# Supporting Information for: Decoupling Strain and Ligand Effects in Ternary Nanoparticles for Improved ORR Electrocatalysis

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#### **Dimer Studies**

Dimer bond lengths are shown in Table S1, giving an indication of the complex interplay between the various elements in the ternary nanoparticles. The change in strain and ligand effects will be predominantly related to the M-M and M-Au bond characteristics. Any changes in the Pt-Au bond effects will then be directly related to changes in the core region of the particle as otherwise, the Pt-Au interface remains constant across all compositions. Changes to the RMSD across the various compositions will be related to the potential changes in all possible elemental bonding pairs, e.g. M-M, M-Au, Au-Au, Au-Pt and Pt-Pt. Thus, singling out reasons for specific changes to the RMSD can be complex as potential changes to bonding properties for certain interactions can be cancelled out, or enhanced by other interactions.

It is found that, in general, all homoatomic M-M bond lengths are reduced with respect to M-Au. The single exception to this is the Zn-Zn dimer, where the bond length is elongated slightly, while the greatest reduction in the M-M bond length relative to Au-Au is for the Cr dimer. There is also a general reduction in M-M bond lengths with respect to Pt, the exceptions being the Sc, Zn and of course Au dimers. This gives an indication as to why there is a general reduction in the Pt shell strain for the multimetallic particles compared to the pure Pt and binary PtAu nanoparticles. It is somewhat more difficult to single out effects that cause the Ti, Mn and Zn containing particles to exhibit very low displacements compared to the Pt<sub>309</sub> nanoparticle. Neither the M-M or M-Au bond lengths tend to be that similar to the Pt-Pt bond length. Thus, it is likely that the culmination of bonding properties leads to the reduced overall displacement within the particles.

Μ	M-M (Å)	M-Au (Å)	$\Delta M$ -M(Au)	$\Delta M$ -M(Pt)	$\Delta$ M-Au(Au)
Sc	2.456	2.506	-0.119	0.082	-0.069
Ti	1.991	2.456	-0.584	-0.383	-0.119
V	1.824	2.432	-0.751	-0.550	-0.143
Cr	1.579	2.408	-0.996	-0.795	-0.167
Mn	1.749	2.398	-0.826	-0.625	-0.177
Fe	1.837	2.389	-0.738	-0.537	-0.186
Co	2.004	2.386	-0.571	-0.370	-0.189
Ni	2.097	2.368	-0.478	-0.277	-0.207
Cu	2.262	2.392	-0.313	-0.112	-0.183
Zn	2.844	2.466	0.269	0.470	-0.109
Pt	2.374	2.518	-0.201	-	-0.057
Au	2.575	-	-	0.201	-

Tab. S1: Homoatomic (M-M) and heteroatomic (M-Au) dimer bond lengths. The M-M bond lengths are then compared to the Au-Au ( $\Delta$ M-M(Au)) and Pt-Pt ( $\Delta$ M-M(Pt)) bond lengths as well as the M-Au bond compared to the Au-Au dimer ( $\Delta$ M-Au).

#### **Mixing Energies**

The mixing energies are calculated to assess the formation stability of the ternary nanoparticle, relative to the pure nanoparticles, as in Equ. 1. In this case, a negative mixing energy suggests formation of the ternary nanoparticle is favoured over formation of the pure nanoparticles.

$$E_m = \frac{1}{N} \left( E_{PtAuM} - \left( n_{Pt} \frac{E_{Pt}}{N} \right) - \left( n_{Au} \frac{E_{Au}}{N} \right) - \left( n_M \frac{E_M}{N} \right) \right)$$
(1)

 $E_{PtAuM}$  is the energy of the ternary Pt<sub>162</sub>Au<sub>92</sub>M<sub>55</sub> nanoparticle,  $E_{Pt/Au/M}$ , the energy of the pure e.g. M<sub>309</sub> nanoparticle, N is the total number of atoms in the nanoparticle and  $n_{Pt/Au/M}$  is the number of e.g. M atoms in the ternary nanoparticle. Mixing energies are calculated as they largely removes the energetic penalties of moving from a bulk to finite system, but retain descriptions of e.g. preferential chemical ordering associated with surface energy.

The resulting mixing energies for the ternary nanoparticles are shown in Figure S1. The mixing energies of the  $Pt_{162}Au_{92}V_{55}$  and  $Pt_{162}Au_{92}Cr_{55}$  are not shown as the optimisation of the pure  $V_{309}$  and  $Cr_{309}$  nanoparticles would not converge to the icosahedral structure of interest. The least stable nanoparticle is the binary  $Pt_{162}Au_{147}$ , with a mixing energy of around 0.12 eV per atom. As discussed in the main manuscript, it is well known that formation of a Pt-shell on Au-core is contrary to what would be expected, giving rise to the positive mixing energy. However, as referenced in the text, several experimental groups have successfully produced these conformations and demonstrated good kinetic stability under operational conditions. Therefore, it is encouraging to note that for the majority of the nanoparticles of interest, the mixing energy is reduced to below 0.04 eV per atom suggesting that they will be more stable than the binary  $Pt_{162}Au_{147}$  nanoparticle.



Fig. S1: Mixing energies calculated for various Pt<sub>162</sub>Au<sub>92</sub>M<sub>55</sub> nanoparticles.

#### **DOS Analysis**

F. Abild-Pedersen *et al* have discussed the use of the *d*-band edge as a descriptor of the likely catalytic properties of a system. The *d*-band edge is defined as the highest peak position resulting from the Hilbert transform of the *d*-band. This is suggested to be an electronic descriptor that is less susceptible to dramatic changes in the *d*-band shape. For  $Pt_{309}$ , the *d*-band edge is the same for both the edge-bridge and atop sites at 0.36 eV. In general, all other *d*-band edge values calculated for the various multimetallic nanoparticles are negative, aside from the  $Pt_{162}Au_{92}Mn_{55}$  nanoparticle, with an edge at 0.06 eV. Irrespective of this, all multimetallic nanoparticles exhibit a downshift when using the *d*-band edge as a descriptor. This fits well when considering OH binding on the constrained  $Pt_{162}Au_{92}M_{55}^*$  nanoparticles, where for both the edge-bridge and atop sites there is a weakening of the Pt-OH bond. However, while the *d*-band edge shifts in the expected direction when comparing the pure  $Pt_{309}$  nanoparticle with the Au containing nanoparticles, there is only a weak correlation between Pt-OH binding and *d*-band edge across the range of multimetallic nanoparticles.

Μ	<i>d</i> -centre	d-width	Occupation	Fractional Filling	Skewness	Kurtosis	d-band Edge
	(eV)	(eV)					(eV)
Sc	-1.16	2.27	9.06	0.88	0.45	9.50	-0.20
Ti	-1.25	2.34	9.06	0.88	0.30	9.33	-0.20
V	-1.32	2.39	9.05	0.88	0.20	9.34	-0.19
Cr	-1.34	2.40	9.04	0.88	0.17	9.26	-0.16
Mn	-1.20	2.38	8.79	0.86	0.31	10.07	0.06
Fe	-1.33	2.42	9.01	0.88	0.17	9.65	-0.09
Co	-1.37	2.43	9.05	0.88	0.14	9.45	-0.13
Ni	-1.47	2.42	9.21	0.89	0.01	8.71	-0.13
Cu	-1.37	2.40	9.05	0.88	0.10	9.28	-0.16
Zn	-1.33	2.34	9.05	0.88	0.10	8.98	-0.19
Pt	-1.32	2.37	9.05	0.88	0.22	9.01	-0.01
Au	-1.27	2.34	9.05	0.88	0.28	9.10	-0.17
Pt <sub>309</sub>	-1.61	2.47	9.05	0.88	-0.31	9.98	0.36

Tab. S2: DOS analysis for the edge-bridge site on the  $Pt_{162}Au_{92}M_{55}^*$  nanoparticles.

М	<i>d</i> -centre	d-width	Occupation	Fractional Filling	Skewness	Kurtosis	d-band Edge
Sc	-1.26	2.26	8.99	0.87	0.22	8.36	-0.23
Ti	-1.37	2.35	8.99	0.87	0.01	8.34	-0.24
V	-1.43	2.41	8.98	0.87	-0.08	8.39	-0.23
Cr	-1.46	2.43	8.99	8.87	-0.12	8.42	-0.19
Mn	-1.33	2.40	8.82	0.86	0.00	9.01	-0.12
Fe	-1.44	2.45	8.96	0.87	-0.10	8.76	-0.14
Co	-1.49	2.47	8.99	0.87	-0.17	8.65	-0.15
Ni	-1.57	2.47	9.13	0.88	-0.25	8.08	-0.17
Cu	-1.49	2.44	8.99	0.87	-0.18	8.33	-0.22
Zn	-1.42	2.34	8.99	0.88	-0.18	8.10	-0.22
Pt	-1.31	2.36	8.99	0.87	0.10	8.67	-0.17
Au	-1.27	2.32	9.00	0.88	0.19	8.41	-0.21
Pt <sub>309</sub>	-1.67	2.50	9.01	0.88	-0.38	8.93	0.36

Tab. S3: DOS analysis for the atop site on the  $Pt_{162}Au_{92}M_{55}^*$  nanoparticles.

The Pt-OH binding energies for the multimetallic nanoparticles are plotted against various *d*-band properties in the supplementary information Figure S4-S5. In all cases, the  $Pt_{309}$ -OH binding energy is not included in the plots as comparisons between characteristics for *d*-bands with significantly different shapes, as discussed above, is unreliable. There is generally little correlation between the various *d*-band characteristics plotted and the Pt-OH binding energy for those bound to the edge-bridge site. There is more significant correlations between *d*-band characteristics and binding energy at the atop site. As the edge-bridge atoms are relatively under-coordinated compared to facet atoms, it is likely that electronic effects play a greater role in changes to Pt-OH binding, thus the disproportionate shape of the *d*-band has greater effect at the edge-bridge site leading to reduced correlation. Conversely, it is found that even though there is an unexpected up-shift in the absolute value of the *d*-centre towards the Fermi energy when comparing the multimetallic nanoparticles to the pure  $Pt_{309}$  nanoparticle, the trends within the range of multimetallic nanoparticles studies holds true to the *d*-band model by Hammer and Nørskov for the atop site.

### **Density Differences**

Fig. S2: Density differences for *d*-band character of the Pt<sub>309</sub> nanoparticle subtracted from that of the PtAuM nanoparticle for the edge-bridge site. This demonstrates the different shape of the *d*-band for the pure Pt<sub>309</sub> nanoparticle compared to the Au containing particles. Negative values show where there is excess intensity from the Pt<sub>309</sub> nanoparticle and positive values show excess intensity from the multimetallic particles.



(a) Pt<sub>162</sub>Au<sub>92</sub>Sc<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(b)  $Pt_{162}Au_{92}Sc_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(c) Pt<sub>162</sub>Au<sub>92</sub>Ti<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(d) Pt<sub>162</sub>Au<sub>92</sub>Ti<sub>55</sub> averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(e) Pt<sub>162</sub>Au<sub>92</sub>V<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(f) Pt<sub>162</sub>Au<sub>92</sub>V<sub>55</sub> averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(g) Pt<sub>162</sub>Au<sub>92</sub>Cr<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(h)  $Pt_{162}Au_{92}Cr_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(i) Pt<sub>162</sub>Au<sub>92</sub>Mn<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(j)  $Pt_{162}Au_{92}Mn_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(k) Pt<sub>162</sub>Au<sub>92</sub>Fe<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(l)  $Pt_{162}Au_{92}Fe_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(m) Pt<sub>162</sub>Au<sub>92</sub>Co<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(n)  $Pt_{162}Au_{92}Co_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(0) Pt<sub>162</sub>Au<sub>92</sub>Ni<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(p)  $Pt_{162}Au_{92}Ni_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(q) Pt<sub>162</sub>Au<sub>92</sub>Cu<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(r) Pt<sub>162</sub>Au<sub>92</sub>Cu<sub>55</sub> averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(s) Pt<sub>162</sub>Au<sub>92</sub>Zn<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(t)  $Pt_{162}Au_{92}Zn_{55}$  averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(u) Pt<sub>162</sub>Au<sub>92</sub>Pt<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(v) Pt<sub>162</sub>Au<sub>92</sub>Pt<sub>55</sub> averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.



(w) Pt<sub>162</sub>Au<sub>92</sub>Au<sub>55</sub> density differences showing original *d*-band character as well as the subtracted character. Plotted with narrow smeqaring to more accurately show *d*-band character.



(x) Pt<sub>162</sub>Au<sub>92</sub>Au<sub>55</sub> averaged density difference with the averaging performed over approximately 1 eV. This is equivalent to increased smearing to better show the disparity in *d*-band shape.

#### **Bader Charge Analysis**

A Bader charge analysis has been performed on the trimetallic  $Pt_{162}Au_{92}M_{55}$  nanoparticles, as well as the strained  $Pt_{309}Au_{xyz}M_{xyz}$  nanoparticles. Significant difference in the charge transfer makes it difficult to compare d-band values. Charge transfer was calculated and then averaged over each shell (1, 12, 42, 92, 162 atoms) within the nanoparticle, the structure of which is in Figure S3. Comparisons between the ternary and strained nanoparticles give further indication of changes induced through forming the alloyed nanoparticles.

Averaged charges for the ternary  $Pt_{162}Au_{92}M_{55}$  nanoparticles are in Table S4. In all case there is relatively constant transfer of negative charge to the outer Pt-shell of between 0.05 and 0.02 |e|. Further, in all cases, the central atom also becomes negatively charged though the charge varies significantly for early, generally gaining greater negative charge, to late d-metals. There is variation across the d-metals for shells 2-4, though generally atoms in shell 2 also gain a negative charge, whilst those in shell 3 generally gain a positive charge. For shell 4, there is typically a shift with early d-metals gaining negative charge and late d-metals gaining positive charge.

Averaged charges for the strained  $Pt_{309}Au_{xyz}M_{xyz}$  nanoparticles are in Table S5. As with the multimetallic nanoparticles, the outer shell and central atom gain negative charge, though there is no variation in the charge gained by the



Fig. S3: Cross section of the nanoparticle showing the various shells.

Tab. S4: Charges averaged over the various atomic shells for the Pt<sub>162</sub>Au<sub>92</sub>M<sub>55</sub> ternary nanoparticles.

outer shell and less variation in the charge gained by the central atom when compared to the multimetallic nanoparticle. For the strained nanoparticles, shells 3 and 4 both become positively charged whilst there is variation across shell 2. As would be expected when comparing the multimetallic nanoparticles to the strained nanoparticles, there is greater variation in the amount of charge transferred as well as the transfer between shells comparing the various d-metal nanoparticles.

The charge transfer between the various multimetallic nanoparticles is relatively modest, thus it is unlikely that the discrepancies in relation between *d*-centre and Pt-OH binding can be attributed to significant variation in charge transfer. Further, the Bader analysis demonstrates that altering the core of the ternary  $Pt_{162}Au_{92}M_{55}$  nanoparticles can have a moderate effect on the electronic properties of the Pt-shell though there is a more significant effect at the M-Au interface. Finally, the strain effects exhibit little change in the charge transfer at the surface of the  $Pt_{309}Au_{xyz}M_{xyz}$ nanoparticles, though there is slight variation of the charge transfer in the core region.

М	Shell						
	1	2	3	4	5		
Sc	-0.09	-0.08	0.00	+0.08	-0.01		
Ti	-0.12	-0.05	+0.01	+0.07	-0.01		
V	-0.05	+0.02	+0.02	+0.06	-0.01		
Cr	0.00	+0.02	+0.02	+0.06	-0.01		
Mn	-0.02	0.00	+0.01	+0.06	-0.01		
Fe	-0.04	+0.04	+0.02	+0.05	-0.01		
Co	-0.02	+0.06	+0.03	+0.05	-0.01		
Ni	-0.03	+0.04	+0.03	+0.05	-0.01		
Cu	-0.05	+0.02	+0.02	+0.06	-0.01		
Zn	-0.08	-0.03	+0.01	+0.07	-0.01		
Pt	-0.08	-0.03	0.00	+0.07	-0.01		
Au	-0.09	-0.05	0.00	+0.08	-0.01		

Tab. S5: Charges averaged over the various atomic shells for the Pt<sub>309</sub>Au<sub>xyz</sub>M<sub>xyz</sub> strained nanoparticles.

## **Density Binding Relations**

Fig. S4: Characteristics of the *d*-band plotted against the Pt-OH binding energy for the edge-bridge site. The Pt-OH binding energy for the pure nanoparticle is not plotted as the difference in *d*-band sahape make direct comparisons between the  $Pt_{309}$  and multimetallc nanoparticles difficult. Instead all binding energies are plotted relative to the  $Pt_{309}$ -OH binding energy. Lines of best fit and  $R^2$  values are also shown, though there is little correlation.



(a) The *d*-band centre of the various nanoparticles plotted against the respective Pt-OH binding energy.



(b) The *d*-band width of the various nanoparticles plotted against the respective Pt-OH binding energy.



(c) The *d*-band skewness of the various nanoparticles plotted against the respective Pt-OH binding energy.



(d) The *d*-band edge of the various nanoparticles plotted against the respective Pt-OH binding energy.

Fig. S5: Characteristics of the *d*-band plotted against the Pt-OH binding energy for the atop site. The Pt-OH binding energy for the pure nanoparticle is not plotted as the difference in *d*-band sahape make direct comparisons between the Pt<sub>309</sub> and multimetallc nanoparticles difficult. Instead all binding energies are plotted relative to the Pt<sub>309</sub>-OH binding energy. Lines of best fit and R<sup>2</sup> values are also shown.



(a) The *d*-band centre of the various nanoparticles plotted against the respective Pt-OH binding energy.



(b) The *d*-band width of the various nanoparticles plotted against the respective Pt-OH binding energy.



(c) The *d*-band skewness of the various nanoparticles plotted against the respective Pt-OH binding energy.



(d) The *d*-band edge of the various nanoparticles plotted against the respective Pt-OH binding energy.