Crystal-plane-dependent metal–support interaction in Au/TiO$_2$†

Lichen Liu, a Chengyan Ge, a Weixin Zou, a Xianrui Gu, a Fei Gao* b and Lin Dong* b

Metal–support interactions between Au and TiO$_2$ are studied based on Au/TiO$_2$ catalysts with different TiO$_2$ crystal planes exposed. With ex situ XPS, TEM and in situ DRIFTS, we have investigated the crystal-plane-dependent metal–support interaction effects on the physiochemical properties of Au/TiO$_2$ catalysts. Based on the structural characterization and spectroscopic results, we can observe chemical oscillations (including the electronic structures of Au nanoparticles and the interaction between Au/TiO$_2$ catalysts and CO molecules) during alternate H$_2$ and O$_2$ pre-treatments. Their variation tendencies of oscillations are greatly dependent on the crystal planes of TiO$_2$ and the pre-treatment temperature. Furthermore, their surface and electronic changes after H$_2$ and O$_2$ pre-treatments can be well correlated with their catalytic activities in CO oxidation. Electron-transfer processes across the Au–TiO$_2$ interface are proved to be the origin accounting for their changes after H$_2$ and O$_2$ pre-treatments. The different electronic structures of different TiO$_2$ crystal planes should have relationships with the crystal-plane-dependent metal–support interaction effects in Au/TiO$_2$.

Metal nanoparticles (NPs) supported on metal oxides are widely used heterogeneous catalysts in many industrial applications including chemical, food, pharmaceutical, environmental and petrochemical industries.¹ The superior catalytic performances are usually related to the metal–support interaction between metal NPs and metal oxide supports.² The classic strong metal–support interaction (SMSI) effect was firstly revealed from the interaction between Group VIII metals and TiO$_2$.³ Under a reductive atmosphere (usually H$_2$) at high temperature, electrons will transfer from the TiO$_2$ support to metal NPs, leading to the encapsulation of metal NPs by thin shells of TiO$_2$.⁴ Associated with these electronic and geometric changes, the chemisorption behaviors and catalytic properties are affected.⁵,⁶ On the other hand, the SMSI effect between the metal NPs and metal oxide supports can be tuned through tuning the electronic structures of the metal oxide supports.⁷,⁸ Based on numerous studies, SMSI is proved to play a crucial role in the catalytic properties of metal/oxide catalysts.

However, previous studies on SMSI are mainly focused on Group VIII metals (Pt, Pd, Rh etc.), while few works have discussed the metal–support interaction of Au NPs supported on oxides.

Metal–support interactions between Au and TiO$_2$ are studied based on Au/TiO$_2$ catalysts with different TiO$_2$ crystal planes exposed. With ex situ XPS, TEM and in situ DRIFTS, we have investigated the crystal-plane-dependent metal–support interaction effects on the physiochemical properties of Au/TiO$_2$ catalysts. Based on the structural characterization and spectroscopic results, we can observe chemical oscillations (including the electronic structures of Au nanoparticles and the interaction between Au/TiO$_2$ catalysts and CO molecules) during alternate H$_2$ and O$_2$ pre-treatments. Their variation tendencies of oscillations are greatly dependent on the crystal planes of TiO$_2$ and the pre-treatment temperature. Furthermore, their surface and electronic changes after H$_2$ and O$_2$ pre-treatments can be well correlated with their catalytic activities in CO oxidation. Electron-transfer processes across the Au–TiO$_2$ interface are proved to be the origin accounting for their changes after H$_2$ and O$_2$ pre-treatments. The different electronic structures of different TiO$_2$ crystal planes should have relationships with the crystal-plane-dependent metal–support interaction effects in Au/TiO$_2$.

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Au NPs supported on metal oxides have shown excellent catalytic performances in many reactions.⁹,¹⁰ And the fantastic activities of Au NPs have been proved to be related with interaction Au NPs and the support.¹¹,¹² Goodman has proposed that Au/TiO$_2$ may be another example of SMSI through comparing the similarities and discrepancies in the catalytic behaviors of Au/TiO$_2$ and Group VIII metals/TiO$_2$.¹³ Takeda et al. have studied the dynamic changes of Au/TiO$_2$ catalysts by in situ environmental TEM under the reaction atmosphere. Au NPs can be encapsulated by TiO$_2$–x shells under an O$_2$ atmosphere and electron irradiation.¹⁴ The electron transfer from Au NPs to TiO$_2$ support also has been in situ observed when Au/TiO$_2$ is exposed to O$_2$, which is different with the situation in H$_2$-pretreated Pt/TiO$_2$.¹⁵,¹⁶ These works imply that SMSI should also exist in Au/TiO$_2$ although it may work in a different mechanism. So, studying the metal–support interaction in Au/TiO$_2$ can provide further insights into the catalytic properties.

What’s more, for the classic SMSI model, the interface between the metal and oxide support is thought to be the reaction zone.¹⁷,¹⁸ The surface structures and electronic structures of the metal–oxide interface will show significant effects on the SMSI between metal and oxide. As we know, the catalytic activities of metal NPs are greatly dependent on the crystal planes of oxide supports.¹⁹,²⁰ However, to the best of our knowledge, this crystal-plane effect on the metal–support interaction has not been studied, which is probably due to the difficulties in obtaining single oxide crystals with different crystal planes exposed. Considering their different surface structures and electronic structures of different crystal planes of metal oxides,²²
it will be meaningful to study the crystal-plane effect on metal-support interaction.

In this work, we have prepared TiO₂ nanocrystals with different crystal planes (⟨100⟩, ⟨101⟩ and ⟨001⟩) exposed as a support of Au NPs to study the crystal-plane effect on the metal–support interaction in Au/TiO₂ catalysts. With the help of ex situ XPS and in situ DRIFTS, the dynamic changes of Au NPs supported on different TiO₂ crystal planes under a reaction atmosphere are investigated. We have found some similar phenomenon like traditional SMSI in as-prepared Au/TiO₂ catalysts as well as some differences. More interestingly, the results show that the responses of Au/TiO₂ catalysts to different atmospheres at different temperatures will vary with the crystal planes of TiO₂ nanocrystals. This work may provide some new insights into the Au–TiO₂ interaction and the working mechanism, especially the interfacial interaction in the reaction atmosphere.

TiO₂ nanocrystals with different crystal planes exposed are synthesized according to our recent works through an anion-assisted method. ²³ The as-prepared TiO₂ nanocrystals show typical XRD patterns of anatase TiO₂ without other peaks. These TiO₂ nanocrystals show regular shapes and similar sizes. Based on the TEM and HRTEM images, their dominant crystal facets are identified as ⟨100⟩, ⟨101⟩ and ⟨001⟩ facets, and the percentages of specific crystal planes are as high as ca. 80%, which suggests that they are ideal model supports. Structural characterizations on the Au/TiO₂ catalysts with different TiO₂ crystal planes exposed can also be found in our recent work. ²⁴ Au NPs are loaded on these TiO₂ nanocrystals through a deposition-precipitation method. We can figure out that Au NPs (average size is ca. 3.6 nm) are located on specific crystal facets of TiO₂ nanocrystals. Therefore, these Au/TiO₂ catalysts can be used as model catalysts to investigate the crystal-plane-dependent metal–support interaction effect.

According to previous studies, SMSI is usually induced by the pre-treatments of a reductive or oxidative atmosphere at high temperature. The interfacial electron transfer will be caused by these pre-treatments and will further have great influences on the electronic and surface structures of the catalysts. Firstly, we use ex situ XPS to investigate the interfacial electron transfer across the Au–TiO₂ interface during the pre-treatments at high temperature. The XPS spectra of the Au 4f region are shown in Fig. S1–S3 (ESI†). In order to clarify the dynamic changes of Au NPs during the alternate pre-treatments, the percentages of cationic Au species (denoted as Au⁺) are calculated according to the fitting results. ²⁵,²⁶ As displayed in Fig. 1, the chemical states of Au will change with the atmosphere. The percentages of Au⁺ in three Au/TiO₂ samples show different variation tendencies under the H₂ and O₂ atmospheres. For Au/Ti-100 and Au/Ti-101, the percentages of Au⁺ are very sensitive to the atmosphere at 250 °C and 300 °C (as shown in Fig. 1a and b). When they are pre-treated with H₂, the percentages of Au⁺ will decrease compared with those under a N₂ atmosphere. When the atmosphere is shifted to O₂, the percentages of Au⁺ are dramatically improved. Therefore, a chemical oscillation of chemical states of Au will appear. However, the variation tendency will change for Au/Ti-001. At the relative low temperature (250 °C and 300 °C), Au/Ti-001 still shows insensitivity to the atmosphere. The percentages of Au⁺ are kept below 10% no matter pre-treated by H₂ or O₂. When the pre-treatment temperature increases to 350 °C, the percentage of Au⁺ can be significantly improved by O₂ oxidation. Furthermore, the content of Au⁺ will subsequently decrease after H₂ treatment. Thus, an oscillation of chemical states of Au can be also observed in Au/Ti-001 if the temperature is high enough, which may be caused by the high energy barrier for charge transfer between Au NPs and TiO₂ ⟨001⟩ planes. Moreover, the high temperature also has a dramatic effect on Au/Ti-100 and
Au/Ti-101. As displayed in Fig. 1c, the percentages of Au\(^{5+}\) in Au/Ti-100 and Au/Ti-101 are still very high after the second H\(_2\) pre-treatment, which shows great contrast with their dramatic variation at 250 °C and 300 °C. The oscillation of chemical states of Au should be originated from the charge transfer between Au NPs and TiO\(_2\) support under a reductive or oxidative atmosphere. During H\(_2\) pre-treatment, electrons will transfer from TiO\(_2\) to Au NPs, resulting in the decrease of percentages of Au\(^{5+}\). While during O\(_2\) pre-treatment, electrons will flow from the Au NPs to TiO\(_2\) support, leading to the increase of percentages of Au\(^{5+}\). The charge transfer processes should have relationships with the electronic properties of different TiO\(_2\) crystal planes, therefore three Au/TiO\(_2\) catalysts show different variation tendencies during the alternate H\(_2\) and O\(_2\) pre-treatments.

In order to figure out the structural changes in these samples during the pre-treatment in O\(_2\), we use TEM to study them after O\(_2\) pre-treatment. When three Au/TiO\(_2\) samples are pretreated in O\(_2\) at 250 °C and 300 °C, no obvious morphological changes can be found (as shown in Fig. S4–S6, ESI†). Au NPs are still located on the corresponding crystal planes of TiO\(_2\) without obvious growth of particle size. However, Au NPs will be encapsulated by a TiO\(_2\) shell after O\(_2\) treatment at 350 °C (Fig. 2a–d). This encapsulation may be caused by the strong interaction between Au and TiO\(_2\) at high temperature in the O\(_2\) atmosphere.\(^{14,29}\) Driven by the oxidative atmosphere at high temperature, electrons will flow to the TiO\(_2\) support, forming TiO\(_{2-x}\) at the Au–TiO\(_2\) interface.\(^{30}\) Then TiO\(_{2-x}\) will crawl along Au NPs, resulting in the encapsulation of Au NPs by TiO\(_2\). Due to the encapsulation, the percentage of Au\(^{5+}\) species cannot fall after H\(_2\) treatment. Interestingly, this encapsulation is not observed in Au/Ti-001 (Fig. 2e and f). No TiO\(_2\) can be found at the Au–{001} plane interface, indicating that TiO\(_2\) will not crawl along Au NPs in the O\(_2\) atmosphere at 350 °C.

Therefore, the Au\(^{5+}\) species in Au/Ti-001 can be reduced by H\(_2\) at 350 °C. Specially, the mechanism of encapsulation of Au NPs observed in our work is different from classic SMSI models. The encapsulation of Au NPs in our work is induced by O\(_2\) pre-treatment while the encapsulation of Group VIII metal NPs in previous studies is induced by H\(_2\) pre-treatment.\(^{30,31}\) Nevertheless, these Au NPs are still covered by TiO\(_{2-x}\) shells after H\(_2\) treatment under 350 °C (see Fig. S7, ESI†), suggesting that the encapsulation is irreversible, which is also different from the classic SMSI. This large discrepancy may be caused by the different electronic structure of Au compared with Group VIII metals.\(^{32}\) However, the encapsulation of Au NPs may also be caused by the surface reconstruction of the TiO\(_2\) support. At high temperature, surface structures of metal oxides will be reconstructed, which may also lead to the encapsulation of metal NPs.\(^{31,32}\) A similar encapsulation phenomenon of Au NPs is also found in some other systems which are also induced by high-temperature treatment under an O\(_2\) atmosphere.\(^{29,32–37}\) Further investigations need to be done to figure out the encapsulation mechanism of Au NPs supported on TiO\(_2\).

Based on the \textit{ex situ} XPS and TEM results, we can understand the In Au/Ti-100 and Au/Ti-101, the electron transfer between Au NPs and TiO\(_2\) is facilitated due to the stronger interactions between Au NPs and {100} planes and {101} planes. Therefore, the percentages of Au\(^{5+}\) will show evident oscillation during the alternate pre-treatments at 250 °C and 300 °C. As to Au/Ti-001, the charge transfer across the Au–TiO\(_2\) interface is not propitious, which makes the percentage of Au\(^{5+}\) stable at 250 °C and 300 °C during pre-treatment processes. However, the situation will change when the pre-treatment temperature is increased to 350 °C. In Au/Ti-100 and Au/Ti-101, Au NPs will be encapsulated by TiO\(_{2-x}\) shells, which may hinder the electron transfer process between Au NPs and TiO\(_2\).\(^{38,39}\) As a consequence, the percentages of Au\(^{5+}\) remain stable after O\(_2\) pre-treatment at 350 °C. For Au/Ti-001, the encapsulation does not occur. What’s more, the electron-transfer process between Au NPs and {001} facets is facilitated by the high temperature, which causes the obvious oscillation of Au\(^{5+}\) percentage.

With the help of \textit{ex situ} XPS and TEM, we have studied the crystal-plane effects on the electron-transfer process between Au NPs and TiO\(_2\) supports. Then, \textit{in situ} DRIFTS are used to study the effects of H\(_2\) and O\(_2\) pre-treatments on the interactions between CO molecules and Au NPs supported on different TiO\(_2\) crystal planes. At first, the effects of H\(_2\) pre-treatments are discussed. As shown in Fig. S8–S10 (ESI†), two peaks appear in all the three Au/TiO\(_2\) catalysts after N\(_2\) pretreatment. They can be ascribed to Au\(^{5+}\)–CO (2110–2120 cm\(^{-1}\)) and Au\(^0\)–CO (2070–2080 cm\(^{-1}\)), respectively.\(^{38,39}\) Notably, the peaks corresponding to Au\(^{5+}\)–CO will disappear and new adsorption signals (2063–2067 cm\(^{-1}\)) can be observed after H\(_2\) reduction. The new adsorption peaks are corresponding to Au\(^{5+}\)–CO, which should result from the CO adsorbed on negative charged Au NPs.\(^{40}\) The intensity of Au\(^0\)–CO will decrease with the increase of temperature. \textit{Ex situ} XPS have proved that electrons will transfer from TiO\(_2\) to Au NPs during H\(_2\) pre-treatment, leading to the accumulation of negative charge in Au NPs. After pre-treatment by H\(_2\) at higher temperature, more
electrons will transfer to Au NPs, which is not favoured for the adsorption of CO.\textsuperscript{29,40} For negatively charged Au NPs, CO adsorption is not facilitated, which have already been reported in some previous studies.\textsuperscript{41,42} For Au/Ti-100 and Au/Ti-101, the adsorption of CO is very weak after high temperature reduction. For Au/Ti-001, the peak corresponding to Au$^3$-CO is still fairly strong, implying that the amounts of negative charges accumulated in Au NPs may vary with the crystal planes of TiO$_2$. Under the H$_2$ pretreatment at the same temperature, more electrons may flow to Au NPs on \{100\} and \{101\} planes than those on \{001\} planes.

What's more, we also track the influences of O$_2$ pretreatments on the adsorption properties of Au/TiO$_2$ catalysts to the
CO molecule. Three Au/TiO$_2$ catalysts are firstly pretreated in the O$_2$ atmosphere at different temperature and then the spectra of CO adsorption on Au/TiO$_2$ are collected every minute. The experimental results of Au/Ti-100 are presented in Fig. 3a. Two peaks corresponding to Au$^{0+}$–CO (2110–2120 cm$^{-1}$) and Au$^{+}$–CO (2070–2080 cm$^{-1}$) can also be observed. Interestingly, as the time prolongs, the intensity of Au$^{0+}$–CO gradually goes down and the intensity of Au$^{+}$–CO grows up. The transformation of Au$^{+}$ to Au$^{0+}$ should be caused by the reduction of Au$^{+}$ by CO. When the temperature increase from 250 °C to 300 °C, the intensity of Au$^{0+}$–CO at the beginning stage (0 min) becomes stronger, indicating that O$_2$ pre-treatment at higher temperature will produce more surface Au$^{0+}$ species. However, when the temperature increases to 350 °C, the intensities of the CO adsorption peaks decrease dramatically (it should be noted that the scale bar is different in Fig. 3a – 350 °C). As shown in Fig. 2,Au NPs will be encapsulated by TiO$_2$ when Au/TiO$_2$ catalysts are pretreated with O$_2$ at 350 °C. These TiO$_2$–Au shells will prevent the adsorption of CO on Au NPs, which results in weak adsorption of CO. The in situ DRIFTS results of Au/Ti-101 are shown in Fig. 3b. The changing tendencies of these curves are similar to those of Au/Ti-100, which is consistent with the results obtained in activity tests and TEM images. The initial intensities of Au$^{0+}$–CO peaks in Au/Ti-100 are stronger than the corresponding peaks in Au/Ti-001 (Fig. 3c), because there are more Au$^{0+}$ species in the Au/Ti-100 sample according to ex situ XPS. As for Au/Ti-001, the intensity of Au$^{0+}$–CO peak at the starting stage is much weaker than those of Au/Ti-100 and Au/Ti-101, which is consistent with the low percentages of Au$^{0+}$ in ex situ XPS. When Au/Ti-001 is pre-treated with O$_2$ under 350 °C, a much stronger Au$^{0+}$–CO peak can be observed when CO is just pumped in. This change can be well correlated with the sudden increase of Au$^{0+}$ percentage in ex situ XPS after O$_2$ pre-treatment at 350 °C.

At last, we use H$_2$ and O$_2$ to pre-treat three Au/TiO$_2$ catalysts and employ CO oxidation as a probe reaction to investigate the relationships between Au–TiO$_2$ interaction and the catalytic properties. During the H$_2$ and O$_2$ pre-treatments, electrons will transfer across the Au–TiO$_2$ interface driven by the atmosphere at high temperature. In Fig. 4, the CO oxidation activity of Au/TiO$_2$ catalysts are tested at 30 °C after different pre-treatments at three temperatures 250 °C, 300 °C and 350 °C. After the pre-treatments, the sample is kept in reaction steam for 15 min to reach the balance before measuring the activity. Obviously, three catalysts show distinct variation tendencies under alternant reductive and oxidative pre-treatments at different temperatures. At 250 °C and 300 °C, for Au/Ti-001, only small changes in activity can be observed, suggesting that Au NPs supported on {001} planes of TiO$_2$ are not sensitive to the pre-treatments at those conditions. For Au/Ti-101 and Au/Ti-100, the CO conversion will slightly decrease after H$_2$ pre-treatments at 250 °C and 300 °C because of the weak adsorption of CO. However, an O$_2$ pre-treatment will remarkably improve the CO conversion of Au/Ti-101 and Au/Ti-100. After O$_2$ pre-treatment, electrons will flow from Au NPs to TiO$_2$ supports, resulting in the formation of Ti$^{3+}$ sites around Au NPs. Theoretical studies have proved that O$_2$ activation will be facilitated by the Au$^{+}$–Ti$^{3+}$ structure. Thus, activity oscillations can be observed for Au/Ti-101 and Au/Ti-100 when they are pre-treated with H$_2$ and O$_2$ before CO oxidation tests, which is similar to their oscillations of Au$^{+}$ percentages. According to our previous work and related references, the percentages of cationic Au species can be well correlated with the CO oxidation activities. Therefore, Au$^{+}$ species should be the major active species in CO oxidation in our samples. Notably, Au/Ti-100 shows higher CO conversions than Au/Ti-101 both after H$_2$ and O$_2$ treatments, which should be related with their different Au–TiO$_2$ interface structures as we discussed in our previous work. There are more surface hydroxyl groups on the {100} planes than {101} and {001} planes, which would facilitate the CO oxidation at the Au–TiO$_2$ interface. But the situation changes when the pre-treatment temperature increases to 350 °C. The inert Au/Ti-001 sample shows enhanced CO oxidation activity after O$_2$ pre-treatment at 350 °C, which is in accordance with its increase of Au$^{+}$ percentages. And the activity will fall back after H$_2$ treatment, which is similar to the behaviours of Au/Ti-100 and Au/Ti-101 when they are pre-treated at 250 °C and 300 °C. As for Au/Ti-100 and Au/Ti-101, both H$_2$ and O$_2$ pre-treatments at 350 °C will deactivate the catalysts. The CO conversion decrease to below 10% after O$_2$ pre-treatment at 350 °C. The improvement of O$_2$ treatment seems ineffective at high temperate for Au/Ti-100 and Au/Ti-101, which is totally different with their variation tendencies at 250 °C and 300 °C. Combining the above ex situ XPS, TEM and in situ DRIFTS results, we can infer that the encapsulation of Au NPs should be the reason for the low CO oxidation activities after O$_2$ pre-treatments at 350 °C.

According to the above analysis based on structural and spectroscopic characterizations and activity measurements, we
can have a comprehensive discussion on the crystal-plane-dependent metal–support interaction effects on Au/TiO₂ catalysts. A schematic illustration about the structural changes of three Au/TiO₂ catalysts during pre-treatments under H₂ and O₂ atmosphere at different temperatures are displayed in Fig. S11 (ESI†). For Au/Ti-100 and Au/Ti-101, electrons can be flexibly transferred between Au NPs and \{100\} and \{101\} planes driven by H₂ and O₂ pre-treatments at 250 °C and 300 °C. As a result, the
percentages of Au\(^{\text{+X}}\) and CO oxidation activities will show oscillations during alternate pre-treatments. For Au/Ti-001, the electron-transfer process between Au NPs and \{001\} facets are not favoured at 250 °C and 300 °C. No apparent oscillations can be found in the percentages of Au\(^{\text{+X}}\) and CO oxidation activities can be observed. These results show that the metal–support interaction effects are greatly dependent on the crystal planes of TiO\(_2\) supports. The charge-transfer process between Au NPs and TiO\(_2\) supports are affected by the electronic structures of TiO\(_2\). When the pre-treatment temperature increases to 350 °C, the situation changes. Much stronger metal–support interaction effects occurred due to the high-temperature pre-treatments. So, the Au–TiO\(_2\) interaction is also related to the temperatures because the electron-transfer processes should be driven by high heating. Apparent oscillations of the percentages of Au\(^{\text{+X}}\) and CO oxidation activities can be observed in Au/Ti-001 at 350 °C. However, the Au NPs will be encapsulated by TiO\(_2\) in Au/Ti-100 and Au/Ti-101, leading to the deactivation of Au NPs and disappearance of chemical oscillations. Herein, it should be noted that although we have observed some similar phenomenon like traditional SMSI in Group VIII metals, we still cannot confirm that we have observed SMSI in Au/TiO\(_2\) catalysts.

The physiochemical origins of metal–support interaction effects in Au/TiO\(_2\) catalysts are the electron-transfer processes between Au and TiO\(_2\) supports. The band structure diagram of different TiO\(_2\) crystal planes are different according to theoretical calculations and experimental measurements.\(^{23,47}\) These TiO\(_2\) nanocrystals show the same valence band positions and different conduct band positions. Because of their different band structures, the electronic interactions between Au NPs and different TiO\(_2\) crystal planes under H\(_2\) and O\(_2\) pre-treatments will be distinct with each other. We can use a band energy scheme to demonstrate the changes of electronic structures under H\(_2\) and O\(_2\) pre-treatments. At first, charge equilibriums between Au NPs and TiO\(_2\) nanocrystals with different crystal planes exposed (as shown in Fig. 5) after Au NPs are loaded on TiO\(_2\) nanocrystals. When Au/TiO\(_2\) catalysts are exposed to O\(_2\) or H\(_2\), band bending will occur in the Au–TiO\(_2\) heterojunction, leading to electron transfer across the Au–TiO\(_2\) interface.\(^{48,49}\) When Au/TiO\(_2\) samples are pre-treated with O\(_2\), the Fermi energy of Au NPs (denoted as \(E_{\text{F}}(\text{Au})\)) will become higher than that of TiO\(_2\) nanocrystals (denoted as \(E_{\text{F}}(\text{TiO}_2)\)).\(^{50}\) The degrees of bending of the energy band (equal to the work function differences between Au NPs and TiO\(_2\) nanocrystals) may be larger between Au NPs and \{100\} planes and \{101\} planes than \{001\} planes, leading to a more favoured electron transfer from Au NPs to TiO\(_2\) nanocrystals.\(^{51}\) When Au/TiO\(_2\) samples are pre-treated with H\(_2\), \(E_{\text{F}}(\text{Au})\) will be lower than \(E_{\text{F}}(\text{TiO}_2)\), resulting in an opposite electron transfer from TiO\(_2\) nanocrystals to Au NPs.\(^{50}\) The accumulated electrons in TiO\(_2\) nanocrystals with flow back to Au NPs. As a consequence, chemical oscillations will appear after alternate pre-treatments. At relative low temperature (250 °C and 300 °C), the more apparent chemical oscillation can be observed in Au/Ti-100 and Au/Ti-101 because of their larger degrees of bending of the energy band than Au/Ti-001. At higher temperature (350 °C), the degree of bending of the energy band in between Au NPs and TiO\(_2\) nanocrystals will become larger. So, apparent chemical oscillations can also be observed in Au/Ti-001. For Au/Ti-100 and Au/Ti-101, driven by high temperature, the Au NPs are encapsulated by TiO\(_2\)–x shells, leading to the loss of catalytic activities.

In summary, we have studied the crystal-plane-dependent metal–support interactions in Au/TiO\(_2\) using TiO\(_2\) nanocrystals with specific crystal planes exposed as model supports. Using \textit{ex situ} XPS, TEM and \textit{in situ} DRIFTS, we have found that chemical oscillations can be observed during alternate H\(_2\) and O\(_2\) pre-treatments. These chemical oscillations are greatly dependent on the crystal planes of TiO\(_2\) nanocrystals. As a consequence of these chemical oscillations, their CO oxidation activities also show corresponding variations to the pre-treatments. Considering the discrepancies of different TiO\(_2\) crystal planes in electronic structures, the electronic interactions between Au NPs and TiO\(_2\) nanocrystals will be distinct from each, which should be the origins for their different metal–support interaction effects. However, much work still need to be done to further investigate the crystal-plane effects on the metal–support interaction mechanism Au/TiO\(_2\) at a molecular level. Maybe theoretical calculations\(^{52-54}\) and studies on surface model catalysts\(^{55}\) will provide some more information. We think the present study will provide some new insights to understand the metal–support interaction effects in Au/TiO\(_2\) and may help to design more active Au/TiO\(_2\) catalysts based on suitable pre-treatments.

Conflicts of interest
The authors declare no competing financial interests.

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