Electronic Supplementary Material (ESI) for Nanoscale.

A Visualized Probe Method for Localization of Surface Oxygen Vacancy on TiO$_2$: Au *in-situ* Reduction

Supporting information

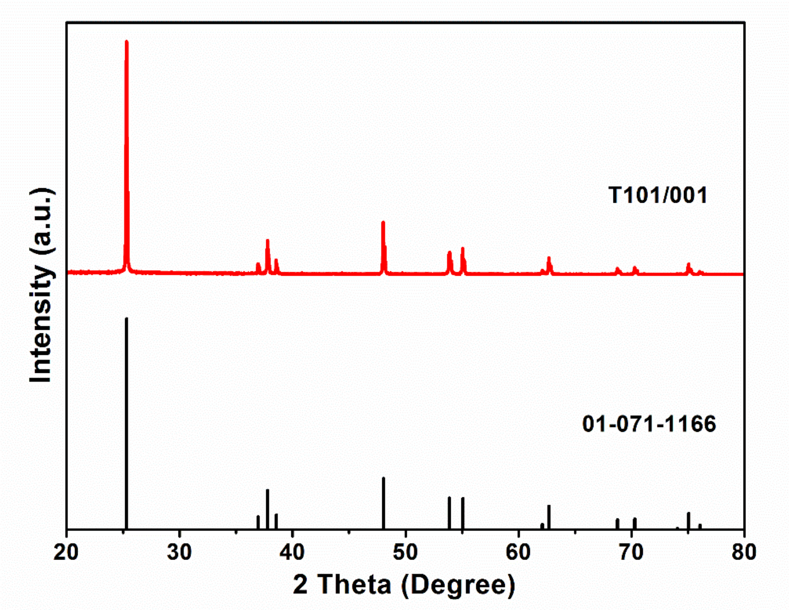

Figure S1 X-ray diffraction pattern of T101/001

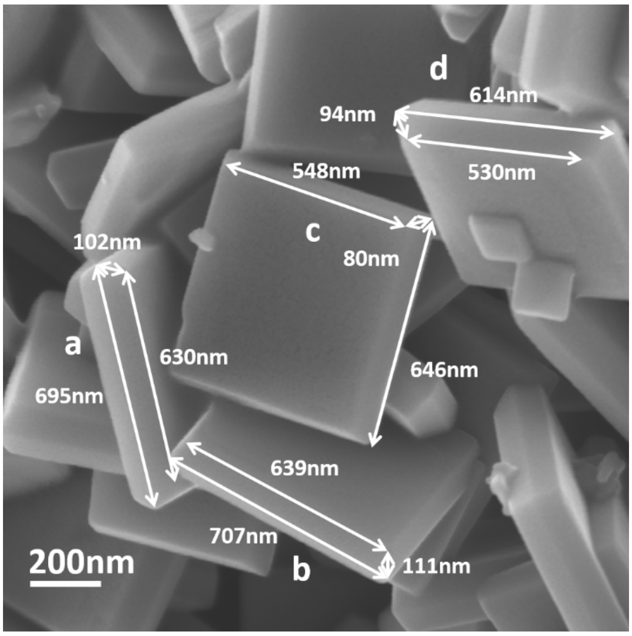

Figure S2 FESEM image of T101/001

Table S1 percentage of different facet on T101/001 observed in Figure 2

	Percentage of {101} facets	Percentage of {001} facets
a	39%	61%
b	40%	60%
c	37%	63%
d	41%	59%
Average	39.25%	60.75%

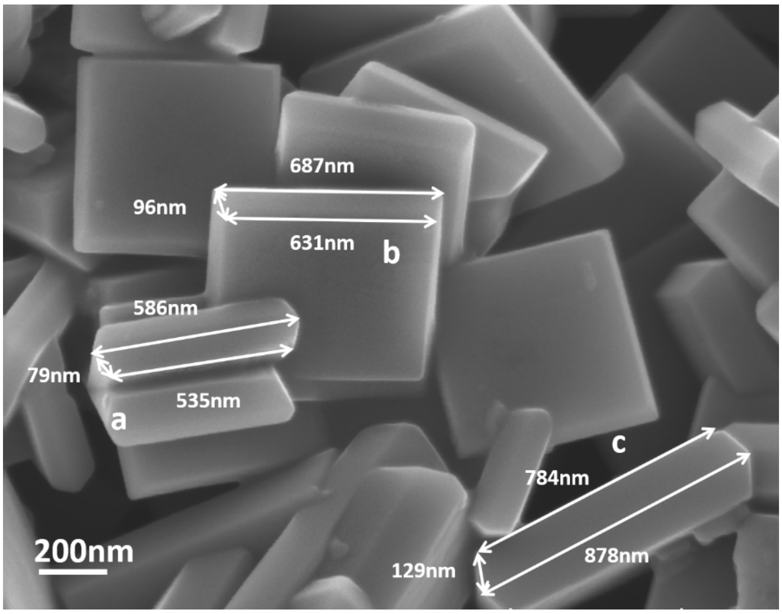

Figure S3 FESEM image of T101/001

Table S2 percentage of different facet on T101/001 observed in Figure 3

	Percentage of {101} facets	Percentage of {001} facets
a	36%	64%
b	37%	63%
c	39%	61%
Average	37.3%	62.7%

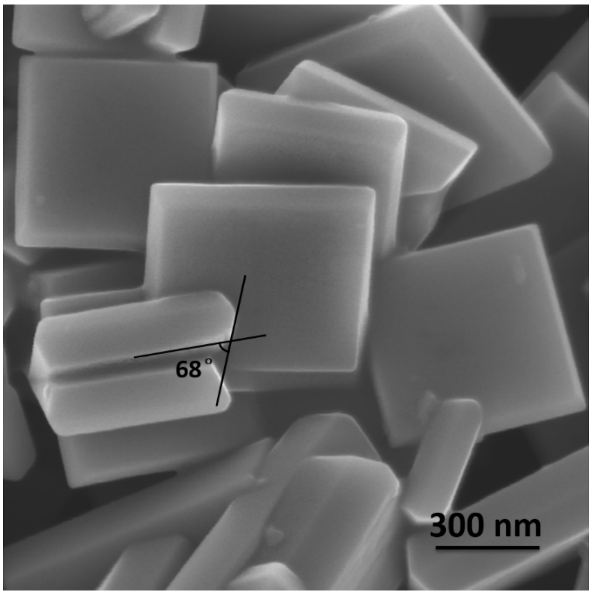

Figure S4 FESEM image of T101/001

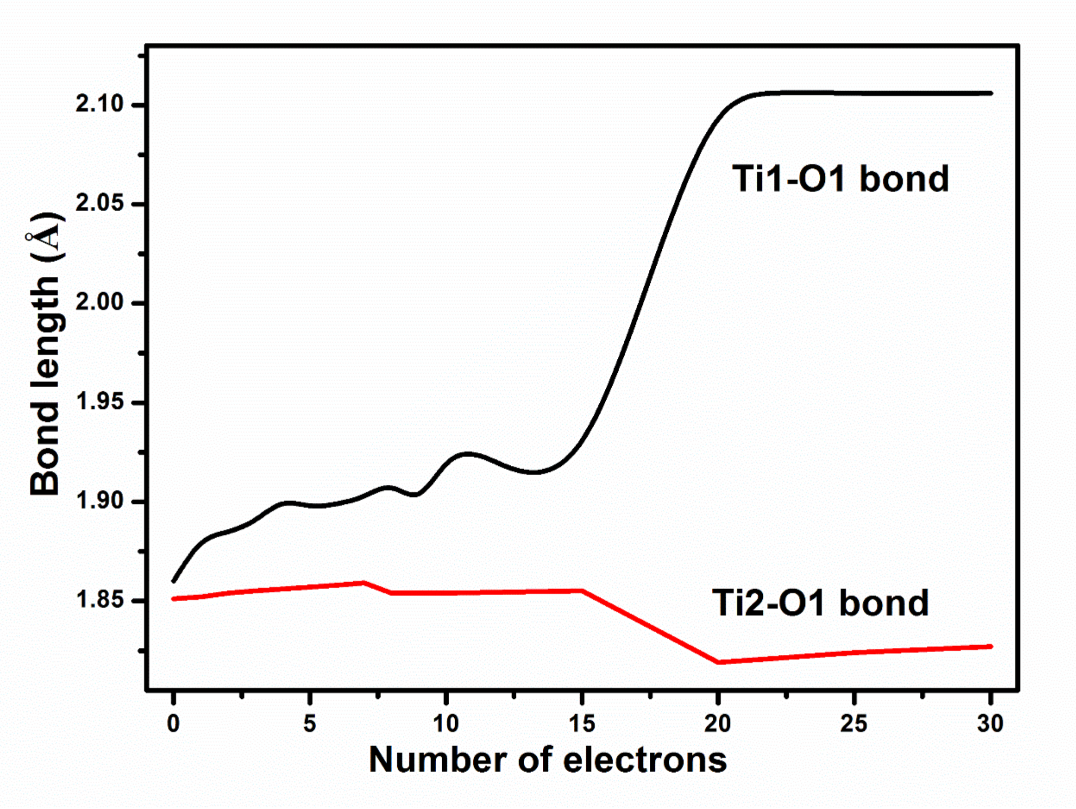

Figure S5 Variation chart of bond length of Ti1-O1, Ti2-O1 caused by extra electrons.

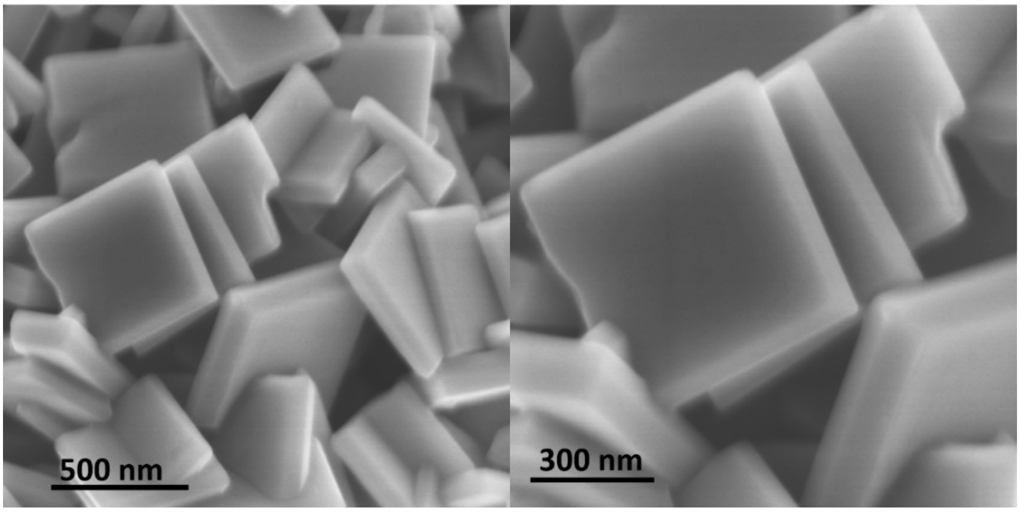

Figure S6 SEM image of Au-T101/001

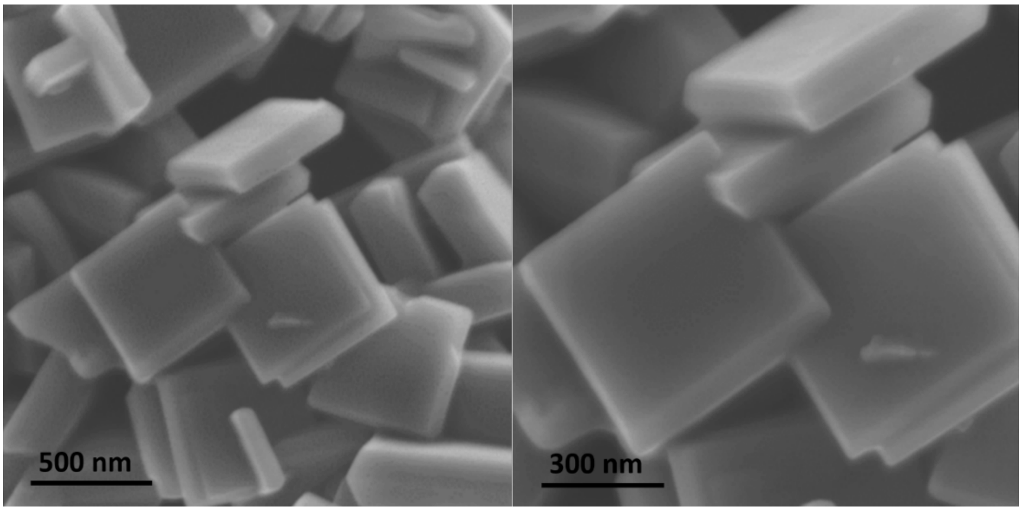

Figure S7 SEM image of Au T101-O_v-R /001

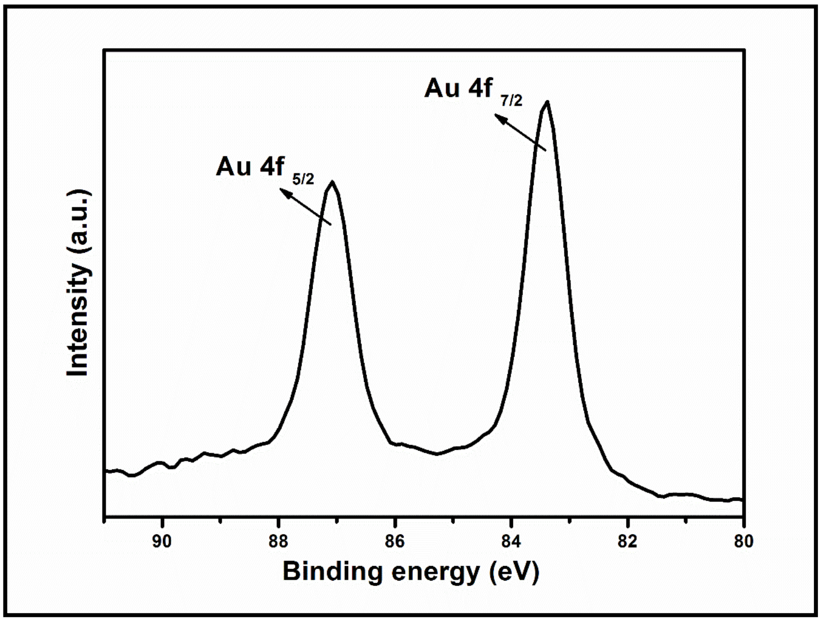

Figure S8 Au $4f_{7/2}$ XPS spectrogram of T101-O_v -Au /001

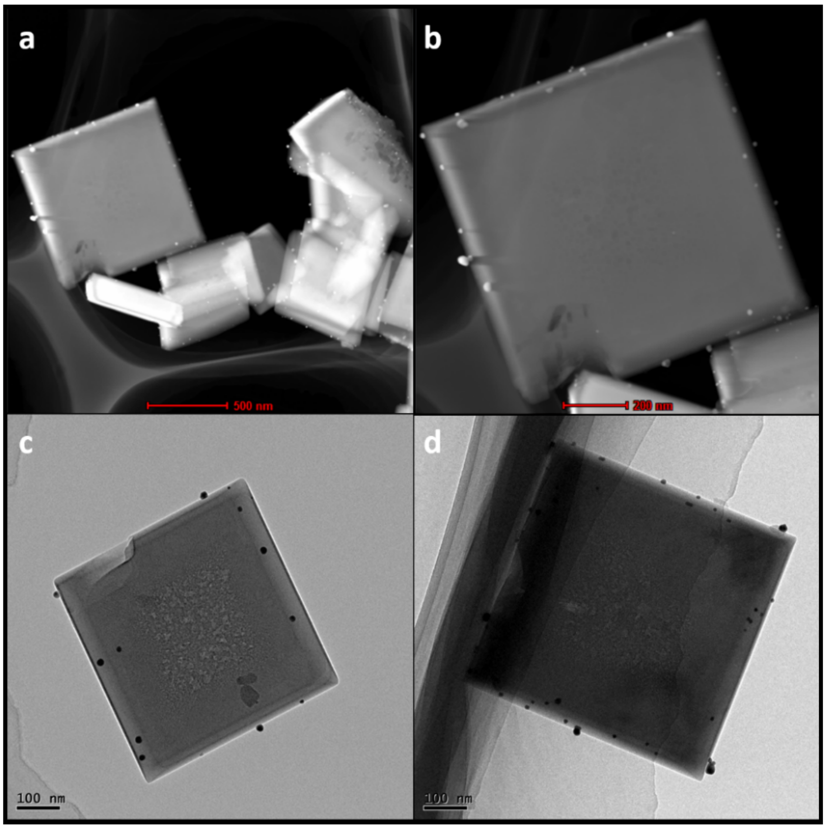

Figure S9 a, b) STEM images and c, d) TEM images of T101-O_v-Au /001 by using $HAuCl_4$ as Au resource.

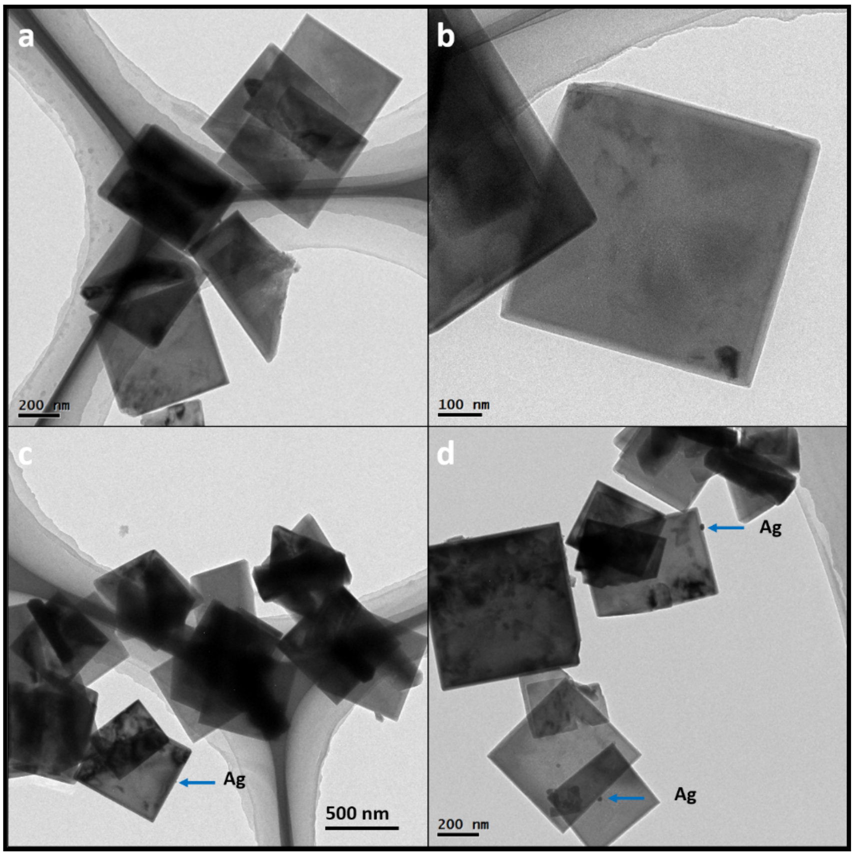

Figure S10 TEM images of T101-O_v-Ag /001 by using $AgNO_3$ as Ag resource.

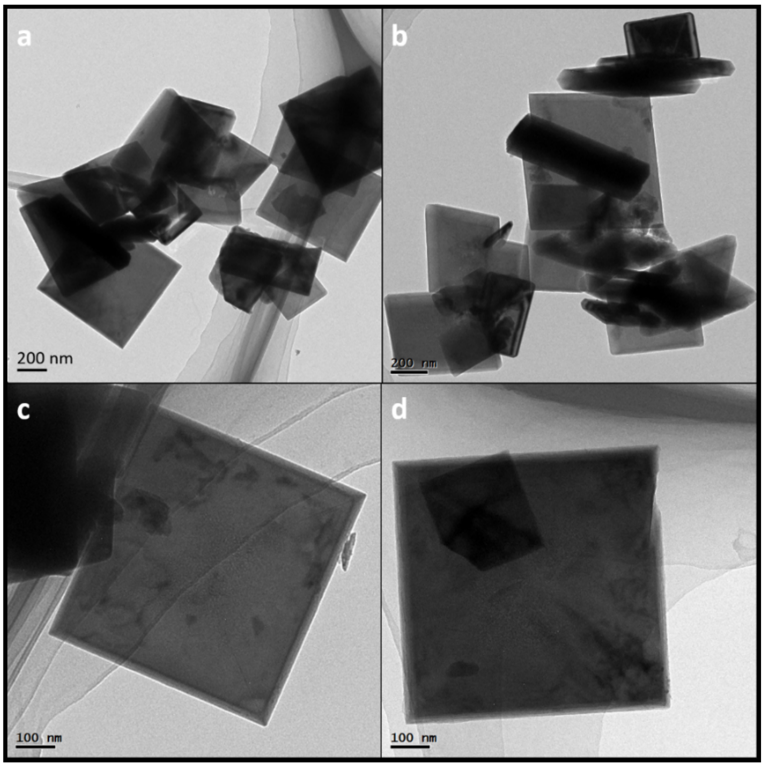

Figure S11 TEM images of T101-O_v-Pt^+ /001 by using $[Pt(NH_3)_4](NO_3)_2$ as Pt resource.

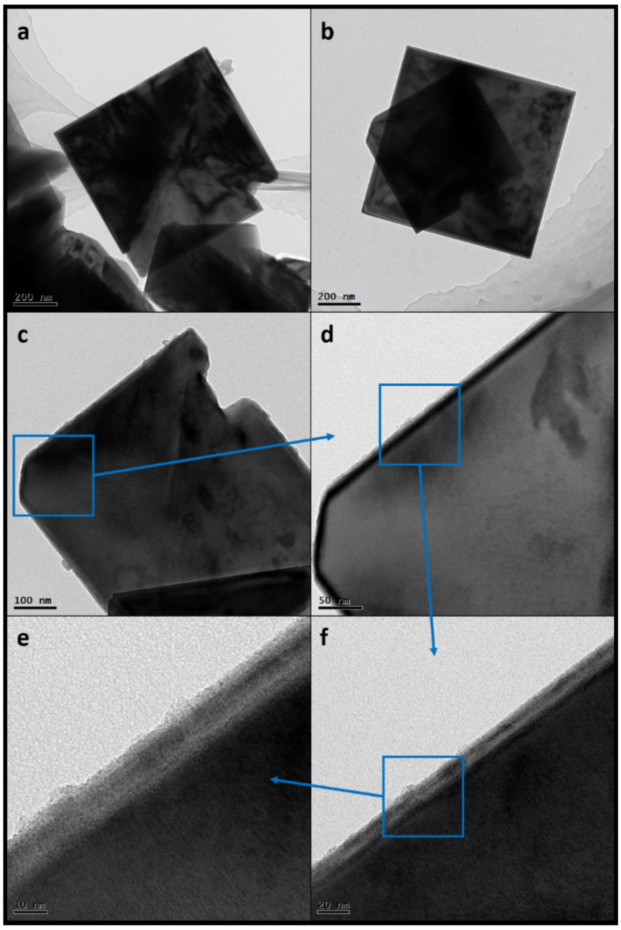

Figure S12 TEM images of T101-O_v-Pt^- /001 by using H_2PtCl_6 as Pt resource.

Generally speaking, the deposition of Au ions in liquid is depending on several conditions. Firstly, the reducing reaction should be allowed by the laws of thermodynamics. It has been conclusively claimed that energy level gap between oxygen vacancy state and conductive band in TiO_2 is 0.75 eV[1-3]. On the base of this data and potential value of the conductive band, the reduction potential of oxygen vacancy is 0.46 eV vs. NHE[2, 4], which is lower than that of the $HAuCl_4$, $AgNO_3$, $[Pt(NH_3)_4](NO_3)_2$ and H_2PtCl_6 in principle[1, 5]. Therefore, in theory, while these noble metal ions contact with TiO_2 surface defect, the photogenerated electrons will shift spontaneously from oxygen vacancies to them. Oxidative noble metal ions will be reduced by electrons. At this point, all these noble metal ions can be used in our method.

Secondly, the reducing reaction should be allowed by the laws of kinetics. Usually, the deposition of noble metal ions need directly attaching between ions and surface of base material. Thus, the surface property would play an important role in this condition. Hence, $HAuCl_4$, $AgNO_3$, $[Pt(NH_3)_4](NO_3)_2$ and H_2PtCl_6 are employed as noble metal resource and corresponding samples are named as T101-O_v-Au/001, T101-O_v-Ag /001, T101-O_v-Pt^+/001 and T101-O_v-Pt^-/001, respectively. Among these four noble metal ions, $HAuCl_4$ and $AgNO_3$ own higher reduction potential than $[Pt(NH_3)_4](NO_3)_2$ and H_2PtCl_6 but with opposite charge. $[Pt(NH_3)_4](NO_3)_2$ and H_2PtCl_6 show opposite charge and low reduction potential. To be noticed, all four noble metal ions can be reduced by oxygen vacancy allowed by the laws of thermodynamics. Therefore, in theory, all these four metal ions should be reduced by oxygen vacancy and metal particles should be observed.

However, characterizations of T101-O_v-Au/001, T101-O_v-Ag /001, T101-O_v-Pt^+/001 and T101-O_v-Pt^-/001 show different results (See Figure S9, Figure S10, Figure S11 and Figure S12). A lot of Au particles show up while only part of Ag particles present, suggesting both Au and Ag ions can be reduced by oxygen vacancy. The possible reason for only part of Ag particles are observed is the different charge. Generally speaking, surface with oxygen vacancy usually present positive charge. According to the fundamental laws that like charges repel but opposite charges attract, it is very difficult for Ag ions to be absorbed on this surface. Then without effective absorption, only part of Ag ions can be reduced by oxygen vacancy. But for Au ions, which are negative charge, are very easy absorbed on the surface and reduced by oxygen vacancy. No sight of Pt particle presents no matter which charge the ions concerning Pt element owned. However, it has been reported that the reduction reaction can happen while heating at 100 °C in an oil bath with magnetic stirring for 2 h[1]. Hence, this phenomenon probably caused by the unknown kinetics reason.

In summary, to apply our method, two basic rules, thermodynamics and kinetics, should be allowed. The reduction potential of the surface defect should be low enough to reduce the noble metal ions. And the noble metal ions should be easily absorbed on the surface and reduced by surface defect. In the further application of this method, the reduction potential, the zeta potential, the charge of noble metal ion and the reaction time and temperature should be carefully considered.

References:

1. X. Pan and Y.-J. Xu, *J. Phys. Chem. C*, 2013, 117, 17996-18005.
2. X. Pan and Y.-J. Xu, *Appl. Catal. A-Gen.*, 2013, 459, 34-40.
3. M. K. Nowotny, L. R. Sheppard, T. Bak and J. Nowotny, *J. Phys. Chem. C*, 2008, 112, 5275-5300.
4. Z. Pei, L. Ding, W. Feng, S. Weng and P. Liu, *Phys. Chem. Chem. Phys.*, 2014, 16, 21876-21881.
5. X. Pan and Y. J. Xu, *ACS Appl Mater Interfaces*, 2014, 6, 1879-1886.