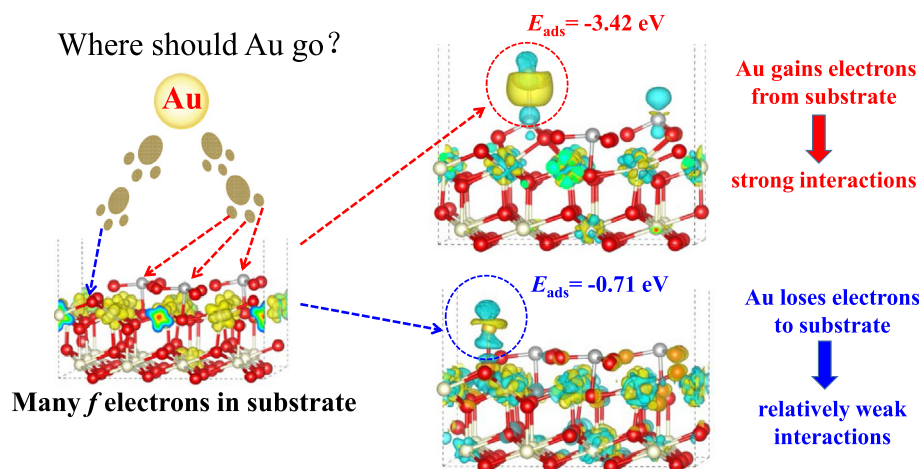


## Regular Article

## A new insight into the theoretical design of highly dispersed and stable ceria supported metal nanoparticles

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## GRAPHICAL ABSTRACT



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## ABSTRACT

How to design and develop ceria supported metal nanoparticles (M/CeO<sub>2</sub>) catalysts with high performance and sintering resistance is a great challenge in heterogeneous catalysis and surface science. In the present work, we propose two ways to improve the anti-sintering capability of M/CeO<sub>2</sub> catalysts. One is to introduce Ti atom on CeO<sub>2</sub> (1 1 1) to form monatomically dispersed Ti, TiO<sub>x</sub> or TiO<sub>2</sub>-like species on ceria. Density functional theory calculations show that the much stronger interactions between Au and Ti modified CeO<sub>2</sub> (1 1 1) occur compared with that on CeO<sub>2</sub> (1 1 1). According to the electronic analysis, the strong interactions are attributed to the electron transfer from the Ti modified ceria substrate to Au. The other is to dope Ti into CeO<sub>2</sub> (1 1 1) to form Ti<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub>. This also leads to the interaction enhancement between Au and Ti<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub> (1 1 1). Electronic analysis indicates that the charge protuberance of surface O atoms near Ti atom results in the strong interactions between metal and ceria. This work provides new ideas for preparing M/CeO<sub>2</sub> catalysts with high dispersity and stability, and sheds light into the theoretical design of catalysts.

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## 1. Introduction

Ceria supported metal nanoparticles (M/CeO<sub>2</sub>) has been widely applied into the purification of automatic exhaust, elimination of volatile organic compounds, water-gas shift reaction, as well as fuel cell [1–11]. How to design and develop M/CeO<sub>2</sub> catalysts with high performance and sintering resistance is a great challenge in heterogeneous catalysis [12,13]. Generally, metal nanoparticles with high activity should highly disperse on ceria to obtain the small particles with more unsaturated active sites as much as possible [14,15]. However, the highly dispersed metal particles tend to aggregate and deactivate slowly upon usage [16–20]. To solve this paradox, great efforts have been devoted by researchers in heterogeneous catalysis and surface science [21–26].

The general way is to reduce the mobility of metal nanoparticles by increasing the interaction between metal and ceria on the basis of the modification of metal or support [27–29]. In view of ceria modification, Zhou et al. found that the proper reduction of ceria produces surface oxygen vacancy. It can provide the nucleation site for metal nanoparticles, which strengthens the interactions between ceria and metals, such as Ni [25], Rh [30], Au [22,31] and Pt [32]. Correspondingly, the anti-sintering abilities of metal nanoparticles are improved. Similar conclusion was obtained by other researchers in Ag [33] and Pd [34]. Weststrate et al. [24] reported that the rough surface with more step sites on ceria can also greatly improve the dispersion of Au nanoparticles due to more nucleation centers at the step sites. In addition, the introduction of Zr ion into ceria to form Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> solid solution is also proved to be an effective way to increase the dispersion of metal nanoparticles in theory [35] and experiment [23]. Another important way to lower the mobility of metal nanoparticles is the confinement effect in mesoporous ceria. It is reported by Yuan et al. [21] that Au/mesoporous-ceria exhibits the higher stability

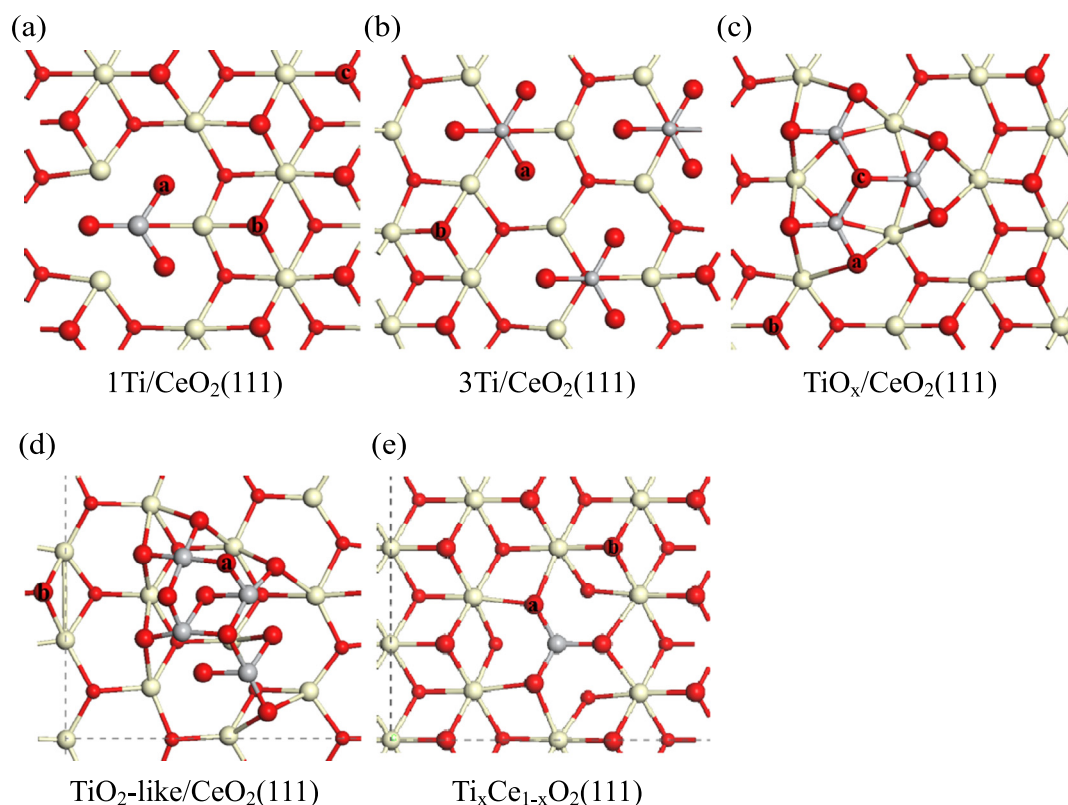
and catalytic activity of CO oxidation than that on other nanostructured ceria due to the confinement effect of the mesoporous structure.

In view of metal nanoparticles, Zhou et al. [22] reported that the anti-sintering capability of Au nanoparticles deposited on the Pt/CeO<sub>2</sub> (1 1 1) to form Au-Pt alloy significantly increases upon heating compared with that deposited on CeO<sub>2</sub> (1 1 1). Similar results was observed for the Co-Au alloy nanoparticles on ceria [36]. This is attributed to the increase of the interactions between alloy particles and ceria support.

Is there any other way to improve the anti-sintering of metal nanoparticles on ceria? It is reported that Ti can be used to modify ceria support, which might monatomically disperse or form TiO<sub>x</sub> or TiO<sub>2</sub>-like species on ceria [37,38], as well as doping into ceria [31]. Can the Ti modified ceria improve the stability of metal nanoparticles? What is the mechanism in electronic nature? In the present work, we systematically investigate the interactions between metal and Ti modified CeO<sub>2</sub> (1 1 1) by using Au as the probe metal, which has been extensively used and studied in gold catalysis. The great improvement in the interactions between Au and Ti modified ceria surfaces are verified in theory. Based on these works, we propose two ways to improve the anti-sintering capability of M/CeO<sub>2</sub> catalysts and explore the electronic nature in detail. This work sheds light into the theoretical design of the anti-sintering M/CeO<sub>2</sub> catalysts at an atomic level.

## 2. Method and models

Spin-polarized DFT calculations with plane-wave basis sets were carried out using the Vienna *ab initio* Simulation package (VASP) [39–42]. We used the generalized gradient approximation with the PW91 functional to describe the exchange-correlation energy of electrons [43]. Ionic cores were treated by the



**Fig. 1.** Ti modified CeO<sub>2</sub> (1 1 1) models. a, b and c represent the oxygen sites near, next near and in the middle of Ti atom. Grey white, red and grey spheres represent the Ce, O and Ti atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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