Supplementary Information

The Dome of Gold Nanolized for Catalysis

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PART 1 | The global minima of Au\textsubscript{n}O\textsubscript{m}/TiO\textsubscript{2}

Supplementary Figure S1 | The slab model for calculated and most stable Au\textsubscript{n} structures on stoichiometric and defective TiO\textsubscript{2} surfaces from SSW-NN global search, including the GM structures of Au\textsubscript{12}O\textsubscript{4}/TiO\textsubscript{2}(n=12, 18, 24); the GM structures of Au\textsubscript{n}/TiO\textsubscript{2}(n=12, 18, 24). The upper two figure show the slab model of p(9×3) rutile (110) surface that used in the global potential energy surface exploration of Au\textsubscript{n}O\textsubscript{m}/TiO\textsubscript{2} catalysts.

As shown in Figure S1, the GMs of Au\textsubscript{12}O\textsubscript{4}/TiO\textsubscript{2} and Au\textsubscript{n}/TiO\textsubscript{2} (n=12, 18 and 24) all exhibit stick configurations growing in the groove between two protruding rows of bridge O (O\textsubscript{br}) on TiO\textsubscript{2}(110) along [1\bar{1}0], anchored by eight Au-O\textsubscript{br} bonds. For all Au\textsubscript{n}O\textsubscript{m}/TiO\textsubscript{2} catalysts, the configuration of Au is largely the same as the corresponding Au\textsubscript{n}/TiO\textsubscript{2}, but it is noted that the Au particles are at the distal site away from the surface O\textsubscript{br} vacancy, which is different from very small clusters (e.g. Au\textsubscript{2} to Au\textsubscript{3}) that sits at the O\textsubscript{br} vacancy.\textsuperscript{13}
Supplementary Figure S2 | The most stable Au_{n}O_{m} structures on TiO_{2} surfaces from SSW-NN global search, including the GM structures of Au_{12}O_{2}/TiO_{2}(n=12, 18) and the GM structure of Au_{30}O_{4}/TiO_{2} (n=30, 35, 52)

For O-containing Au particles (Figure S2), the GMs of Au_{12}O_{2}/TiO_{2} and Au_{18}O_{2}/TiO_{2} contain two Au-O_{24}-Ti_{35} species at the interface. Comparing with Au_{12}/TiO_{2} and Au_{18}/TiO_{2}, the O-containing particles, although still in the groove between two rows of O_{2r}, become less spreading along [1 1 0] (forming only six Au-O_{2r} bonds) and thus higher with respect to surface. The particles have hollow voids but sealed at the bottom (Au_{18}O_{2}). The GM of Au_{30}O_{4} cluster (G_{f} = -0.035) can be regarded as an in-between structure from Au_{22}O_{4} (G_{f} = 0.037) to Au_{30}O_{4} (G_{f} = -0.033). For the GM of Au_{32}O_{4}, the Au particle is 1.3 nm in diameter and 1.01 nm in height with 5 atomic layers. The top 4 layers are close packed regular-square-pyramid, exposing (100) surface at the bottom. The pyramid then links with the bottom (5^{th}) layer, a close-packed (111) plane, that is in contact with TiO_{2}.

- The coverage of Au particles on the TiO_{2} (110) surface.

The coverage is defined by the total number of Au atoms in particle (3D structure) as previously used in the literature. Hence, the coverage of 71% is in fact not high and here it corresponds to the case of supported Au_{52}, which still have a separation of 9.38 Å between adjacent clusters. The Au_{22}O_{4} clusters corresponds to a coverage of 33% in this definition, which have a separation of 9.5 Å between clusters.
The formation energy of Au₉O₇ (Gᵢ) computation.

The formation energies of gold are calculated using equation (S1), where G[X] is the approximate Gibbs free energy of X. For solids, the free energy is approximated by its DFT total energy. For molecules, the free energy is calculated as equation (S2), including the DFT total energy [X], the zero-point-energy (ZPE) and the thermodynamic correction terms. G[Au(111)] is the free energy of a surface Au atom on Au(111).

\[
\Delta G_{Au} = [G[Au_{9}O_{7}TiO_{2}] - G[TiO_{2}] - n \times G[Au(111)]] / n
\]

\[
G[X](p, T) = E[X] + ZPE[X] + \{H[X](p^0,T) - H[X](p^0,0K) - T \times S[X](T, p^0) + k_B T \ln \frac{p}{p^0}\}
\]

The determination of the optimal O contents on/in Au particles

To determine the optimal oxygen content on/in Au particles, we have computed the differential adsorption energy of O₉₉ atom (ΔG) on the Au₉O₇/TiO₂ catalysts using equation (S3) under ambient condition. G[Au₉O₇/TiO₂] and G[Au₉O₇/TiO₂] are the total energy of the identified GM structures. The result is shown in Table S1, where the positive value means that the oxygen is more stable in the gas phase than on the surface.

\[
\Delta G_{O_9} = G[Au_{9}O_{7}/TiO_{2}] - G[Au_{9}O_{7-1}/TiO_{2}] - 1/2*G[O_{2}]
\]

| Supplementary Table S1 | The differential adsorption energies of O in Au₉O₇/TiO₂. |
|-------------------------|----------------------------------------------------------|
|                         | Au₉         | Au₁₂        | Au₁₈        | Au₂₄        |
| ΔG₁₀                   | -0.30       | -1.27       | -1.15       | -1.02       |
| ΔG₂₀                   | 0.26        | -0.62       | -1.09       | -1.39       |
| ΔG₃₀                   | /           | 1.17        | 0.12        | -0.72       |
| ΔG₄₀                   | /           | /           | /           | -0.32       |
| ΔG₅₀                   | /           | /           | /           | 0.80        |

The LUMO wavefunction of Au₂₄O₄ and Au₃₇O₄,

In Supplementary Figure S3 and S4, we show the LUMO wavefunction of the nano-domes, Au₂₄O₄/TiO₂ and Au₃₇O₄, and compare them with the HOMO and LUMO of Au₃₂ hollow cage in the gas phase. We found that the LUMO of the dome structures has the delocalized characteristics, demonstrating the aromaticity similar to Au₃₂ cage. The density of states plotted in Supplementary Figure S4 indicates that the HOMO of Au₃₂ cage is composed mainly by 5d orbitals but the LOMO is contributed from both 5d and 6s orbitals.

Supplementary Figure S3 | Lowest unoccupied orbital (LUMO) for Au₂₄O₄/TiO₂ and Au₃₇O₄. This state is critical since it helps to stabilize O₉₉ vacancy.
Supplementary Figure S4 | HOMO (left), LUMO (middle) and p-DOS of Au$_{32}$ hollow cage (right).
The HOMO of Au$_{32}$ is mainly contributed by Au 5d orbitals and LUMO have contributions from both 6s and 5d orbitals.

In Supplementary Figure S5, we show the initial and final snapshots of Au$_{24}$O$_4$/TiO$_2$, Au$_{24}$/TiO$_2$ from MD simulation at 800 K for 1 ns. The morphology of Au$_{24}$O$_4$/TiO$_2$ catalyst basically keeps the configuration of the GM. For Au$_{24}$/TiO$_2$, the cluster has completely lost its original dome-like morphology, migrating away from the original site. We have also shown the initial and final snapshots of Au$_{24}$O$_4$/TiO$_2$ and Au$_{19}$/TiO$_2$ from MD simulation at 300 K for 1 ns, where the clusters basically maintain its original morphology which atoms slightly vibration around its initial position.
Supplementary Figure S5 | The initial (left panel) and final snapshots (right panel) for Au$_{24}$, Au$_{24}$O$_4$ and Au$_{37}$O$_4$ particles with (w/) or without the adsorption of CO from MD simulations at 800K or 300K for 1ns. A movie corresponds to the MD trajectory of Au$_{24}$O$_4$ / TiO$_2$ is also present where each frame corresponds to 10 ps.
PART 2 | Energetics data and microkinetic simulation details for CO oxidation on Au\(_n\)O\(_m\)/TiO\(_2\)

Supplementary Table S2 lists the formation energy of O\(_{\text{br}}\) vacancy, the adsorption energy of CO and the reaction barrier for CO to react with the O\(_{\text{br}}\) of different Au\(_n\)O\(_m\)/TiO\(_2\) catalysts. Table S3 lists the reaction energy barrier and reaction rate constant used for microkinetic simulation of CO oxidation on Au/TiO\(_2\) at p(CO)= 0.01atm, p(O\(_2\)) = 0.21atm and 300K.

**Supplementary Table S2** | Formation energy of O\(_{\text{br}}\) vacancy next to Au particle (E\(_{\text{f-O}}\)), the adsorption energy of CO (E\(_{\text{ad-CO}}\)) and the barrier of CO to react with O\(_{\text{br}}\) (E\(_{\text{b}}\)). All are in the unite of eV.

|          | AuO | Au\(_2\)O\(_2\) | Au\(_3\)O\(_2\) | Au\(_2\)O\(_4\) | Au\(_3\)O\(_4\) | Au\(_5\)O\(_4\) |
|----------|-----|----------------|----------------|----------------|----------------|----------------|
| E\(_{\text{f-O}}\)^* | 2.31 | 2.70           | 2.63           | 1.66           | 2.08           | 2.21           |
| E\(_{\text{ad-CO}}\)^* | 1.15 | 1.33           | 0.53           | 1.01           | 0.22           | 0.23           |
| E\(_{\text{b}}\)^* | 0.93 | 0.93           | 0.45           | 0.61           | 0.16           | 0.17           |

*a: E\(_{\text{ad}}\) of CO in the initial state of the first reaction step, CO\(^*\)+O\(_{\text{br}}\).  
b: The reaction barrier for CO to react with O\(_{\text{br}}\) (the first step, CO\(^*\)+O\(_{\text{br}}\)).

* PBE+U functional is utilized for computing the O vacancy formation energy.

**Supplementary Table S3** | The free energy barrier (G\(_{\text{a},+}\) and G\(_{\text{a},-}\)) and reaction rate constant (k\(_{+}\), k\(_{-}\)) used for microkinetic simulation of CO oxidation on Au/TiO\(_2\) at p(CO)= 0.01atm, p(O\(_2\)) = 0.21atm and 300K. The initial coverage for Au sites (*) and reactive O\(_{\text{br}}\) (O\(_{\text{br}}\)) are set to 1. The initial coverage for O\(_2\) (O\(_2\)) and O\(_{\text{br}}\) (O\(_{\text{br}}\)) are set to zero.

| Elementary step Au\(_{24}\)O\(_4\) | G\(_{\text{a},+}\) | G\(_{\text{a},-}\) | k\(_{+}\) | k\(_{-}\) |
|---------------------|----------------|----------------|--------|--------|
| CO + * -> CO\(^*\)  | 0.52           | 1.10           | 1.15E+01 | 2.07E-06 |
| CO\(^*\) + O\(_2\) -> CO\(_2\) + * + $ | 0.57 | 2.17 | 1.66E+03 | 2.19E-24 |
| O\(_2\) + $ + * -> O\(_2\) + ^ | 0.54 | 1.01 | 5.29E+03 | 6.73E-05 |
| CO + ^ -> CO\(^^\) | 0.52 | 0.81 | 1.15E+04 | 4.83E-02 |
| CO\(^^\) + O\(_2\) + ^ -> OCOO\(^^\) + ^ | 0.32 | 0.48 | 3.87E+07 | 5.39E+04 |
| OCOO\(^^\) -> CO\(_2\) + O\(_2\) + * | 0.29 | 4.43 | 1.21E+07 | 2.35E-62 |

| Elementary step Au\(_{37}\)O\(_4\) | G\(_{\text{a},+}\) | G\(_{\text{a},-}\) | k\(_{+}\) | k\(_{-}\) |
|---------------------|----------------|----------------|--------|--------|
| CO + * -> CO\(^*\)  | 0.52           | 0.26           | 1.15E+01 | 2.68E+08 |
| CO\(^*\) + O\(_2\) -> CO\(_2\) + * + $ | 0.13 | 1.27 | 4.09E+10 | 2.88E-09 |
| O\(_2\) + $ + * -> O\(_2\) + ^ | 0.54 | 1.77 | 5.29E+03 | 1.15E-17 |
| CO + ^ -> CO\(^^\) | 0.52 | 0.18 | 1.15E+04 | 5.91E+09 |
| CO\(^^\) + O\(_2\) + ^ -> OCOO\(^^\) + ^ | 0.28 | 0.68 | 1.24E+08 | 2.35E+01 |
| OCOO\(^^\) -> CO\(_2\) + O\(_2\) + * | 0.34 | 4.58 | 1.21E+07 | 7.10E-65 |

The reaction condition is set as p(CO)= 0.01atm, p(O\(_2\)) = 0.21 atm, and a series of temperature utilized in simulations, ranging from 200 to 300 K. The catalysts initially have all the interfacial Au sites occupied by adsorbed CO; the surface is in stoichiometry without O\(_{\text{br}}\) and O\(_2\) coverage on surface is zero.

**Computation for reaction rate (mol\(_{CO}\) g\(_{Au}\)\(^{-1}\)s\(^{-1}\)).** The reaction rate of CO\(_2\) production on Au\(_{24}\)O\(_4\) and Au\(_{37}\)O\(_4\) is obtained from equation S4, where R\(_{mk}\) is the rate obtained from microkinetic simulation. Each Au\(_n\) (n=24, 37) particle has two active sites at the interface and the Au molar mass is 197 g/mol.

\[
R(Au_n, n=24, 37) = R_{mk}*2/n/197 = 4.50*10^{-2} \text{ mol}_{CO}\text{ g}_{Au}^{-1}\text{ s}^{-1}\]  

**RMSD computation.** The RMSD of Au particle during MD simulation is calculated by equation (S5), where \(q_i\) is the cartesian coordinates of atom i.

\[
\text{RMSD} = \sqrt{\frac{\sum (q_i^f - q_i^0)^2}{n_{Au}}} \]  

(S5)
Supplementary Table S4 | The benchmark of the dispersion effect (with Grimme’s D3 dispersion correction, PBE-D3)\textsuperscript{a}, the dipole effect and the layer effect.

|                  | PBE+U | PBE+U, D3 | PBE+U, D3, Dipole\textsuperscript{g} | PBE+U, D3, SL\textsuperscript{d, g} | PBE+U | PBE+U, D3 |
|------------------|-------|----------|------------------------------------|-----------------------------------|-------|----------|
| $E_{ad}$ CO\textsuperscript{a} | 1.10  | 1.11     | 1.12                               | 1.14                             | 0.26  | 0.29     |
| $E_{b1}$\textsuperscript{b}     | 0.57  | 0.55     | 0.57                               | 0.57                             | 0.13  | 0.15     |
| $E_{ad}$ CO\textsuperscript{c} | 0.81  | 0.76     | 0.79                               | 0.78                             | 0.18  | 0.16     |
| $E_{ad}$ O\textsubscript{2}\textsuperscript{c} | 1.01  | 1.04     | 1.02                               | 1.05                             | 1.77  | 1.76     |
| $E_{b2}$\textsuperscript{b}     | 0.32  | 0.27     | 0.28                               | 0.25                             | 0.28  | 0.32     |
| $E_{b3}$\textsuperscript{c}     | 0.29  | 0.32     | 0.30                               | 0.26                             | 0.34  | 0.32     |

\textsuperscript{a} $E_{ad}$ of CO in the initial state of the first reaction step, CO*+O\textsubscript{2}.
\textsuperscript{b,e,f} The reaction barrier for three steps.
\textsuperscript{c} $E_{ad}$ of CO and O\textsubscript{2} in the state of the second reaction step.
\textsuperscript{d} SL indicates the TiO\textsubscript{2} with 5 layers.
\textsuperscript{g} a single point energy is computed using the configuration from PBE+U+D3.

As shown in Table S4, the variation of the adsorption energy and energy barrier of key reactions are within 0.05 eV with or without dispersion correction and dipole correction, which doesn’t affect the main conclusion.

PART 3 | Training dataset and benchmark of the AuTiO and AuTiCO G-NN potential

To cover all the likely compositions of Au-Ti-O our SSW simulations have been carried out for different structures (including bulk, layer and particle), compositions and atom number per unit cell (4 ~ 524) for Ti, TiO, Au, AuO\textsubscript{x} and Au-Ti-O. Overall, these exhaustive SSW simulations generate more than 10\textsuperscript{7} structures on global PES. The final global dataset that is computed from high accuracy DFT calculation contains 44,541 structures screened from global PES, as detailed in SI Table S4.

To pursue a high accuracy for PES, we have adopted a large set of power-type structure descriptors (PTSDs), which contains 198 descriptors for every element with only power-type structure descriptors, including 82 two-body, 96 three-body, 20 four-body descriptors, and compatibly, the network utilized is also large involving two-hidden layers (198-50-50-1 network), equivalent to 37,753 network parameters in total. Min-max scaling is utilized to normalization the training data sets. Hyperbolic tangent activation functions were used for the hidden layers, while a linear transformation was applied to the output layer of all networks. The limited-memory Broyden-Fletcher-Goldfarb-Shannon (L-BFGS) method is used to minimize the loss function to match DFT energy, force and stress. The final energy and force criterions of the root mean square errors are around 6.3 meV/atom and 0.155 eV/Å respectively. To confirm the accuracy of G-NN PES for Au particles on TiO\textsubscript{2}, we also select key Au/TiO\textsubscript{2} structures to compare G-NN results with DFT calculations. It has a max energy error of 3.89 meV/atom, which is quite standard for NN potentials and accurate enough (correct energy ordering) for searching the stable structure candidates. This benchmark results can be found in SI Table S6.

Finally, SSW-NN simulation is performed over a wide range of composition and structures, both for the global dataset generation in Fig. 1 and for the PES. For the data in Fig. 1, they are taken from the global minima of AuTiO as identified from the SSW-NN simulation, where each composition is simulated in the unit cells of 330 ~ 525 atoms and explored to visit more than 10\textsuperscript{5} minima on PES.
by SSW. Thus, a large variety of structures have been obtained from SSW-NN simulation. All the low energy structure candidates from SSW-NN exploration are finally fully optimized and verified by DFT calculations.

Supplementary Table S4 lists the structure information in the first principles global dataset for AuTiO G-NN potential training. Taking this dataset as basic training set, we then add extra data involving carbon element, including CO and O$_2$ adsorbed on identified Au$_{24}$O$_4$ and Au$_{37}$O$_4$ clusters. Supplementary Table S5 lists the structure information in the first principles global dataset for AuTiCO G-NN potential training. Benchmark between G-NN and DFT calculations for several supported Au$_n$O$_m$/TiO$_2$ catalysts are listed in Table S6.

### Training dataset of the AuTiO G-NN potential

All the structures included in the dataset are sorted in the sequence of number of C, O, Ti, Au atoms, where the structures obtained from the Bayesian optimization are listed at the bottom. All the training data sets are available online.

**Supplementary Table S5 | Structure information in the first principles global dataset.** Listed data are the number of the structures in the global dataset, as distinguished by the chemical formula, the number of atoms (N), the type of structures (cluster, bulk, layer).

| Species     | Natm | cluster | layer | bulk | total |
|-------------|------|---------|-------|------|-------|
| Au8         | 8    | 0       | 125   | 0    | 125   |
| Au14        | 14   | 0       | 3     | 56   | 59    |
| Au15        | 15   | 135     | 5     | 69   | 209   |
| Au16        | 16   | 1365    | 218   | 8165 | 9746  |
| Au28        | 28   | 0       | 2     | 68   | 70    |
| Au29        | 29   | 0       | 37    | 30   | 67    |
| Au30        | 30   | 59      | 26    | 121  | 206   |
| Au31        | 31   | 0       | 75    | 75   |       |
| Au32        | 32   | 30      | 2     | 225  | 257   |
| Au45        | 45   | 25      | 0     | 0    | 25    |
| O1-Au16     | 17   | 0       | 1     | 133  | 134   |
| O2-Au16     | 18   | 47      | 33    | 86   | 166   |
| O4          | 4    | 0       | 15    | 0    | 15    |
| O4-Au16     | 20   | 0       | 86    | 174  | 260   |
| O4-Au24     | 28   | 76      | 18    | 109  | 203   |
| O6-Au4      | 10   | 0       | 0     | 2918 | 2918  |
| O6-Au16     | 22   | 0       | 5     | 187  | 192   |
| O6-Ti4      | 10   | 0       | 0     | 44   | 44    |
| O7-Au8      | 15   | 0       | 0     | 1158 | 1158  |
| O7-Ti4-Au2  | 13   | 0       | 103   | 0    | 103   |
| O7-Ti4-Au5  | 16   | 0       | 261   | 13   | 274   |
| O8-Au8      | 16   | 0       | 0     | 2361 | 2361  |
| O8-Au16     | 24   | 0       | 66    | 40   | 106   |
| O8-Ti4      | 12   | 2115    | 190   | 11379| 13684 |
| O8-Ti4-Au2  | 14   | 0       | 115   | 0    | 115   |
| O8-Ti4-Au5  | 17   | 0       | 306   | 12   | 318   |
| O9-Ti4-Au1  | 14   | 0       | 153   | 0    | 153   |
| O9-Ti4-Au5  | 18   | 0       | 46    | 240  | 286   |
| O10-Au16    | 26   | 0       | 63    | 19   | 82    |
| O10-Ti5-Au9 | 24   | 0       | 3     | 867  | 870   |
| O11         | 11   | 0       | 78    | 24   | 102   |
| Compound         | X  | Y  | Z  | Value1 | Value2 |
|------------------|----|----|----|--------|--------|
| O11-Ti5-Au8      | 24 | 0  | 0  | 893    | 893    |
| O11-Ti6-Au2      | 19 | 0  | 52 | 99     | 151    |
| O11-Ti6-Au5      | 22 | 0  | 52 | 40     | 92     |
| O12-Au16         | 28 | 0  | 8  | 118    | 126    |
| O12-Ti4-Au8      | 24 | 0  | 0  | 1237   | 1237   |
| O12-Ti6-Au1      | 19 | 0  | 38 | 117    | 155    |
| O12-Ti6-Zn5      | 23 | 0  | 78 | 196    | 274    |
| O12-Ti8          | 20 | 0  | 0  | 378    | 378    |
| O13-Ti6          | 19 | 0  | 144| 476    | 620    |
| O13-Ti6-Au1      | 20 | 0  | 11 | 177    | 188    |
| O13-Ti6-Au5      | 24 | 0  | 26 | 1585   | 1611   |
| O13-Ti7          | 20 | 0  | 40 | 19     | 59     |
| O14-Au16         | 30 | 0  | 0  | 122    | 122    |
| O14-Ti7          | 21 | 0  | 0  | 1      | 1      |
| O14-Ti8          | 22 | 0  | 0  | 198    | 198    |
| O15-Au16         | 31 | 0  | 0  | 142    | 142    |
| O15-Ti9          | 24 | 0  | 2  | 283    | 285    |
| O16-Ti8          | 24 | 0  | 127| 538    | 665    |
| O17-Au16         | 33 | 0  | 8  | 103    | 111    |
| O18-Ti7          | 25 | 0  | 0  | 1      | 1      |
| O18-Ti8          | 26 | 0  | 0  | 3      | 3      |
| O18-Au12         | 30 | 0  | 349| 17     | 366    |
| O22-Au16         | 38 | 0  | 0  | 199    | 199    |
| O24-Au16         | 40 | 0  | 0  | 14     | 14     |
| O31-Ti16-Au4     | 51 | 0  | 93 | 0      | 93     |
| O31-Ti16-Au8     | 55 | 0  | 64 | 0      | 64     |
| O32-Ti16-Au4     | 52 | 0  | 98 | 0      | 98     |
| O32-Ti16-Au8     | 56 | 0  | 58 | 0      | 58     |
| O32-Ti16-Au16    | 64 | 0  | 151| 0      | 151    |
| O33-Ti16-Au5     | 54 | 0  | 182| 0      | 182    |
| O33-Ti16-Au7     | 56 | 0  | 57 | 0      | 57     |
| O33-Ti16-Au16    | 65 | 0  | 125| 0      | 125    |
| O47-Ti24-Au2     | 73 | 0  | 70 | 0      | 70     |
| O47-Ti24-Au3     | 74 | 0  | 48 | 6      | 54     |
| O47-Ti24-Au8     | 79 | 0  | 49 | 0      | 49     |
| O47-Ti24-Au20    | 91 | 0  | 48 | 0      | 48     |
| O48-Ti24-Au1     | 73 | 0  | 69 | 0      | 69     |
| O48-Ti24-Au3     | 75 | 0  | 69 | 0      | 69     |
| O48-Ti24-Au8     | 80 | 0  | 52 | 0      | 52     |
| O48-Ti24-Au12    | 84 | 0  | 43 | 0      | 43     |
| O52-Ti24-Au1     | 77 | 0  | 68 | 0      | 68     |
| O52-Ti24-Au2     | 78 | 0  | 65 | 0      | 65     |
| O52-Ti24-Au12    | 88 | 0  | 43 | 0      | 43     |
| O52-Ti24-Au20    | 96 | 0  | 101| 0      | 101    |
| O63-Ti32-Au8     | 103| 0  | 77 | 0      | 77     |
| O63-Ti32-Au14    | 109| 0  | 22 | 0      | 22     |
| O64-Ti32-Au8     | 104| 0  | 50 | 0      | 50     |
| O64-Ti32-Au14    | 110| 0  | 13 | 0      | 13     |
| O64-Ti32-Au8     | 105| 0  | 77 | 0      | 77     |
| O65-Ti32-Au14    | 111| 0  | 24 | 0      | 24     |
### Training dataset of the AuTiCO G-NN potential

Supplementary Table S6 | Structure information in the first principles global dataset utilized in G-NN training. Listed data are the number of the structures in the global dataset, as distinguished by the chemical formula, the number of atoms (N), the type of structures (cluster, bulk, layer).

| Species          | Nats | cluster | layer | bulk | total |
|------------------|------|---------|-------|------|-------|
| Au8              | 8    | 0       | 125   | 0    | 125   |
| Au14             | 14   | 0       | 3     | 56   | 59    |
| Au15             | 15   | 135     | 5     | 69   | 209   |
| Au16             | 16   | 1362    | 217   | 8165 | 9744  |
| Au28             | 28   | 0       | 2     | 68   | 70    |
| Au29             | 29   | 0       | 37    | 30   | 67    |
| Au30             | 30   | 59      | 26    | 121  | 206   |
| Au31             | 31   | 0       | 0     | 75   | 75    |
| Au32             | 32   | 30      | 2     | 225  | 257   |
| Au45             | 45   | 25      | 0     | 0    | 25    |
| O1               | 1    | 1       | 0     | 0    | 1     |
| O1-Au16          | 17   | 0       | 1     | 133  | 134   |
| O2               | 2    | 5       | 0     | 0    | 5     |
| O2-Au16          | 18   | 0       | 49    | 187  | 236   |
| O3-Au16          | 19   | 47      | 33    | 86   | 166   |
| O4               | 4    | 0       | 15    | 0    | 15    |
| O4-Au16          | 20   | 0       | 85    | 174  | 259   |
| O4-Au24          | 28   | 76      | 18    | 109  | 203   |
| O6-Au4           | 10   | 0       | 0     | 2918 | 2918  |
| O6-Au16          | 22   | 0       | 5     | 169  | 174   |
| O6-Ti4           | 10   | 0       | 0     | 44   | 44    |
| O7-Au8           | 15   | 0       | 0     | 1158 | 1158  |
| O7-Ti4-Au2       | 13   | 0       | 103   | 0    | 103   |
| O7-Ti4-Au5       | 16   | 0       | 261   | 13   | 274   |
| O8-Au8           | 16   | 0       | 0     | 2361 | 2361  |
| O8-Au16          | 24   | 0       | 65    | 39   | 104   |
| O8-Ti4           | 12   | 2115    | 190   | 11379| 13684 |
| O8-Ti4-Au2       | 14   | 0       | 115   | 0    | 115   |
| O8-Ti4-Au5       | 17   | 0       | 306   | 12   | 318   |
| O9-Ti4-Au1       | 14   | 0       | 153   | 0    | 153   |
| O9-Ti4-Au5       | 18   | 0       | 46    | 240  | 286   |
| O10-Au16         | 26   | 0       | 61    | 19   | 80    |

**total** -- 3580 4969 35722 44541
| Bond          | Start | End | Value1 | Value2 |
|---------------|-------|-----|--------|--------|
| O10-Ti5-Au9   | 24    | 0   | 3      | 867    |
| O11-Ti5-Au8   | 24    | 0   | 0      | 893    |
| O11-Ti6-Au2   | 19    | 0   | 52     | 99     |
| O11-Ti6-Au5   | 22    | 0   | 52     | 40     |
| O12-Au16      | 28    | 0   | 7      | 105    |
| O12-Ti4-Au8   | 24    | 0   | 0      | 1237   |
| O12-Ti6-Au1   | 23    | 0   | 78     | 196    |
| O12-Ti8       | 20    | 0   | 0      | 378    |
| O13-Ti6       | 19    | 0   | 144    | 476    |
| O13-Ti6-Au1   | 20    | 0   | 11     | 177    |
| O13-Ti6-Au5   | 24    | 0   | 26     | 1585   |
| O13-Ti7       | 20    | 0   | 40     | 19     |
| O14-Au16      | 30    | 0   | 0      | 119    |
| O14-Ti7       | 21    | 0   | 0      | 1      |
| O14-Ti8       | 22    | 0   | 0      | 198    |
| O15-Au16      | 31    | 0   | 0      | 133    |
| O15-Ti9       | 24    | 0   | 2      | 283    |
| O16-Ti8       | 24    | 0   | 127    | 538    |
| O17-Au16      | 33    | 0   | 8      | 99     |
| O18-Ti7       | 25    | 0   | 0      | 1      |
| O18-Ti8       | 26    | 0   | 0      | 3      |
| O18-Au12      | 30    | 0   | 349    | 17     |
| O22-Au16      | 38    | 0   | 0      | 199    |
| O24-Au16      | 40    | 0   | 0      | 14     |
| O31-Ti16-Au4  | 51    | 0   | 93     | 0      |
| O31-Ti16-Au8  | 55    | 0   | 64     | 0      |
| O32-Ti16-Au4  | 52    | 0   | 98     | 0      |
| O32-Ti16-Au8  | 56    | 0   | 58     | 0      |
| O32-Ti16-Au16 | 64    | 0   | 150    | 0      |
| O33-Ti16-Au5  | 54    | 0   | 181    | 0      |
| O33-Ti16-Au7  | 56    | 0   | 57     | 0      |
| O33-Ti16-Au16 | 65    | 0   | 125    | 0      |
| O47-Ti24-Au2  | 73    | 0   | 70     | 0      |
| O47-Ti24-Au3  | 74    | 0   | 48     | 6      |
| O47-Ti24-Au8  | 79    | 0   | 49     | 0      |
| O48-Ti24-Au20 | 91    | 0   | 48     | 0      |
| O48-Ti24-Au1  | 73    | 0   | 69     | 0      |
| O48-Ti24-Au3  | 75    | 0   | 69     | 0      |
| O48-Ti24-Au8  | 80    | 0   | 52     | 0      |
| O48-Ti24-Au12 | 84    | 0   | 43     | 0      |
| O52-Ti24-Au1  | 77    | 0   | 68     | 0      |
| O52-Ti24-Au2  | 78    | 0   | 65     | 0      |
| O52-Ti24-Au12 | 88    | 0   | 43     | 0      |
| O52-Ti24-Au20 | 96    | 0   | 101    | 0      |
| O63-Ti32-Au8  | 103   | 0   | 77     | 0      |
| O63-Ti32-Au14 | 109   | 0   | 22     | 0      |
| O64-Ti32-Au8  | 104   | 0   | 50     | 0      |
| O64-Ti32-Au14 | 110   | 0   | 13     | 0      |

S12
### Benchmark between G-NN and DFT calculations for supported AuₙOₘ/TiO₂ catalysts.

Supplementary Table S7: Benchmark between G-NN and DFT calculations for supported Au/TiO₂ systems. The lowest energy in each sequence is the GM, defined as zero. Listed data include the compositions, total atom number (N_{atom}), DFT energy, NN energy and energy differences between DFT energy and NN energy (E_{diff}, meV/atom).

| composition                  | N_{atom} | DFT-en (eV) | NN-en (eV) | en-diff (meV/atom) |
|------------------------------|----------|-------------|------------|-------------------|
| 0                            |          | -1.185      | 2.332      |                   |
| total                        |          | 3855        | 9751       | 40531             | 54127             |

- Benc mark between G-NN and DFT calculations for supported AuₙOₘ/TiO₂ catalysts.
| System          | Energy | Volume | Pressure | Temperature |
|-----------------|--------|--------|----------|-------------|
| Au<sub>18</sub>O<sub>2</sub>/TiO<sub>2</sub> | 506    | 0.917  | -0.803   | 3.398       |
|                 |        | 1.293  | -0.625   | 3.791       |
| Au<sub>24</sub>O<sub>4</sub>/TiO<sub>2</sub> | 514    | 0.476  | -1.415   | 3.698       |
|                 |        | 0.733  | -1.298   | 3.891       |
| Au<sub>30</sub>O<sub>2</sub>/TiO<sub>2</sub> | 518    | 0.007  | -1.811   | 3.509       |
|                 |        | 0.041  | -1.750   | 3.456       |
| Au<sub>24</sub>O<sub>2</sub>/TiO<sub>2</sub>-CO | 354    | 0.230  | -1.170   | 3.966       |
|                 |        | 0.699  | -0.944   | 4.633       |
| Au<sub>37</sub>O<sub>4</sub>/TiO<sub>2</sub>-5CO | 537    | 0      | -2.663   | 4.959       |
| Au<sub>24</sub>O<sub>2</sub>/TiO<sub>2</sub>-4CO | 522    | 0      | -0.700   | 1.341       |
| Au<sub>37</sub>O<sub>4</sub>/TiO<sub>2</sub>-4CO | 535    | 0      | 2.887    | 5.396       |

#### Supplementary References

1. Matthey, D. et al. Enhanced Bonding of Gold Nanoparticles on Oxidized TiO<sub>2</sub>(110). *Science* **315**, 1692 (2007).
2. Wahlstrom, E. et al. Bonding of gold nanoclusters to oxygen vacancies on rutile TiO<sub>2</sub>(110). *Phys. Rev. Lett.* **90** (2003).
3. Chen, M. S. & Goodman, D. W. Catalytically active gold: From nanoparticles to ultrathin films. *Acc. Chem. Res.* **39**, 739-746 (2006).
4. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132** (2010).