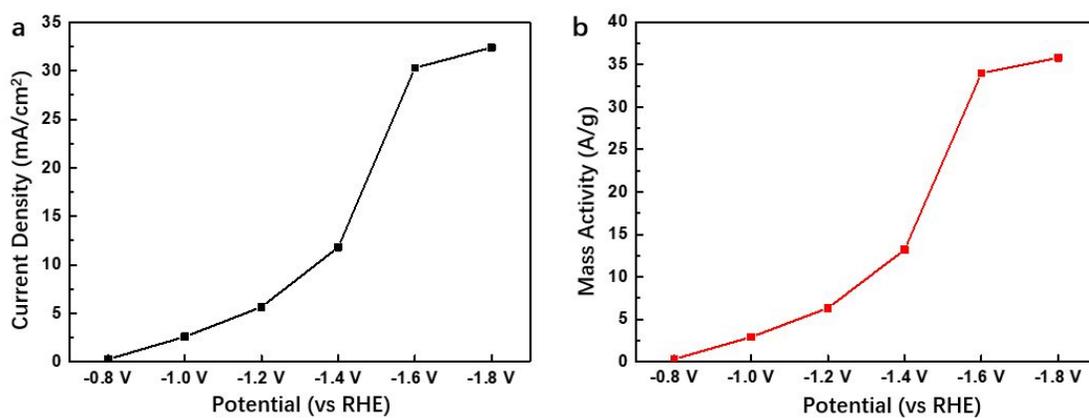
**Figure S5.** Mass change of the  $\text{Cu}_3\text{N}$  NC sample over heating temperature in Ar atmosphere.



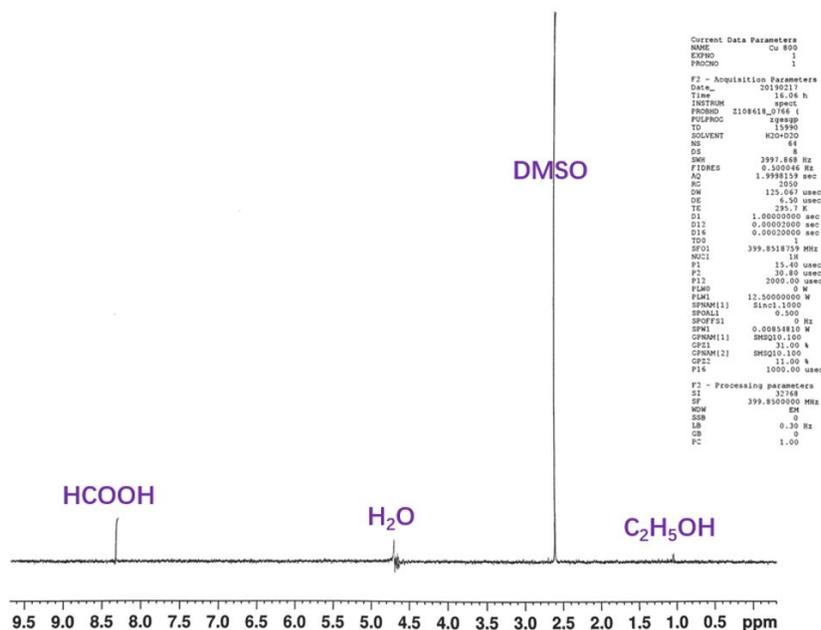
**Figure S6.** TEM image of 25 nm  $\text{Cu}_3\text{N}$  NCs after loaded on carbon support.



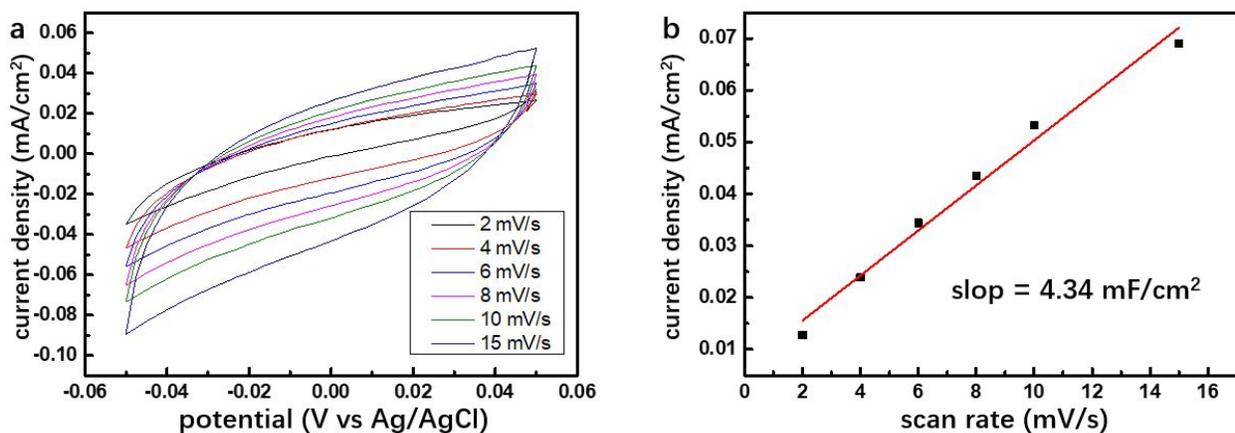
**Figure S7.** CV curves of (a) 10 nm Cu<sub>3</sub>N NCs and (b) Cu<sub>3</sub>N NPs under Ar (black) and CO<sub>2</sub> (red)



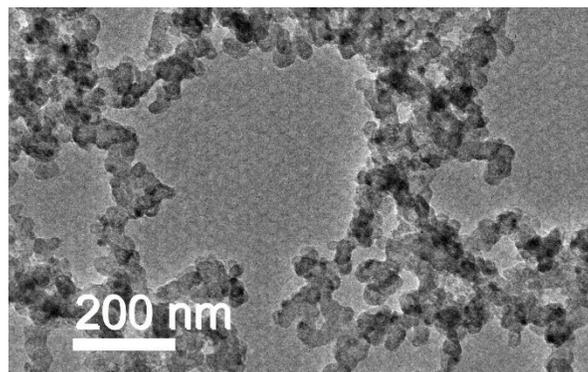
**Figure S8.** (a) Current density and (b) mass activity of 25 nm Cu<sub>3</sub>N NCs at different reduction potentials.



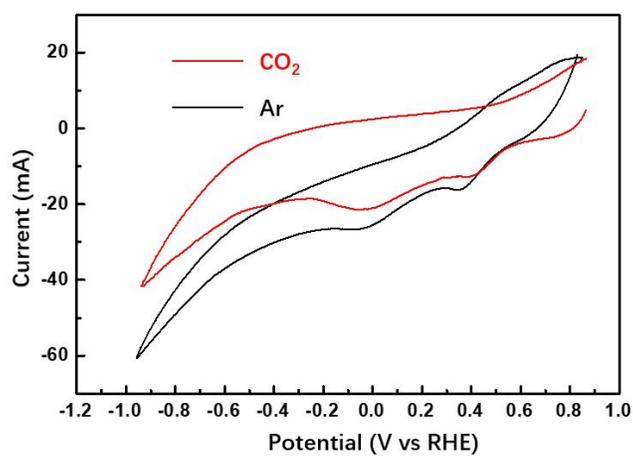
**Figure S9.**  $^1\text{H}$  NMR spectrum of the liquid products obtained from the  $\text{CO}_2\text{RR}$  at  $-1.6$  V. DMSO was used as the internal standard.



**Figure S10.** (a) Potential scan rate (mV/s)-dependent CVs of the  $\text{Cu}_3\text{N}$  catalyst obtained from  $-0.05$  V to  $0.05$  V without Faradaic processes, and (b) plot of the current density of double-layer capacitance charge/discharge vs potential scan rate.



**Figure S11.** TEM image of the carbon-supported 25 nm  $\text{Cu}_3\text{N}$  NCs after 20 h of  $\text{CO}_2\text{RR}$  test.



**Figure S12.** CV curves of 29 nm Cu NCs in Ar (black)- and  $\text{CO}_2$  (red)-saturated 0.1 M  $\text{KHCO}_3$  solution.

## References

- (1) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (2) P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (3) B. Hammer, L. B. Hansen, J. K. Nørskov, *Phys. Rev. B* **1999**, *59*, 7413–7421.
- (4) H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (5) G. Henkelman, H. Jónsson, *J. Chem. Phys.* **2000**, *113*, 9978–9985.
- (6) K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias, R. G. Hennig, *J. Chem. Phys.* **2014**, *140*, 084106
- (7) K. Letchworth-Weaver, T. A. Arias, *Phys. Rev. B* **2012**, *86*, 075140.