

## Supporting Information

### Strain and Ligand Effects on CO<sub>2</sub> Reduction Reactions Over Cu-Metal Heterostructure Catalysts

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It is well known that the GGA overestimates the lattice constants of metals at different levels, and in a lot of cases the DFT (GGA) lattice constants were still used as the basis to study the properties of catalysts. Yet, in some calculations, the experimentally determined lattice constants were used instead.<sup>1</sup> This is because firstly, the difference in two lattice constants is quite small. For example, Delley reported that the error is 0.77%, 0.91%, 2.07%, 1.56%, 1.06% and 1.78% for Ni, Cu, Pd, Rh, Ir, Pt, respectively.<sup>2</sup>

Secondly, the differences in surface properties obtained using two lattice constants are also small. For example, the adsorption of CO on Pt(111) surface has been checked by Gil et. al. using both the experimental lattice constant and the GGA optimized one. Their tested calculations concluded that there is no significant effect on the difference in adsorption energy on the top and hollow sites.<sup>3</sup>

We further check the influence of using GGA optimized (expanded) lattice constants, which are listed in the table below. Usually the difference in lattice constants are small and the over 5% differences come from the choice of the treatment of core electrons implemented in Dmol3.<sup>4</sup> All electron treatment was used for all the calculations, leading to the larger lattice expansion of Pt and Ir.<sup>5-6</sup> The second poorest prediction is for Ir, whose GGA lattice is 5.14% larger than the experimental value. And we choose the Cu(1ML)-Ir(111) heterostructure model as an extreme example. The values of lattice mismatch between the two metals are 9.8% and 6.2% using the GGA values and the experimental data, respectively.

Calculations of the Cu(1ML)-Ir(111) model show that different lattice constants have small influence over adsorptions. For strain-insensitive species \*CO, the adsorption energies are 0.845 eV and 0.812 eV for the GGA and experimental lattices, correspondingly. For strain-sensitive adsorbate \*CHO, the adsorption energies are 1.332 eV and 1.239 eV, respectively.

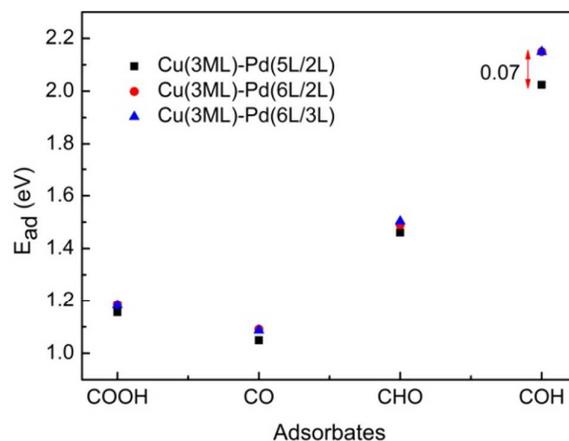
The strain effects on the adsorptions of \*CO and \*CHO are 0.006 eV and -0.233 eV using the GGA lattices, respectively, and -0.034 eV and -0.164 eV using the experimental lattices, correspondingly. The differences in the two strain effects are even smaller, 0.010 eV for \*CO and 0.069 eV for \*CHO. The corresponding ligand effects on the adsorptions of \*CO and \*CHO are -0.111 eV and -0.078 eV using the GGA lattices, and -0.117 eV and -0.090 eV using experimental lattice parameters. The differences in the two ligand effects are also much smaller, 0.006 eV for \*CO and 0.012 eV for \*CHO.

In short, we believe that using experimental lattices instead of GGA ones has little influence of on the stain and ligand effects, thus the use of experimental lattices should not affect the conclusions. We have highlighted the potential confusing point in the Method part. Table S1 and the above explanation have been put into the Supporting Information as well to help clarify the consequence of using experimental lattices.

**Table S1.** Experimental and GGA optimized lattice constants

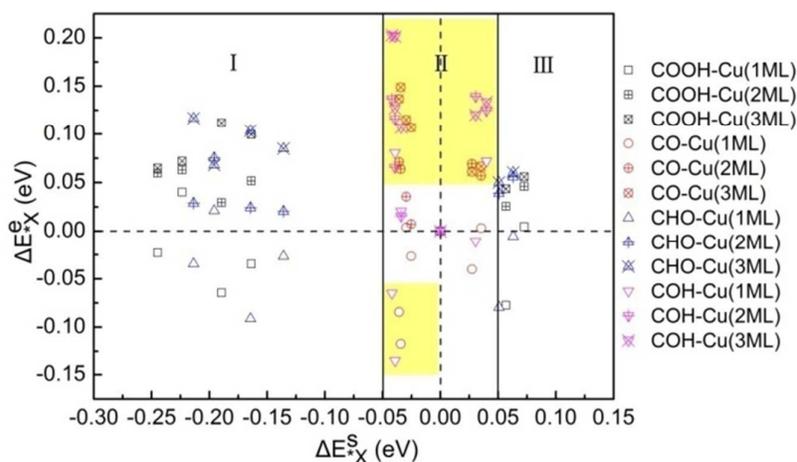
Metal	Experimental lattice constant (Å)	GGA lattice constant (Å)	Error (%)
Ni	3.524	3.5593	1.00
Co	3.544	3.5743	0.85
Cu	3.6147	3.6764	1.71
Rh	3.8044	3.8999	2.51
Ir	3.8389	4.0363	5.14
Pd	3.8907	4.0081	3.07
Pt	3.9239	4.1317	5.29

In our calculations, we use five atomic layers with bottom two fixed as the catalytic slab model to calculate the adsorption energy of the key adsorbates during electroreduction CO<sub>2</sub>. However, the effect of the numbers of total layers and fixed layers on adsorption energy is uncertain. Therefore, we check the adsorption of these adsorbates as a function of the number of total layers with respect to the number of the fixed bottom layers. Here, as an example, only the Cu(3ML)-Pd model is considered, the results are shown in Figure S1. The adsorption energies of COOH, CO and CHO on these model surfaces are very close ( $dE < 0.1$  eV). Moreover, these small differences do not influence any of our conclusions and thus can be ignored. Therefore, the numbers of total layers and the fixed layers used in our slab models are reliable.



**Figure S1.** Adsorption energies of key adsorbates on the Cu(3ML)-Pd(5L/2L), Cu(3ML)-Pd(6L/2L) and Cu(3ML)-Pd(6L/3L) model surfaces. 5L or 6L, 3ML, and 2L or 3L represent total layers, relaxed top overlayers, and fixed bottom layers for the tested slab models, individually.

To compare the ligand and strain effects, we plot their contributions on the adsorption energy of intermediates of CO<sub>2</sub>RR in Figure S3. Three regions are divided based on the magnitude of energy. Region I, for tuning the adsorption energy of COOH and CHO, the strain effect (-0.15 ~ -0.25 eV) is stronger than the ligand effect (-0.1 ~ 0.12 eV). In region III, the strain effect is only slightly larger by ~0.02 eV than the ligand effect in tuning the adsorption of COOH and CHO. While the yellow area in region II marks the regime where the ligand effect (0.05 ~ 0.2 eV) is stronger than that of the strain effect (< 0.05 eV) for the adsorptions of CO and COH.



**Figure S2.** Ligand effect versus strain effect on tuning the adsorption energies of adsorbates of CO<sub>2</sub>RR. Region I: the strain effect is stronger; Region II: the ligand effect is stronger in the yellow rectangles. The boundary lines of  $\pm 0.05$  eV approximately mark the region of negligible strain contribution. Uncolored region, both the ligand and the strain effects are negligible ( $< 0.05$  eV). Region III: the strain effect is slightly larger than the ligand effect. The positive and negative values correspond to weakening and strengthening of adsorption, respectively.

### References:

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