**Interfacial Catalysis**

**Structure Sensitivity of Au-TiO₂ Strong Metal–Support Interactions**

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**Abstract:** Strong metal–support interactions (SMSI) is an important concept in heterogeneous catalysis. Herein, we demonstrate that the Au-TiO₂ SMSI of Au/TiO₂ catalysts sensitively depends on both Au nanoparticle (NP) sizes and TiO₂ facets. Au NPs of ca. 5 nm are more facile undergo Au-TiO₂ SMSI than those of ca. 2 nm, while TiO₂ [001] and [100] facets are more facile than TiO₂ [101] facets. The resulting capsulating TiO₂-x overlayers on Au NPs exhibit an average oxidation state between +3 and +4 and a Au-to-TiO₂-x charge transfer, which, combined with calculations, determines the Ti:O ratio as ca. 6:11. Both TiO₂-x overlayers and TiO₂-x-Au interface exhibit easier lattice oxygen activation and higher intrinsic activity in catalyzing low-temperature CO oxidation than the starting Au-TiO₂ interface. These results advance fundamental understanding of SMSI and demonstrate engineering of metal NP size and oxide facet as an effective strategy to tune the SMSI for efficient catalysis.

**Introduction**

Metal–support interactions play a key role in modulating the structures and catalytic performance of supported metal catalysts. Firstly postulated in Group 8 and noble metals supported on TiO₂,[¹] strong metal–support interactions (SMSI) referring to high-temperature reduction-induced capsulation of supported metal nanoparticles (NPs) by support overlayers,[²] has been recognized as a common phenomenon occurring in reducible oxides-supported Group 8 and noble metals and evolved as one of the most important concepts in heterogeneous catalysis.[³] Recently, the supported metal catalysts exhibiting the SMSI phenomenon have been broadened to oxides and non-oxides supported Au NPs.[⁴] Several methods[⁵] different from the traditional high-temperature reduction approach were reported capable of inducing the capsulation of supported metal NPs by support overlayers. Owing to the capsulation of the catalytic active metal NPs, SMSI generally decreases the catalytic activity of supported metal catalysts but can enhance the stability.[⁶-⁸] Despite the long and extensive studies, the origin of SMSI is still debated due to the lack of solid experimental evidence; meanwhile, the structures of capsulating support overlayers and capsulating support overlayers-metal NPs interfaces remain unclear.[²,³,⁶]

Particle sizes of supported metals[⁹] and facets of oxide support[¹⁰] are the most important structural factors in oxides-supported metal catalysts, but their effects on the SMSI have been seldom explored. Ultrafine Pt NPs (ca. 1 nm) with a tight particle size distribution[¹¹] and Ni clusters of a very small number of atoms[¹²] supported on TiO₂ have been recently observed not capsulated upon high-temperature H₂ reduction and Au NPs supported on TiO₂ has been just reported to exhibit size-dependent H₂-reduction temperatures for a full capsulation,[¹³] indicating the size effect of supported metal NPs for the SMSI. In the present work, employing Au/TiO₂ catalysts with Au NPs of ca. 5 and ca. 2 nm supported on various anatase TiO₂ nanocrystals (NCs) predominantly exposing the [001] (denoted as TiO₂-[001]), [100] (denoted as TiO₂-[100]) and [101] (denoted as TiO₂-[101]) facets, we unambiguously demonstrate that both metal particle size and oxide facet of metal/oxide catalysts exert great influences on the Au-TiO₂ SMSI. Meanwhile, we develop a combined experimental and DFT calculation approach to successfully identify the Ti:O ratio of capsulating TiO₂-x overlayer on Au NPs resulting from the Au-TiO₂ SMSI as around 6:11.

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Results and Discussion

The TiO$_2$[001], TiO$_2$[100], and TiO$_2$[101] NCs with similar BET specific surface areas of ca. 100 m$^2$/g$^{-1}$ (Supporting Information, Table S1) and the proportions of the exposed predominant facets above 80% were prepared following the well-established recipes. It is noteworthy that our as-synthesized TiO$_2$ NCs do not show XPS signals of F, S, and Cl involved during the synthesis.

TEM and HRTEM images (Figure 1 a–c) show that all TiO$_2$ NCs exhibit uniform morphologies and a pure anatase phase. Using the TiO$_2$-fresh NCs as the supports, Au/TiO$_2$-fresh catalysts with a calculated Au loading of 2% (weight ratio) were prepared by deposition-precipitation method and then treated either by calcination in air at 400°C for 4 h or by an initial reduction in 5% H$_2$/ Ar at 500°C for 1 h and subsequent oxidation in 10% O$_2$/Ar at 400°C for 1 h. The actual Au loadings of Au/TiO$_2$-fresh catalysts were analyzed to be close to the calculated loading by inductively coupled plasma atomic emission spectrometry (Supporting Information, Table S2). All Au/TiO$_2$-fresh catalysts only display diffraction patterns of anatase TiO$_2$ in the XRD patterns (Supporting Information, Figure S1). Using the TiO$_2$[101] diffraction peak, the average crystalline sizes of TiO$_2$ in various TiO$_2$ and Au/TiO$_2$ catalysts were calculated from the Debye–Scherer equation to improve with the thermal treatments and vary within ca. 10 and ca. 20 nm (Supporting Information, Table S1). HADDF-STEM images demonstrate that the calcination treatment in air leads to supported Au NPs of around 5 nm (Figure 1d–f; Supporting Information, Figure S3), herein denoted as 5 nm-Au/TiO$_2$-fresh, while the treatment of reduction and subsequent oxidation results in supported Au NPs of around 2 nm (Figure 1g–i; Supporting Information, Figure S3), herein denoted as 2 nm-Au/TiO$_2$-fresh. The reduction of supported Au$^{4+}$ precursor into Au$^0$ was observed to occur at higher temperatures upon calcination in air than upon reduction in H$_2$, resulting in the formation of larger Au NPs. Meanwhile, an O$_2$ atmosphere was reported to exert a stronger enhancement effect on the Ostwald ripening than a H$_2$ atmosphere, facilitating the formation of larger supported metal NPs.

Surface structures of various Au/TiO$_2$-fresh catalysts were probed by CO adsorption at 123 K with $P_{CO}=200$ Pa (Figure 2). Vibrational peaks at ca. 2178, ca. 2127 and ca. 200 Pa were observed, arising from CO adsorbed at the Ti$^4+$ site (CO$_{Ti^4+}$), perimeter Au$^0$ site (CO$_{Au^0}$) and surface Au$^0$ site (CO$_{Au^0}$) of Au NPs, respectively.\[12\]

![Figure 1](link) Microscopic characterizations. a)–c) Representative TEM images with inserted HRTEM images and morphology illustrations of a) TiO$_2$[001]-fresh, b) TiO$_2$[100]-fresh and c) TiO$_2$[101]-fresh NCs. d–i) HADDF-STEM images with inserted Au particle size distributions of d) 5 nm-Au/TiO$_2$[001]-fresh, e) 5 nm-Au/TiO$_2$[100]-fresh, f) 5 nm-Au/TiO$_2$[101]-fresh, g) 2 nm-Au/TiO$_2$[001]-fresh, h) 2 nm-Au/TiO$_2$[100]-fresh, and i) 2 nm-Au/TiO$_2$[101]-fresh catalysts.

![Figure 2](link) CO adsorption. In situ DRIFTS spectra of CO chemisorption on various Au/TiO$_2$-fresh and Au/TiO$_2$-H500 catalysts at 123 K and $P_{CO}=200$ Pa.

2107 cm$^{-1}$ were observed, arising from CO adsorbed at the Ti$^4+$ site (CO$_{Ti^4+}$), perimeter Au$^0$ site (CO$_{Au^0}$) and surface Au$^0$ site (CO$_{Au^0}$) of Au NPs, respectively.\[17\] The strong vibrational peak of CO$_{Au^0}$ species at ca. 2178 cm$^{-1}$ gives rise to the corresponding weak vibrational peak of CO$_{Ti^4+}$ species at ca. 2127 cm$^{-1}$ (Supporting Information, Figure S4). Due to the higher dispersion of supported Au NPs, the 2 nm-Au/TiO$_2$-fresh catalysts exhibit much stronger vibrational peaks of CO$_{Au^0}$ and CO$_{Au^0}$ species than the corresponding 5 nm-Au/TiO$_2$-fresh catalysts. The Au/TiO$_2$-fresh catalysts were treated in 5% H$_2$/Ar at 500°C for 1 h to induce the SMSI. The acquired catalysts, herein denoted as Au/TiO$_2$-H500, were observed to display Au NP size- and TiO$_2$ facet-dependent DRIFTS spectra for CO adsorption (Figure 2; Supporting Information, Figures S5 and S6). All 5 nm-Au/TiO$_2$-H500 catalysts exhibit no CO$_{Au^0}$ vibrational feature and a very tiny CO$_{Au^0}$ vibrational feature. 2 nm-Au/TiO$_2$[001]-H500 and 2 nm-Au/TiO$_2$[100]-H500 exhibit much weaker vibrational features of both CO$_{Au^0}$ and CO$_{Au^0}$ species than 2 nm-Au/TiO$_2$[001]-fresh and 2 nm-Au/TiO$_2$[100]-fresh, respectively, and the CO vibrational features on 2 nm-Au/TiO$_2$[001]-H500 are weaker than on 2 nm-Au/TiO$_2$[100]-H500. However, 2 nm-Au/TiO$_2$[101]-H500 shows vibrational features of CO adsorbed at the Au sites almost identical to 2 nm-Au/TiO$_2$[101]-fresh. Meanwhile, the CO$_{Ti^4+}$ vibrational...
feature weakens upon H₂ reduction at 500°C for Au/TiO₂[001]-fresh catalysts but does not vary much for Au/TiO₂[100]-fresh and Au/TiO₂[101]-fresh catalysts.

CO adsorption at RT under 1 atm of 1% CO/Ar was also characterized on various Au/TiO₂-fresh and Au/TiO₂-H500 catalysts (Supporting Information, Figure S7), during which the H₂ reduction treatments in 5% H₂/Ar at 500°C were carried out in the in situ reaction cell for DRIFTS. CO does not adsorb at the Ti⁴⁺ site at RT, and the CO Au⁴⁺ vibrational feature overlaps with the signals of gaseous CO and cannot be observed. Only CO Au⁴⁺ vibrational features were observed to exhibit results consistent with those of CO adsorption at 123 K. All 5nm-Au/TiO₂-H500 catalysts exhibit no visible CO Au⁴⁺ vibrational feature, whereas 2nm-Au/TiO₂[001]-H500 and 2nm-Au/TiO₂[100]-H500 exhibit significantly weaker vibrational features than 2nm-Au/TiO₂[001]-fresh and 2nm-Au/TiO₂[100]-fresh, respectively, and 2nm-Au/TiO₂[101]-H500 shows the vibrational feature almost identical to 2nm-Au/TiO₂[101]-fresh. The CO adsorption behaviors of 5nm-Au/TiO₂-H500 catalysts are the characteristics of SMSI, evidencing the occurrence of Au-TiO₂ SMSI and the consequent almost full capsulation of Au NPs by TiO₂ overlays. The capacities of Au/TiO₂-H500 catalysts to adsorb CO can fully recover to those of corresponding Au/TiO₂-H500 catalysts after they are oxidized in 10% O₂/Ar at 400°C for 1 h (Figure S7), proving the reversibility of Au-TiO₂ SMSI. However, the Au NPs in 2nm-Au/TiO₂[001]-H500 and 2nm-Au/TiO₂[100]-H500 are partially capsulated, and those in 2nm-Au/TiO₂[101]-H500 are barely capsulated.

HRTEM images of various Au/TiO₂-fresh and Au/TiO₂-H500 catalysts (Figure 3a1–f2) directly visualize that the supported Au NPs are obviously capped in 5nm-Au/TiO₂-H500 catalysts, partially capped in 2nm-Au/TiO₂[001]-H500 and 2nm-Au/TiO₂[100]-H500, and barely capped in 2nm-Au/TiO₂[101]-H500. Uniform Ti and O signals were imaged on the Au NPs in the energy-dispersive X-ray (EDX) mapping image of 5nm-Au/TiO₂[101]-H500 (Supporting Information, Figure S8), proving the full capsulation of Au NPs. Electron energy loss spectra (EELS) analysis of marked areas in HRTEM images of 5nm-Au/TiO₂[101]-H500 and 2nm-Au/TiO₂[101]-H500 (Figure 3g–j; Supporting Information, Figure S9) evidences the presence of both Ti L-edge and O K-edge EELS signals on the surface of Au NP of 5nm-Au/TiO₂[101]-H500 but not on the surface of Au NP of 2nm-Au/TiO₂[101]-H500. This further supports that Au NP of 5nm-Au/TiO₂[101]-H500 are capped by TiO₂ overlayers while those of 2nm-Au/TiO₂[101]-H500 are not. Comparing the EELS spectra of TiO₂ from TiO₂ to TiO₂[100], the EELS features of TiO₂ support in 5nm-Au/TiO₂[101]-H500 and 2nm-Au/TiO₂[101]-H500 are the typical features of TiO₂, while the EELS feature of capsulating TiO₂ overlayers on Au NP of 5nm-Au/TiO₂[101]-H500 is similar to that of TiO₂ with mixed valences of Ti³⁺ and Ti⁴⁺.

The above spectroscopic and microscopic results clearly demonstrate that the Au-TiO₂ SMSI of Au/TiO₂ catalysts sensitively depends on the Au NP size and the TiO₂ facet. Supported Au NPs with a size of ca. 5 nm are more facile to undergo the Au-TiO₂ SMSI than those of ca. 2 nm, and the TiO₂[001] and [100] facets are more facile than the TiO₂[101] facets. Such a structure sensitivity of Au-TiO₂ SMSI in Au/TiO₂ catalysts, as far as we know, represents the first unambiguous and comprehensive example of structure sensitivity of SMSI.
The reducibility of various TiO$_2$-fresh and Au/TiO$_2$-fresh catalysts was examined using H$_2$-TPR measurements. TiO$_2$-[001]-fresh NCs are more difficult to be reduced than TiO$_2$-[100]-fresh and TiO$_2$-[101]-fresh NCs (Supporting Information, Figure S10), consistent with the DFT calculation results of oxygen vacancy formation energies of anatase TiO$_2$ [001], [100], and [101] surfaces as 4.57, 4.0, and 4.15 eV, respectively.[19] The loading of Au NPs induces Au$_{np}$-TiO$_2$ interactions and subsequently promotes the reduction of TiO$_2$ NCs (Figure 4 a–c). The TiO$_2$ in Au/TiO$_2$-[001]-fresh and Au/ higher binding energies by the same value of 0.3 eV (Supporting Information, Figure S11 and Table S3). This suggests the occurrence of downward surface band bending with similar extents for all TiO$_2$-H500 NCs, which, based on the corresponding ESR measurements (Supporting Information, Figure S12), results from the reduction-induced formation of large quantities of bulk F$^-$ centers. The Au 4f$_{7/2}$ binding energy of Au/TiO$_2$-fresh catalysts locates at 83.5–83.7 eV (Figures 4 d; Supporting Information, Figure S13 and Table S4). It shifts toward higher binding energies after H$_2$ reduction at 500 °C and the amplitudes vary with the catalysts. Based on the Ti 2p and O 1s XPS results (Supporting Information, Figure S14 and Table S4), no surface band bending occurs for TiO$_2$ of Au/TiO$_2$-fresh catalysts, while the downward surface band bending occurs in 5nm-Au/ TiO$_2$-[101]-H500 and 2nm-Au/TiO$_2$-H500 catalysts but not in 5nm-Au/TiO$_2$-[001]-H500 and 5nm-Au/TiO$_2$-[100]-H500 catalysts. The corresponding ESR results (Supporting Information, Figure S15) show the presence of bulk F$^-$ centers, bulk Ti$^{3+}$ species, and surface O$_2^-$ species in Au/TiO$_2$-fresh and Au/ TiO$_2$-H500 catalysts, but no Ti$^{2+}$ features could be observed in the Ti 2p XPS and UPS spectra (Supporting Information, Figures S16 and S17). Au/TiO$_2$-[001]-H500, 5nm-Au/TiO$_2$-[100]-H500 and 5nm-Au/TiO$_2$-[101]-H500 catalysts exhibit much stronger defect signals than corresponding Au/TiO$_2$-fresh catalysts, while 2nm-Au/TiO$_2$-[100]-H500 and 2nm-Au/ TiO$_2$-[101]-H500 catalysts show weaker defect signals than corresponding Au/TiO$_2$-fresh catalysts. Therefore, the surface band bending of TiO$_2$ in Au/TiO$_2$-H500 catalysts seems not dependent on the defect density. We propose that the defects in 5nm-Au/TiO$_2$-[001]-H500 and 5nm-Au/TiO$_2$-[100]-H500 catalysts are so localized not as to induce the downward surface band bending of TiO$_2$, while those in other Au/TiO$_2$-H500 catalysts are homogeneously distributed and induce the downward surface band bending of TiO$_2$.

Figure 4 e illustrates the Au 4f$_{7/2}$, Ti 2p$_{3/2}$, and O 1s binding energy shifts of various Au/TiO$_2$-H500 catalysts comparing to corresponding Au/TiO$_2$-fresh catalysts, and Figure 4 f shows the Au 4f$_{7/2}$ binding energy shifts of various Au/TiO$_2$-H500 catalysts comparing to corresponding Au/TiO$_2$-fresh catalysts after the corrections of corresponding surface band bending effects. It can be seen that the H$_2$ treatment at 500 °C induces the positive shifts in the Au 4f binding energy of supported Au NPs for all Au/TiO$_2$-fresh catalysts. The charger transfer between supported Au NPs and TiO$_2$ support is well established.[20] Charge transfer occurs obviously from surface oxygen vacancies of reduced TiO$_2$ surface to supported Au NPs but is negligible between supported Au NPs and stoichiometric TiO$_2$ surface. Therefore, the observed positive shifts in the Au 4f binding energy of Au/TiO$_2$-H500 catalysts should result from the charge transfer from capsulated Au NPs to capsulating TiO$_2$ overlayers. Similar charge transfer was previously observed from capsulated Pt NPs to capsulating TiO$_2$ overlayers due to the Pt-TiO$_2$ SMSI.[21] The Au 4f binding energy shift amplitudes vary with both the size of supported Au NPs and the TiO$_2$ facets in the same trends to the SMSI effect. Supported on the same type of TiO$_2$ support, 5 nm Au NPs exhibit larger Au 4f binding energy shifts and more extensive Au-TiO$_2$ SMSI than 2 nm Au NPs; with
similar sizes, Au NPs supported on TiO$_2$[001] exhibit larger Au 4f binding energy shifts and more extensive Au-TiO$_2$ SMSI than on TiO$_2$[100] and TiO$_2$[101]. A larger Au 4f binding energy shift points to a more extensive Au$_{5s}$-to-TiO$_2$ charge transfer at the TiO$_2$-Au$_{5s}$ interface and consequently a stronger TiO$_2$-Au$_{5s}$ interactions, triggering a more extensive Au-TiO$_2$ SMSI.

In the Au-TiO$_2$ SMSI process, the H$_2$ reduction at 500°C induced-transformation of the Au$_{5s}$-TiO$_2$ interface of Au/ TiO$_2$-fresh catalysts to the TiO$_2$-Au$_{5s}$ interface of Au/TiO$_2$-H500 catalysts via the removal of the O atom, can be described by the chemical equation of xH$_2$ + Au$_{5s}$-TiO$_2$ → TiO$_2$-Au$_{5s}$ + xH$_2$O. Thermodynamically, the occurrence of SMSI between supported Au NP and TiO$_2$ support is favored for Au/TiO$_2$ catalyst with a strong TiO$_2$-Au$_{5s}$ interfacial interactions, a weak Au$_{5s}$-TiO$_2$ interfacial interactions, and a weak Ti–O bond. The Ti–O bond strength can be related to the reducibility of TiO$_2$ in Au/TiO$_2$ catalysts. As shown in the H$_2$-TPR profiles, TiO$_2$ in Au/TiO$_2$[001]-fresh and Au/TiO$_2$[100]-fresh is more easily to be reduced than in Au/TiO$_2$[101]-fresh, thus the Ti–O bond is weaker in Au/TiO$_2$[001]-fresh and Au/TiO$_2$[100]-fresh than in Au/TiO$_2$[101]-fresh. The strength of both Au$_{5s}$-TiO$_2$ and TiO$_2$-Au$_{5s}$ interfacial interactions can be related to the interfacial charge transfer. As demonstrated by the Au 4f binding energy, all Au/TiO$_2$-fresh catalysts exhibit similar Au$_{5s}$-TiO$_2$ interfacial interactions, while 5nm-Au/TiO$_2$-H500 exhibits stronger TiO$_2$-Au$_{5s}$ interfacial interactions than corresponding 2nm-Au/ TiO$_2$-H500 and Au/TiO$_2$[001]-H500 exhibits stronger TiO$_2$-Au$_{5s}$ interfacial interactions than corresponding Au/TiO$_2$[100]-H500 and Au/TiO$_2$[101]-H500. Therefore, 5 nm Au NPs supported on TiO$_2$ are more facile to undergo the Au-TiO$_2$ SMSI than 2 nm Au NPs, and the TiO$_2$[001] facet is more facile to undergo the Au-TiO$_2$ SMSI than the TiO$_2$[100] facet and then the TiO$_2$[101] facet. Our observation that 2 nm Au NPs supported on TiO$_2$[101] do not exhibit the Au-TiO$_2$ SMSI could be the reason for the absence of Au-TiO$_2$ SMSI in Au/ TiO$_2$ catalysts since the sizes around 2 nm are very common for Au NPs supported on TiO$_2$ and the [101] facets are predominant on spherical or irregular anatase TiO$_2$ particles following the Wulff construction.[22]

The Au particle size-dependent Au$_{5s}$-to-TiO$_2$, charge transfer at the TiO$_2$-Au$_{5s}$ interface can be associated with the size-dependent electronic structures of Au NPs. Resulted from the interplay of quantum-size and surface effect,[23] the lattice contracts, and the d charge at the metal atom site depletes relative to the bulk metal as the size of metal particles decreases. Supported Au NPs of 2–3 nm were previously reported to exhibit such a metal-to-nonmetal transition.[15,24] Therefore, 2 nm Au NPs with the contracting lattice and the depleted d charge exhibit extensive Au$_{5s}$-to-TiO$_2$, charge transfer at the TiO$_2$-Au$_{5s}$ interface than 5 nm Au NPs and consequently are less able to trigger the Au/ TiO$_2$ SMSI. These results provide unambiguous experimental evidence for directly correlating the TiO$_2$-Au$_{5s}$ interface formation with the occurrence of Au-TiO$_2$ SMSI.

Catalytic CO oxidation is very sensitive to structures of employed catalysts.[25] Catalytic activity of various Au/TiO$_2$-fresh and Au/TiO$_2$-H500 catalysts was evaluated in low-temperature CO oxidation (Figure 5a–f). Supporting Information, Figure S18). The 5nm-Au/TiO$_2$-H500 catalysts with almost fully capsulated Au NPs are less active than the corresponding 5nm-Au/TiO$_2$-fresh catalysts, whereas the 2nm-Au/TiO$_2$-H500 catalysts with partially capsulated Au NPs are more active than the corresponding 2nm-Au/TiO$_2$-fresh catalysts. The best catalyst, 2nm-Au/TiO$_2$[101]-H500, exhibits a Au mass-specific CO reaction rate as high as 2.75 mol CO$_2$·mol$^{-1}$·h$^{-1}$ at 30°C. All Au/TiO$_2$-fresh catalysts with the Au$_{5s}$-TiO$_2$ interface as the active structure exhibit similar apparent activation energies around 42.2 ± 2.2 kJ mol$^{-1}$, while all Au/TiO$_2$-H500 catalysts exhibit similar apparent activation energies of 29.0 ± 2.1 kJ mol$^{-1}$ (Figure 5g; Supporting Information, Figures S19, S20 and Table S5). Thus, the active structures of all Au/TiO$_2$-H500 catalysts, which could be the TiO$_2$-Au interface or the capsulating TiO$_2$$_x$ overlays on Au NPs, are intrinsically more active in catalyzing CO oxidation than the Au$_{5s}$-TiO$_2$ interface of Au/TiO$_2$-fresh catalysts. These observations also suggest that, although supported Au NPs on 2nm-Au/TiO$_2$[101]-fresh are not capsulated upon a H$_2$ treatment at 500°C, the interface structure should change from the original Au$_{5s}$-TiO$_2$ interface to the capsulating TiO$_2$$_x$, resulting from the reduction of TiO$_2$. The reaction order against CO of Au/TiO$_2$-H500 catalysts is generally larger than that of corresponding Au/TiO$_2$-fresh catalysts (Supporting Information, Figures S21, S22 and Table S5), except that 5nm-Au/TiO$_2$[001]- H500 with a very small amount of surface Au sites exhibits almost identical reaction order against CO to 5nm-Au/ TiO$_2$[001]-fresh. The reaction order against O$_2$ of Au/TiO$_2$-H500 catalysts is similar to that of corresponding Au/TiO$_2$-fresh catalysts.

Using Au/TiO$_2$[101]-fresh catalysts as an example, CO treatments of 5nm-Au/TiO$_2$[101]-fresh and 2nm-Au/TiO$_2$[101]-fresh at 500°C also demonstrate the similar Au NP size-dependent Au-TiO$_2$ SMSI, in which the treated 5 nm- Au/TiO$_2$[101]-CO500 exhibits the Au-TiO$_2$ SMSI whereas the treated 2nm-Au/TiO$_2$[101]-CO500 does not (Supporting Information, Figure S23). Meanwhile, Au/TiO$_2$[101]-CO500 and Au/TiO$_2$[101]-H500 show similar catalytic activity and apparent activation energy in catalyzing low-temperature CO oxidation.
oxidation (Supporting Information, Figure S24). These results further confirm the structure sensitivity of Au-TiO2 SMI.

DFT calculations were used to probe charge transfer processes between the AuNP-TiO2 and TiO2-x-AuNP interfaces using two-layer Au rod supported on anatase TiO2(101) surface and Ti12Ox4+/Au clusters (x = 0–6) on Au(111) as the models (Figure 6), respectively. The two-layer Au nanorod

![Image](52x526 to 291x687)

**Figure 6**: Calculated structures and interfacial charge transfer of Au/TiO2 and TiO2-x/Au (a–e) Top and (f–j) side views of optimized Au/TiO2 and Ti12Ox4+/Au (x = 0–6) structures. The Au yellow, Ti blue, O red spheres. The direction and amount of charge transfer between Ti12Ox4+ and Au are indicated below the structures.

binds TiO2(101) surface with the average Au–O and Au–Ti bond lengths, respectively of 2.47 and 3.43 Å, indicating weak Au-TiO2 interactions. However, large structure reconstructions occurred when one-layer Ti12Ox4+/Au clusters (x = 0–6) structure with the feature of TiO2(101) surface were deposited on Au(111) surface due to formations of multiple Au–Ti and Au–O bonds. Charge transfer occurs barely at the AuNP-TiO2 interface, consistent with previous calculation results[20] but it occurs obviously at the TiO2-x-AuNP interfaces with both direction and amplitude sensitively depending on the TiO2-x composition. As summarized in Table S6, eight Ti4+/four Ti4+, six Ti3+/six Ti4+, six Ti2+/six Ti4+, and two Ti1+/ten Ti1+ are in Ti12Ox4+/Au(111), Ti12Ox4+/Au(111), and Ti12Ox4+/Au(111), respectively; meanwhile, one Au–O bond/two Au–Ti bonds, five Au–O bonds/ten Au–Ti bonds, nine Au–O bonds/six Au–Ti bonds, and seven Au–O bond and five Au–Ti bonds form at Ti12Ox4+/Au(111), Ti12Ox4+/Au(111), and Ti12Ox4+/Au(111), respectively. The Bader charge analysis was carried out within the interfacial Au–O and Au–Ti bonds. Charge transfer always occurs from Au to O within the interfacial Au–O bond, and from Ti to Au within the interfacial Au–Ti bond for the Ti cations. Less Au–Ti bonds and more Au–O bonds formation results in the charge transfer direction changing from TiO2-to-Au to Au-to-TiO2 with increasing O content in Ti12Ox4+/Au(111) (Figure 6). The overall charge transfer occurs from Ti12Ox4+ and Ti12Ox4+ clusters to Au(111) with amplitudes of 0.245 e per (TiO2)_24 and 0.048 e per (TiO2)_24, respectively, whereas from Au(111) to Ti12Ox4+ and Ti12Ox4+ clusters with amplitudes of 0.039 e per (TiO2)_24 and 0.064 e per (TiO2)_24, respectively. O/Au ratio was found as a descriptor for the Ti12Ox4+/Au(111) interfacial charge transfer (Supporting Information, Figure S25).

Experimentally, we observed that the capsulating TiO2-x overlayers on Au NPs exhibit mixed valences of Ti4+ and Ti3+,

and charge transfer occurs from Au to TiO2-x. Correlated with the calculated Ti4+/Ti3+ compositions and charge transfers of Ti12Ox4+/Au(111), it can be identified that the capsulating TiO2-x overlayers on Au NPs in Au/TiO2 catalysts experiencing Au-TiO2 SMI are of a stoichiometric of around Ti12O24. Thus, the combined experimental characterizations and DFT calculations of the oxidation state of capsulating oxide overlayers and the metal-capsulating oxide overlayers charge transfer are able to identify the stoichiometric of capsulating oxide overlayers in metal/oxide catalysts experiencing SMI. This, as far as we know, represents the first approach to identify compositions of capsulating oxide overlayers in metal/oxide catalysts experiencing SMI.

CO oxidation mechanisms were extensively explored over Au/TiO2 and Ti12O24/Au catalysts. It was found that CO oxidation can occur at the Au-TiO2 interface of Au/TiO2(101) surface and the Ti12O24/Au interface and on the Ti12O24 surface of Ti12O24/Au(111) surface, all initiated by the reaction between adsorbed CO and surface lattice O with an activation energy of 0.77, 0.32 and 0.46 eV, respectively (Figure 7; Supporting Information, Figures S26–S31). This produces a CO2 molecule and an oxygen vacancy at which O2 adsorbs. After, two CO oxidation pathways were found, depending on whether O2 dissociates or not.[24] In the direct route, molecularly adsorbed O2(a) dissociates into one surface lattice oxygen and another atomic oxygen and adsorbed CO reacts with the atomic oxygen to produce a CO2 molecule, which completes the CO oxidation cycle. In the alternative indirect pathway, adsorbed CO reacts with O2(a) to form the OOOO intermediate, which subsequently dissociates into a CO2 molecule and a surface lattice oxygen to complete the CO oxidation cycle. The rate-limiting step in the indirect pathway, the reaction of adsorbed CO reacts with O2(a) to form the OOOO intermediate, exhibits similar activation energies of around 1.50 eV at the Ti12O24-Au interface and on the Ti12O24 surface of Ti12O24/Au(111) surface, much larger than the rate-limiting step in the direct pathway, the O2(a) dissociation. Therefore, CO oxidation proceeds via the direct pathway rather than the indirect pathway over Ti12O24/Au(111). In contrast, both CO oxidation pathways can take place at the interface of Au/TiO2, in which CO reacting with lattice oxygen in TiO2 is the rate-determining step. The O2(a) dissociation proceeds with similar activation energies at Ti12O24-Au interface and on Ti12O24 surface of Ti12O24/Au(111), but still lower than that of CO oxidation at the Au-TiO2 interface of Au/TiO2(101). Meanwhile, CO oxidation is endothermic at the interface of Au/TiO2(101) due to the strong Ti–O bond in TiO2, whereas it becomes highly exothermic thus giving lower CO oxidation barriers at Ti12O24-Au interface and on Ti12O24 surface of Ti12O24/Au(111). These DFT calculation results demonstrate that Ti12O24/Au is more active in catalyzing CO oxidation than Au/TiO2 catalyst, consistent with the experimental results that all Au/TiO2-H2SO4 catalysts exhibit lower apparent activation energies in CO oxidation than all Au/TiO2-fresh catalysts.

Inferred from these DFT calculation results, the likely active structure for catalyzing CO oxidation is the capsulating TiO2-x overlayers in 5nm-Au/TiO2-H2SO4 catalysts whose Au NPs are almost entirely capsulated, while the capsulating
Conclusion

The Au-TiO₂ SMSI of Au/TiO₂ catalysts sensitively depends on both Au NP sizes and TiO₂ facets. Au NPs of ca. 5 nm are more facile to undergo the Au-TiO₂ SMSI than those of ca. 2 nm, while TiO₂[100] and [100] facets are more facile to undergo the Au-TiO₂ SMSI than TiO₂[101] facets. The resulting TiO₂-Au interfaces on Au NPs exhibit a Ti:O ratio as around 6:11. Both capsulating TiO₂-Au interfaces on Au NPs and capsulating TiO₂-Au interface of Au/TiO₂ catalysts experiencing the SMSI exhibit more facile lattice oxygen activation and more intrinsically active in catalyzing low-temperature CO oxidation than the starting Au-TiO₂ interface. These results point to a strategy to fabricate highly efficient catalysts by manipulating the SMSI effect via engineering metal particle sizes and oxide morphologies of metal/oxide catalysts.

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Conflict of interest

The authors declare no conflict of interest.

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References


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