Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for

The Charge States of Au on Gold-Substituted $Ce_{1-x}O_2(111)$ Surfaces with Multiple Oxygen Vacancies

Ming-Wen Chang and Wen-Shyan Sheu*

Department of Chemistry, Fu-Jen Catholic University, Xinzhuang, New Taipei City 24205, Taiwan, R. O. C.

*Corresponding author. Tel.: +886 2 29053724; Fax: +886 2 29023209.
E-mail: chem1013@mails.fju.edu.tw (W.-S. Sheu).

Table S1. Calculated and experiment lattice constants of CeO_2 bulk

	CeO_2 /Å
PW91+U(=5.00 eV)	5.49
LDA+U(=6.00 eV)	5.40
HSE06	5.40
[a]Exp.	5.41

a. L. Eyring, in: K.A. Gschneider, L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, North-Holland, Amsterdam, 1979.

Table S2. The Au charges predicted by various methods for selected oxygen vacancy configurations on the $Au@V_{Ce}$ surface with a *p*(3x3) supercell.

Oxygen vacancy configuration	q[Au] / |e|			
	[a]G5//G5 (LC=5.49 Å)	[b]G5//H06 (LC=5.49 Å)	[c]H06//H06 (LC=5.40)	[d]L6//L6 (LC=5.40 Å)
perfect-$Au@V_{Ce}$	1.26	1.36	1.42	1.31
[e]$(V_O1)_{surf}$	1.09	1.24	1.26	1.12
[f]$(V_O1, V_O2)_{surf, surf}$	0.39	0.46	0.45	0.41
[g]$(V_O1, V_O2, V_O3)_{surf, surf, surf}$	0.33	0.40	0.40	0.34

a. Charges obtained in the present PW91+U(= 5.00 eV) calculations.

b. Charges predicted by HSE06 functional calculations at the relaxed surface geometry of the reduced $Au@V_{Ce}$ optimized by the PW91+U(= 5.00 eV) method.

c. Charges predicted by HSE06 functional calculations at the relaxed surface geometry of the reduced $Au@V_{Ce}$ optimized by the HSE06 method.

d. Charges predicted by LDA+U(= 6.00 eV) functional calculations at the relaxed surface geometry of the reduced $Au@V_{Ce}$ optimized by the LDA+U(= 6.00 eV) method.

e. Au-NNN configuration.

f. Linear-like structure.

g. High-Spin configuration.

h. All HSE06 functional calculations were performed at the gamma point.