Supplementary Information for An ab-initio study of silver-titanium interfaces in gas-phase and surface-supported clusters

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Convergence tests

As a first step in our work, we checked some bulk properties, such as lattice parameter, cohesive energy and bulk modulus of hcp Ti. All these quantities were calculated by using a k-point mesh of $10 \times 10 \times 10$. From Table S1 we can conclude that the results obtained by PBE achieve better consistency with the experimental values than PBEsol, therefore, the structure optimizations and related properties calculations of the article were made by the PBE functional.

Table S 1: Bulk properties of hcp Ti calculated by PBE and PBEsol along with previous experimental values. a and c represent the lattice parameters of hcp Ti structure. E_{coh} shows the cohesive energy of Ti which was calculated by subtracting the total energy of bulk Ti from the energy of single Ti atom in the gas phase.

| | a (Å) | c (Å) | Bulk modulus (GPa) | E_{coh} (eV/atom) |
|---------------------------|-------|-------|--------------------|---------------------|
| PBE | 2.936 | 4.642 | 109.1 | 5.276 |
| PBEsol | 2.900 | 4.584 | 121.6 | 5.845 |
| $\operatorname{Exp.}^{1}$ | 2.949 | 4.678 | 105 | 4.85 |

A good sampling of the reciprocal space is a critical factor for obtaining reliable results.

Due to the crystalline symmetry of the hcp lattice that are being compared, the x and y directions need the same density of k-point sampling in the first Brillouin zone of the reciprocal space, and the z direction needs a lower number of k-points, which in this case we take it 1. In Table S2 the convergence study of the total energy of $(4 \times 4 \times 4)$ Ti slab with respect to the number of k-points is presented. We observe that a $4 \times 4 \times 1$ mesh for the k-points is enough to achieve good energy convergence.

| k-points | PBE | PBEsol |
|-----------------------|--------------|--------------|
| $2 \times 2 \times 1$ | -159924.6797 | -158242.3025 |
| $3 \times 3 \times 1$ | -159924.5309 | -158242.1536 |
| $4 \times 4 \times 1$ | -159924.5023 | -158242.1247 |
| $5 \times 5 \times 1$ | -159924.4990 | -158242.1214 |
| $6 \times 6 \times 1$ | -159924.4989 | -158242.1212 |
| $7 \times 7 \times 1$ | -159924.4993 | -158242.1216 |
| $8 \times 8 \times 1$ | -159924.4990 | -158242.1213 |

Table S 2: Total energy of $4 \times 4 \times 4$ Ti(0001) slab for different k-points.

For the bare Ti(0001) surface, we computed some surface properties such as surface energy E_{surf} , work function W_f and surface relaxation (space between the two topmost atomic layers) $\Delta d_{1,2}$ with respect to the bulk value d_0 . The results are summarized in Table S3 in comparison with experiments.¹⁻⁵ The surface energy of Ti(0001) surface presented in Table 3, is calculated as the difference between the total energy of the slab and the total energy of an equal number of Ti units in the bulk phase, divided by the total exposed area. The work function is obtained by subtracting the potential in vacuum from the Fermi energy of the slab. The results of surface energy and work function are in reasonable agreement with the existing experimental values.

Table S 3: Surface properties of hcp Ti(0001) surface calculated by PBE potential together with the previous experimental values. E_{surf} presents the surface energy of Ti(0001) surface and W_f its work function. $\Delta d_{1,2}$ displays the interlayer relaxation percentage between the two topmost layers with respect to the bulk distance d_0 (2.321 Å).

| | $E_{surf} (J/m^2)$ | W_f (eV) | $\Delta d_{1,2}$ (%) |
|------|-----------------------|------------------------------------|----------------------|
| PBE | 1.939 | 4.416 | - 6.388 |
| Exp. | $1.98 - 2.10^{3,6,7}$ | $\left(4.6\pm0.2 ight)^8-4.45^{9}$ | -4.90^{10} |



Figure S 1: Size slab effect on the adsorption of Ti and Ag adatoms. First row represent energy difference ΔE of Ti (a) and Ag (c) adatoms on a slab of 2 × 2 Ti(0001) surface with a thickness of 4, 6 and 8 layers. Second row show Ti (b) and Ag (d) adatoms energy difference on a slab of 4 layers thickness with 2 × 2, 4 × 4 and 6 × 6 Ti(0001) surfaces. Adsorption energies for both adatoms on Top, Bridge, fcc and hcp sites are presented by red circles, green stars, blue down triangles and black up triangles, respectively.

Calculations of convergence of the Ti and Ag adatoms adsorption energy as a function of the Ti thickness and area in the slab were carried out. For all slabs, we adsorb adatom on different sites of Ti(0001) surface such as Top, Bridge, fcc and hcp, conserving always a 18 Å vacuum space separation between slabs along the z direction. The results can be seen in Figure S1. From this figure, it is observed that when changing the slab thickness from 4 to 8 layers (left row of Figure S1), the energy difference of Ti adatom on Ti(0001) surface is less than 0.01 eV. Therefore, the 4-layered model is sufficient for the adsorption process. However, when changing the surface area from 2×2 to 6×6 (right row of Figure S1), the calculations showed that the energy difference is about 0.1 eV. Hence, only the $4 \times$ 4 Ti(0001) surface with four atomic layers slab model was considered as a substrate in our study since it shows a good compromise between accuracy and time consumption.

Gas-phase clusters

Composition stability analysis

For pure nanoclusters, E_{coh} is 4.225 eV/atom for Ti and 2.128 eV/atom for Ag. These values are smaller than their bulk counterparts, meaning that the strength between atoms becomes weaker for small clusters.

| Composition | Configuration | $E \to (eV/atom)$ | $E \cdot (eV/atom)$ |
|-----------------------------------|---------------|---------------------|---------------------|
| | Configuration | L_{coh} (CV/atom) | L_{mix} (CV/atom) |
| $Ti_{53}Ag_2$ | a) | 4.1694 | -0.02024 |
| | b) | 4.1646 | -0.01544 |
| | c) | 4.1561 | -0.00699 |
| | d) | 4.1503 | -0.00117 |
| | e) | 4.1413 | + 0.00787 |
| | f) | 4.1383 | + 0.01081 |
| | g) | 4.1156 | + 0.03351 |
| Ti ₄₂ Ag ₁₃ | a) | 3.7067 | + 0.02300 |
| | b) | 3.6550 | + 0.07464 |
| | c) | 3.4089 | + 0.32074 |
| Ti ₁₃ Ag ₄₂ | d) | 2.8125 | -0.18869 |
| | e) | 2.7873 | -0.16347 |
| | f) | 2.7649 | -0.14104 |
| | g) | 2.4498 | + 0.17408 |
| | h) | 2.2452 | + 0.37864 |

Table S 4: Cohesive and mixing energies per atom for $Ti_{55-m}Ag_m$ icosahedral clusters, where $m \neq 1$. All configurations are represented in Figures 4 and 5 in the main text.

Structural analysis

To gain a deeper insight into the site preference and chemical ordering in gas-phase TiAg clusters, we evaluate the effective coordination concept of atoms in different configurations.^{11–13} For a given atom i, the ECN_i is defined as:

$$ECN_{i} = \sum_{j} \exp\left[1 - \left(\frac{r_{ij}}{d_{av}^{i}}\right)^{6}\right]$$
(1)

where, r_{ij} represent the distances between atoms *i* and *j* taken from the relaxed geometries, while d_{av}^i , is given as:

$$d_{av}^{i} = \frac{\sum_{j} r_{ij} \exp\left[1 - \left(\frac{r_{ij}}{d_{av}^{i}}\right)^{6}\right)\right]}{\sum_{j} \exp\left[1 - \left(\frac{r_{ij}}{d_{av}^{i}}\right)^{6}\right)\right]}$$
(2)

here, d_{av}^i represents a weighted average of the bond distances between atom *i* and its neighbors and it is obtained through a self-consistent iterative procedure.

Here, we present the effective coordination concepts of Ag impurity in Ti Ih and cubo. ECN for each atom of Ih and cubo are shown in Figure S2, whereas weighted bond lengths are in Figure S3.



Figure S 2: Effective coordination number for Ag impurity in different sites of (a) icosahedral and (b) cuboctahedral matrices.

For all configuration of both Ih and Cubo Ti₅₄Ag clusters, the results of ECN_i presented in Figure S4(a) show that the core atoms have an average ECN of ~ 12, corresponding to highly coordinated atoms in the Ih and Cubo cores. However, the ECN values for surface atoms differ significantly between the two geometries. Surface atoms in the icosahedral cluster have an average ECN of ~ 8 at edge sites and ~ 6 at vertices. In contrast, in the cuboctahedral geometry, surface atoms exhibit an average ECN of ~ 8 for atoms located at (100)-like facet sites, ~ 6 at edges and ~ 5 at vertices. This difference reflects a more open surface of the cuboctahedral compared to the more compact and enclosed surface topology



Figure S 3: Average weighted bond lengths for all atoms in the lowest energy chemical ordering (a) icosahedral (a) and (b) cuboctahedral clusters of $Ti_{54}Ag$.

of the icosahedron.



Figure S 4: Effective coordination numbers (a) and weighted bond lengths (b) for all atoms in the lowest energy chemical ordering icosahedral clusters.

Table S 5: Average weighted bond length d_{av} of core and surface atoms with Ag in different sites of Ti icosahedral and cuboctahedral structures together with d_{av} of Ag atom. A, B, C and D represent Ag in center, subsurface, surface vertex and surface edge sites of icosahedral and cuboctahedral structures, respectively. E shows Ag in (100)-like surface site of the cuboctahedron.

| Structure | Atom site | d_{av}^{core} (Å) | d_{av}^{surf} (Å) | d_{av}^{Ag} (Å) |
|---------------------|--------------|----------------------|----------------------|--------------------|
| Ih ₅₅ | _ | 2.8030 | 2.8077 | — |
| Ih ₅₄ Ag | А | 2.8086 | 2.8086 | 2.7900 |
| | В | 2.7975 | 2.8106 | 2.8091 |
| | \mathbf{C} | 2.7979 | 2.8188 | 2.9502 |
| | D | 2.8145 | 2.8158 | 2.8491 |
| Cubo ₅₅ | — | 2.8016 | 2.7605 | _ |
| $Cubo_{54}Ag$ | А | 2.8116 | 2.7566 | 2.8622 |
| | В | 2.8031 | 2.7607 | 2.8228 |
| | \mathbf{C} | 2.8049 | 2.7642 | 2.8974 |
| | D | 2.8038 | 2.7622 | 2.8787 |
| | \mathbf{E} | 2.8064 | 2.7618 | 2.8912 |

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