Modulation of the selectivity of CO2 to CO electroreduction in palladium rich Palladium-Indium nanoparticles

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Reply to: "On the role of metal cations in CO_2 electroreduction reduction"

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Supplementary Information

Supplementary Methods

Density functional theory (DFT) simulations were carried out through the Vienna Ab Initio Simulation Package(VASP).[1,2] We chose the PBE density functional (ref 3) including dispersion through the DFT-D2 method,[4,5] with our reparametrized C_6 coefficients.[6] Inner electrons were represented by PAW pseudopotentials[7,8] and the monoelectronic states for the valence electrons were expanded as plane waves with a kinetic energy cutoff of 450 eV. We employed a 4-layer thick Au(111) (3×3) supercell, with the two innermost Au layers fixed to mimic the bulk and 3 H_2O molecules within the solvation layer. A vacuum thickness of around 8 Å vacuum was included beyond the outermost H_2O molecule. A K^+ was inserted within the solvation layer to assess the "with metal cation" case (see Fig.1a), while no cation was present in the system "without metal cation" (Fig. 1c). To model the case "with metal cation" but "no excess electron", we removed one hydrogen from one H_2O molecule (Fig. 1b), leading to a charge balanced cell with one K^+ and one OH^-. To compute activation angle α (Fig. 1d,e) and Bader charge q (Fig. 1f,g) of the CO_2 unit, we carried out a ionic optimization of the overall system: Au surface, H_2O molecules, cation (if present), and a CO_2 molecule initially adsorbed on the surface and let free to move. Since K^+, CO_2, and the explicit solvation layer were placed only on one side of the slab, we applied an additional dipole correction to remove spurious contributions arising from the asymmetric slab model.[9]

To assess the role of explicit electrostatic effects on CO_2 activation, we applied different intensities of electric field ($\vec{E}_{EDL}$) through a dipole correction (refs. 6,10): –0.2 V Å^{-1}, –0.4 V Å^{-1}, –0.6 V Å^{-1}. Considering a potential of zero charge (U_{PZC}) for polycrystalline gold of +0.2 V vs SHE (ref. 13) and an electrical double layer thickness (d_{EDL}) of 3 Å,[11,12] such electric field intensities correspond roughly to values of electric potential of –0.4 V vs. SHE, –1.0 V vs. SHE, and –1.6 V vs. SHE respectively, Supporting Equation 1.

$$U \text{ (vs. SHE)} = U_{PZC} + \vec{E}_{EDL} \cdot d_{EDL} \tag{1}$$

Supplementary References

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