Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Tuning Pd-Catalyzed Electroreduction of CO_2 to CO with Reduced Overpotential

Zishan Han,[a] Changhyeok Choi,[b] Hengcong Tao,[a] Qun Fan,[a] Yuannan Gao,[a] Shizhen Liu,[a] Alex W. Robertson,[c] Song Hong,[a] Yousung Jung*[b] and Zhenyu Sun*[a]

Electrocatalytically active surface area (ECSA) and ECSA corrected-Tafel slope measurements. The values of ECSA were evaluated on the basis of the reduction charge of surface $Pd(OH)_2$ in the potential region of −0.25 to +1.2 V (*vs*. RHE) on the CVs in a deaerated 0.1 M $HClO_4$ solution with a scanning rate of 50 mV/s. We chose +1.2 V as the appropriate potential limit because +1.2 V is the upper limit for the formation of $Pd(OH)_2$ in a solution of pH = 1.[1] The ECSA value can be determined by

$$\mathrm{ECSA} = \mathrm{GSA} * (Q_\mathrm{R} / Q_\mathrm{F}) \qquad \text{(Eq. S1)}$$

where GSA is the the geometric surface area, Q_R is the charge density for reduction of surface $Pd(OH)_2$ on work electrode and Q_F is the charge density for the formation a fully covered $Pd(OH)_2$ layer which was chosen to be 430 μC cm^{-2}.[2] ECSA-corrected Tafel slopes for CO production (that is, $j_\mathrm{total} \times \eta_\mathrm{CO}/\mathrm{ECSA}$) were calculated from corresponding ECSA-corrected current densities for CO based on the linear sweep voltammetry curves and the CO Faradaic efficiency.

Number of active sites and turn over frequency (TOF) measurements. To further characterize the catalytic activities of 3% Pd/C, 3% Pd_30% CeO_x/C and 3% PdTe (0.15)_30% CeO_x/C, we applied a roughness factor technique to determine the number of active edge sites of the catalysts. Roughness factor (R_f) was estimated by dividing the electrocatalytically active surface area to geometric surface area (0.19625 cm^2 here)[3].

R_f = ECSA/GAS= Q_R / Q_F (Eq. S2)

The calculated number of active sites for each catalyst was obtained using the equation:

Density of active sites for catalyst (sites/cm^2) = Density of active sites for standard sample (sites/cm^2) × R_f (Eq. S3)

We note that the chemical compositions of the Pd-based catalysts remained unchanged during electrochemical CO_2 reduction at applied potentials in the range of -0.6 to -1.2 V (vs. RHE), allowing for estimation of turnover frequency (TOF) in this potential range. The CO formation TOF of active sites for CO_2 reduction reaction was calculated at different overpotentials using Eq. S4[4]:

CO formation TOF (s^{-1}) = i_0 (A cm^{-2}) × CO formation FE /([active sites density (sites/cm^2)] × [1.602 ×10^{-19} (C/e$^-$)] × [2e$^-$/CO_2]) (Eq. S4)

Faradaic efficiency (FE) measurement. The FE values of catalysts were calculated using $E_{Faradaic} = \alpha nF/Q$, where α is the number of electrons transferred (α = 2 for CO and H_2 production), n the number of moles for a given product, F Faraday's constant (96,485 C mol^{-1}), Q all the charge passed throughout the electrolysis process (measured by calculating the curve area of current density vs. time plot). CO and H_2 mole fractions of injected samples were calculated using GC calibration curve.

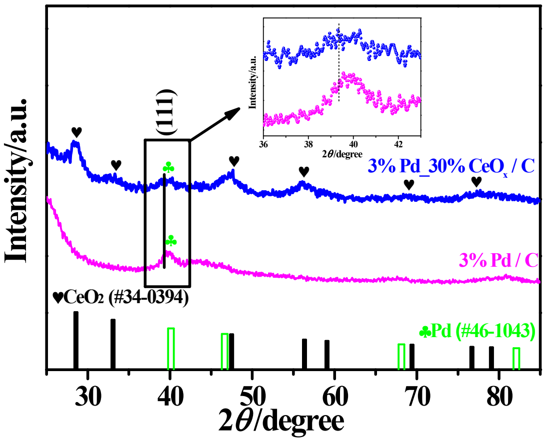


Fig. S1 XRD patterns of 3 wt% Pd/C and 3 wt% Pd_30% CeO_x/C.

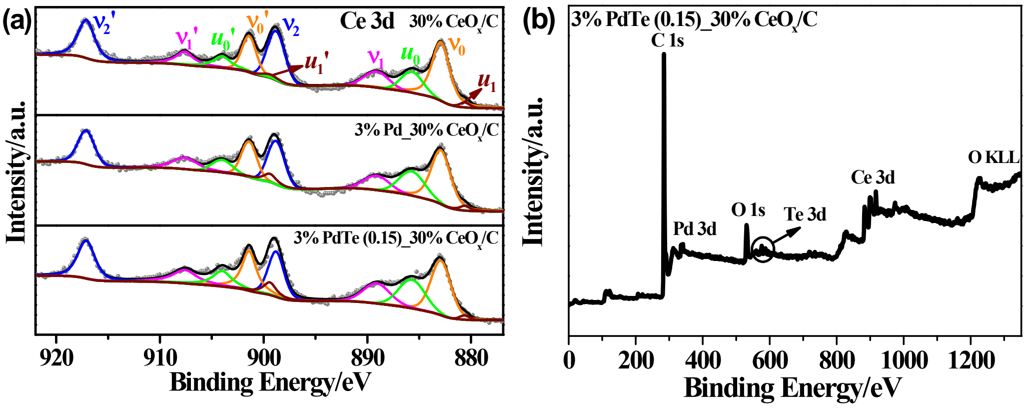


Fig. S2 (a) Ce 3d XPS spectrum of 30% CeO_x/C, 3% Pd_30% CeO_x/C and 3% PdTe (0.15)_30% CeO_x/C. (b) The wide-survey XPS spectrum of 3% PdTe (0.15)_30% CeO_x/C.

Table S1 Charge of Pd and O atom in interface of Pd and CeO_2

Atom	CeO_2	Pd/CeO_2	PdTe/CeO_2
O	-1.068	-1.128	-1.135
Pd		+0.303	+0.095

We proposed that electron transfer occurred from Pd to O through Pd1-O bond. Positive charge of Pd1 was found in Pd/CeO_2 and PdTe/CeO_2, while more negative charge of O was obtained in Pd/CeO_2 and PdTe/CeO_2 than that of CeO_2.

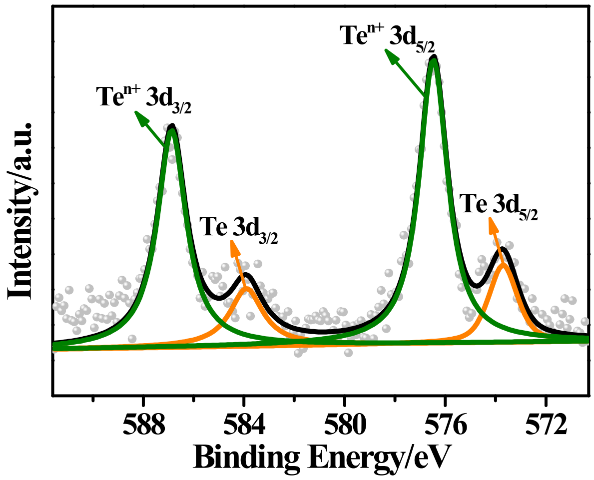
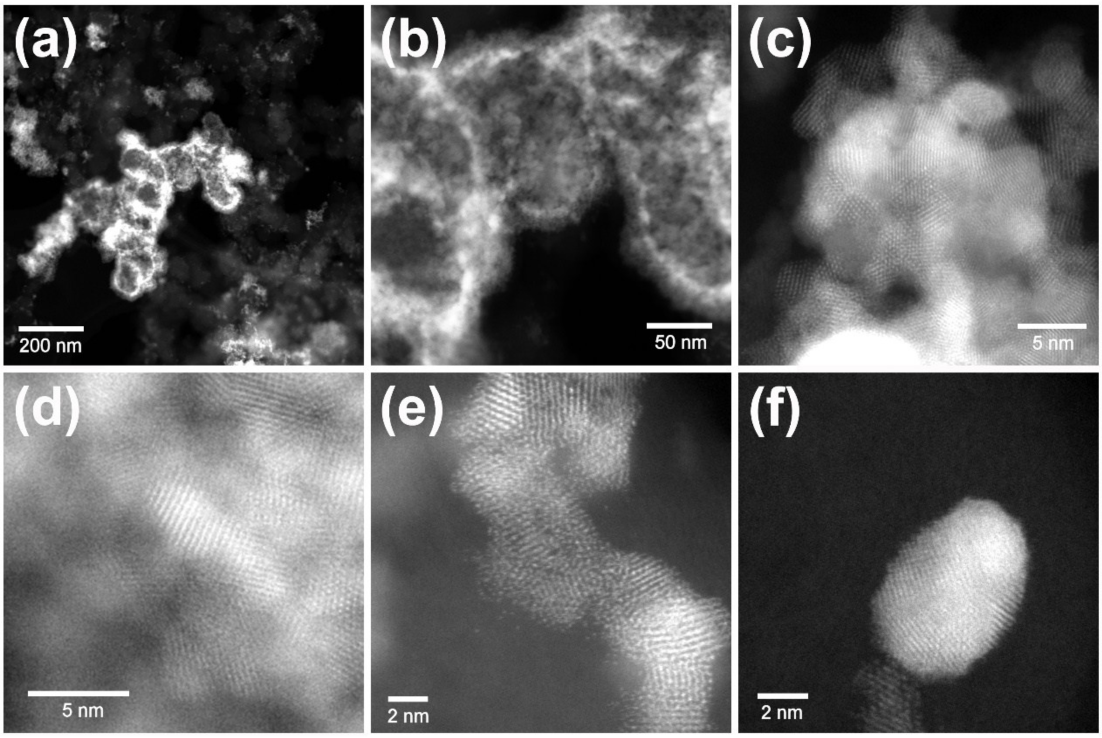


Fig. S3 Te 3d XPS spectrum of 3% PdTe(0.15)_30% CeO_x/C.



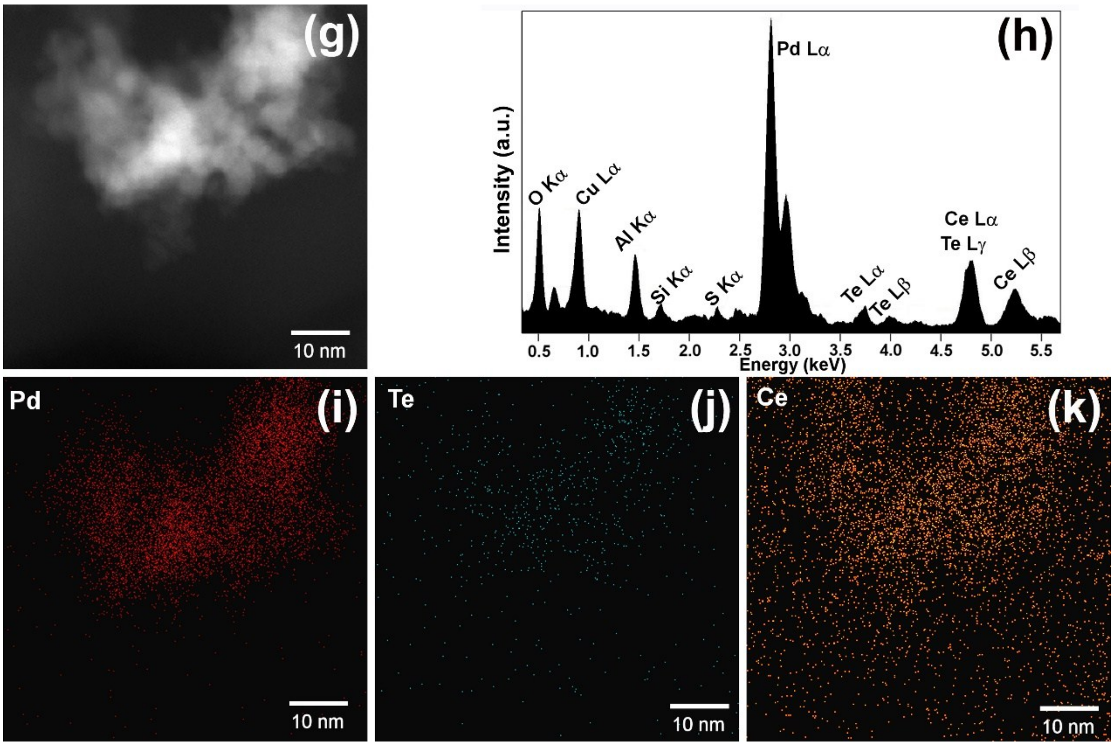


Fig. S4 STEM and EDX characterization of 3% PdTe_30% CeO$_x$/C. (a)-(b) Low-magnification, (c)-(f) high-magnification, and (g) medium-magnification STEM images. (h) EDX spectrum, and (i)-(k) EDX mapping images of Pd, Te, and Ce, respectively, taken from the region shown in (g).

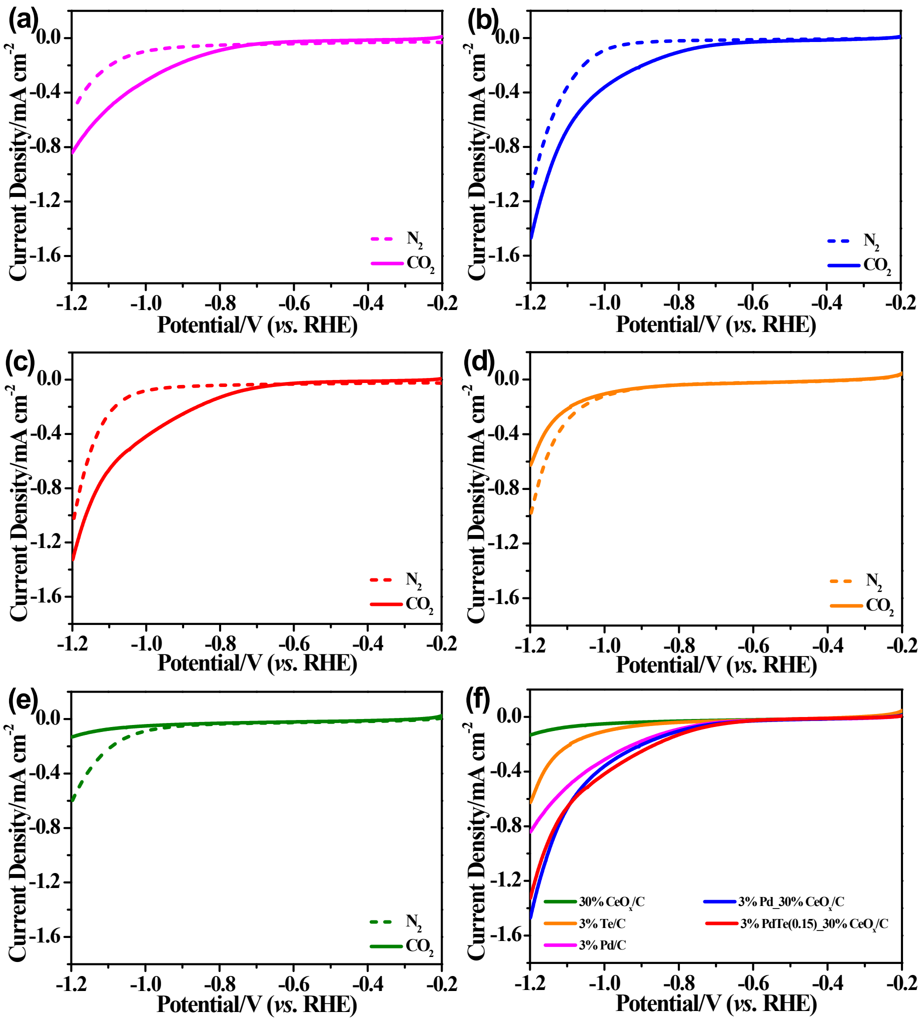


Fig. S5 Current–voltage curves on (a) 3% Pd/C, (b) 3% Pd_30% CeO$_x$/C, (c) 3% PdTe (0.15)_30% CeO$_x$/C, (d) 3% Te/C and (e) 30% CeO$_x$/C electrodes obtained from the LSV scans in CO$_2$- and N$_2$-saturated 0.1 M aqueous KHCO$_3$. (f) LSVs of 30% CeO$_x$/C, 3% Te/C, 3% Pd/C, 3% Pd_30% CeO$_x$/C, and 3% PdTe(0.15)_30% CeO$_x$/C electrodes in CO$_2$-saturated 0.1 M KHCO$_3$. Scan rate: 5 mV s^{-1}.

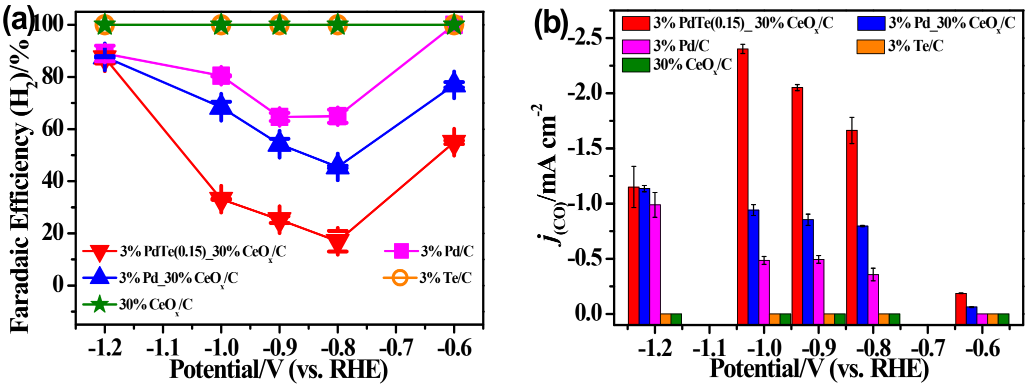


Fig. S6 (a) Faradaic efficiency for H_2 production of 30% CeO$_x$/C, 3% Te/C, 3% Pd/C, 3% Pd_30% CeO$_x$/C and 3% PdTe (0.15)_30% CeO$_x$/C catalysts, and (b) partial current density of CO formation on 30% CeO$_x$/C, 3% Te/C, 3% Pd/C, 3% Pd_30% CeO$_x$/C and 3% PdTe (0.15)_30% CeO$_x$/C catalysts at various applied potentials in 0.1 M aqueous KHCO$_3$.

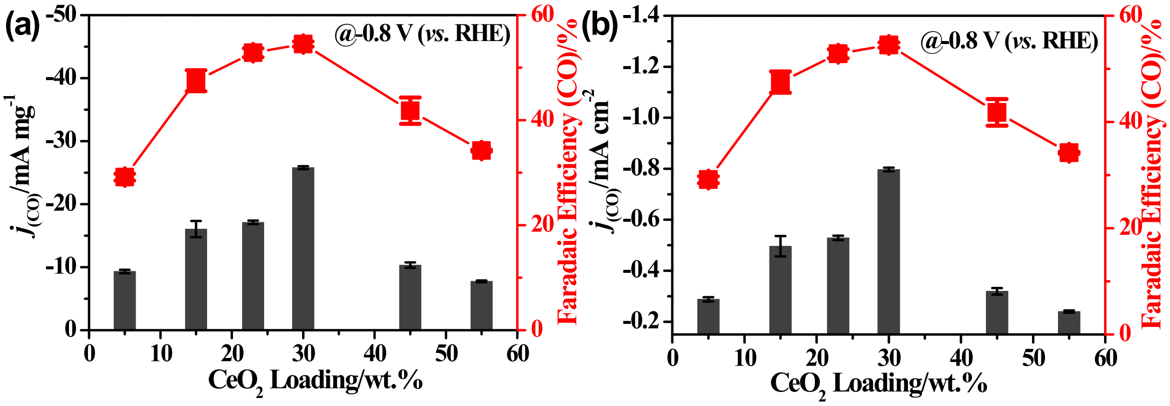


Fig. S7 (a) Mass activities and FEs, and (b) partial current density and FEs on different CeO$_x$ mass loadings at various applied potentials in 0.1 M KHCO$_3$ electrolyte.

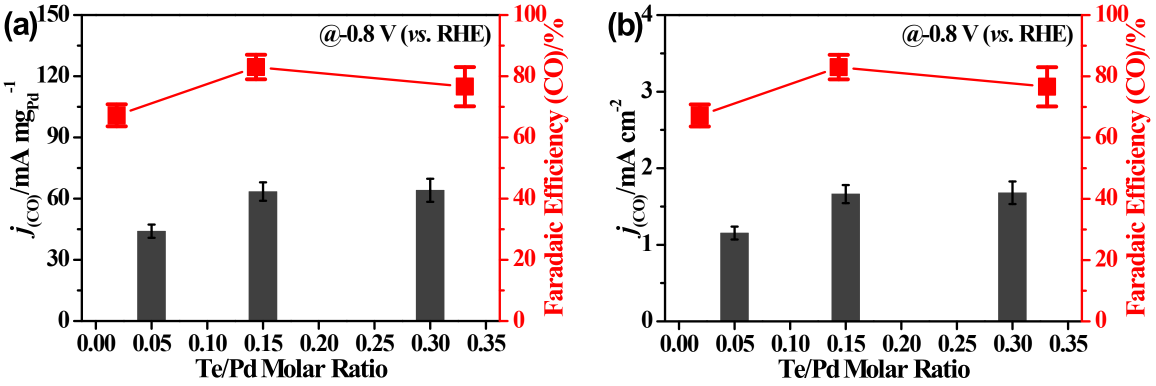


Fig. S8 (a) Mass activities and FEs, and (b) partial current densities and FEs of 3% PdTe_30% CeO_x/C with different Te/Pd molar ratios [Te/Pd (mol/mol) = 0.05, 0.15, 0.3] at various applied potentials in 0.1 M aqueous $KHCO_3$.

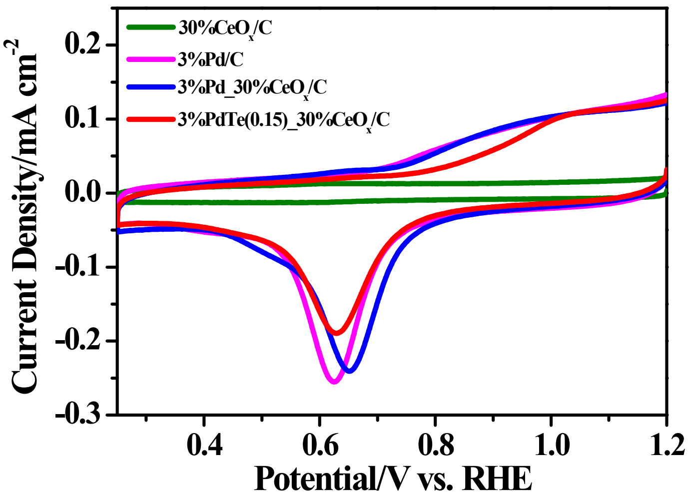


Fig. S9 Representative CVs of 30% CeO_x/C, 3% Pd/C, 3% Pd_30% CeO_x/C and 3% PdTe (0.15)_30% CeO_x/C electrodes in a deaerated 0.1 M $HClO_4$ solution with a scanning rate of 50 mV/s with upper potential limits at 1.2 V *vs*. RHE.

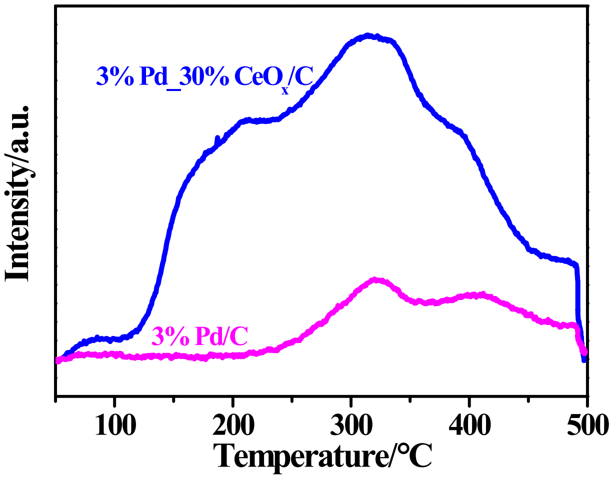


Fig. S10 CO_2-TPD-MS spectra of 3% Pd/C and 3% Pd_30% CeO_x/C.

References

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2. M. Hara, U. Linke and T. Wandlowski, *Electrochim. Acta*, 2007, **52**, 5733-5748.
3. S. Trasatti and O. A. Petrii, *J. Electroanal. Chem.*, 1992, **327**, 353-376.
4. M. Asadi, K. Kim, C. Liu, A. V. Addepalli, P. Abbasi, P. Yasaei, P. Phillips, A. Behranginia, J. M. Cerrato, R. Haasch, P. Zapol, B. Kumar, R. F. Klie, J. Abiade, L. A. Curtiss and A. Salehi-Khojin, *Science*, 2016, **353**, 467-470.