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Tuning the Charge State of Metal Atoms and Clusters Deposited on Oxide Surfaces by Doping. A DFT Study of the Adsorption Properties of Nitrogen- and Niobium-doped TiO_2 and ZrO_2

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SUPPLEMENTARY INFORMATION

1. Distances (Å) Adsorbate-Surface for Au and Ag Atoms and Tetramers

In this section, the distances in Å between the metal atoms and the support are reported. Distances up to 3 Å were taken into account, respectively. "#" denotes the number of bonds found.

1.1 Dopant Free Titania

1.1.1 Atoms

Ag/Stoic	M-O	M-Ti	**Ag/Vo1**	M-O	M-Ti	**Ag/Vo2**	M-O	M-Ti
Distances	2.18	0	Distances	0	2.69	Distances	2.17	0
	2.18				2.89		2.98	
	2.79						2.19	
Average	2.39	0	Average	0	2.79	Average	2.44	0
Au/Stoic	M-O	M-Ti	**Au/Vo1**	M-O	M-Ti	**Au/Vo2**	M-O	M-Ti
Distances	2.28	2.73	Distances	0	2.58	Distances	0	2.49
					2.83			
Average	2.28	2.73	Average	0	2.7	Average	0	2.49

Vo1: O Vacancy at surface position

Vo2: O Vacancy at sub-surface position

1.1.2 Tetramers

Ag/Stoic	M-O	M-Ti	**Ag/Vo1**	M-O	M-Ti	**Ag/Vo2**	M-O	M-Ti
Distances	2.86	0	Distances	2.40	2.87	Distances	2.46	0
	2.48			2.40			2.25	
	2.92			2.91			2.99	
	2.38			2.98				
	2.51			2.98				
				2.40				
				2.65				
				2.65				
				2.40				
Average	2.63	0	Average	2.64	2.87	Average	2.57	0
Au/Stoic	M-O	M-Ti	**Au/Vo1**	M-O	M-Ti	**Au/Vo2**	M-O	M-Ti
Distances	2.30	2.88	Distances	2.30	2.58	Distances	2.28	2.87
	2.99				2.61		2.99	2.98
	2.97						2.08	
	2.09							
Average	2.59	2.88	Average	2.30	2.60	Average	2.45	2.93

Vo1: O Vacancy at surface position

Vo2: O Vacancy at sub-surface position

1.2 N-doped Titania

1.2.1 Atoms

Ag/N-Surf	M-O	M-Ti	M-N	**Ag/N-SubSurf**	M-O	M-Ti	M-N
Distances	2.24	0	2.11	Distances	2.20	0	0
	2.96				2.17		
					2.79		
Average	2.60	0	2.11	Average	2.39	0	0
Au/N-Surf	M-O	M-Ti	M-N	**Au/N-SubSurf**	M-O	M-Ti	M-N
Distances	0	0	1.94	Distances	2.11	0	0
					2.11		
					2.81		
					2.85		
Average	0	0	1.94	Average	2.47	0	0

1.2.2 Tetramers

Ag/N-Surf	M-O	M-Ti	M-N	**Ag/N-SubSurf**	M-O	M-Ti	M-N
Distances	2.31	2.77	2.21	Distances	2.19	0	0
	2.55				2.27		
	2.33				2.84		
	2.99				2.32		
Average	2.54	2.77	2.21	Average	2.41	0	0
Au/N-Surf	M-O	M-Ti	M-N	**Au/N-SubSurf**	M-O	M-Ti	M-N
Distances	2.31	2.99	1.97	Distances	2.10	0	0
	2.99				2.07		

Average	2.65	2.99	1.97	Average	2.08	0	0

1.3 Nb-doped Titania

1.3.1 Atoms

Ag/Nb-Surf	M-O	M-Ti	M-Nb	**Ag/Nb-SubSurf**	M-O	M-Ti	M-Nb
Distances	0	0	2.68	Distances	2.19	0	0
					2.19		
					2.82		
Average	0	0	2.68	Average	2.40	0	0
Au/Nb-Surf	M-O	M-Ti	M-Nb	**Au/Nb-SubSurf**	M-O	M-Ti	M-Nb
Distances	0	0	2.55	Distances	0	2.48	0
Average	0	0	2.55	Average	0	2.48	0

1.3.2 Tetramers

Ag/Nb-Surf	M-O	M-Ti	M-Nb	**Ag/Nb-SubSurf**	M-O	M-Ti	M-Nb
Distances	2.40	0	0	Distances	2.47	0	0
	2.26				2.92		
	2.99				2.40		
	2.99				2.50		
Average	2.66	0	0	Average	2.57	0	0
Au/Nb-Surf	M-O	M-Ti	M-Nb	**Au/Nb-SubSurf**	M-O	M-Ti	M-Nb
Distances	2.21	0	2.96	Distances	2.31	2.88	0
	2.98				2.99		

	2.14				2.97		
					2.09		
Average	2.44	0	2.96	Average	2.59	2.88	0

1.4 Dopant Free Zirconia

1.4.1 Atoms

Ag/Stoic	M-O	M-Zr	**Ag/Vo1**	M-O	M-Zr	**Ag/Vo2**	M-O	M-Zr
Distances	2.30	3.02	Distances	3.30	3.03	Distances	3.34	2.79
				3.30	3.02		3.34	
				3.31	3.03		3.26	
Average	2.30	3.02	Average	3.30	3.03	Average	3.31	2.79
Au/Stoic	M-O	M-Zr	**Au/Vo1**	M-O	M-Zr	**Au/Vo2**	M-O	M-Zr
Distances	2.18	2.83	Distances	3.20	2.93	Distances	3.28	2.66
				3.22	2.92		3.28	
				3.20	2.93		3.22	
Average	2.18	2.83	Average	3.21	2.93	Average	3.26	2.66

1.4.2 Tetramers

Ag/Stoic	M-O	M-Zr	**Ag/Vo1**	M-O	M-Zr	**Ag/Vo2**	M-O	M-Zr
Distances	2.12	3.11	Distances	2.71	2.96	Distances	2.13	2.96
	2.39	3.37		3.21			2.44	
	3.10	2.97		3.25			3.11	
				3.17				
				3.24				
Average	2.54	3.15	Average	3.12	2.96	Average	2.56	2.96

Au/Stoichio	M-O	M-Zr	**Au/Vo1**	M-O	M-Zr	**Au/Vo2**	M-O	M-Zr
Distances	2.04	2.90	Distances	2.75	2.92	Distances	2.05	2.75
	2.13	2.75		2.92	2.80		2.14	2.91
					3.00			
					2.87			
Average	2.09	2.83	Average	2.84	2.90	Average	2.10	2.83

1.5 N-doped Zirconia

1.5.1 Atoms

Ag/N-Surf	M-O	M-Zr	M-N	**Ag/N-SubSurf**	M-O	M-Zr	M-N
Distances	0	0	2.01	Distances	2.98	0	0
					2.28		
					2.28		
Average	0	0	2.01	Average	2.51	0	0
Au/N-Surf	M-O	M-Zr	M-N	**Au/N-SubSurf**	M-O	M-Zr	M-N
Distances	0	0	1.95	Distances	2.16	0	0
					2.16		
					3.16		
					2.86		
Average	0	0	1.95	Average	2.59	0	0

1.5.2 Tetramers

Ag/N-Surf	M-O	M-Zr	M-N	**Ag/N-SubSurf**	M-O	M-Zr	M-N
Distances	2.17	0	2.10	Distances	2.15	0	0

	2.30				2.39		
					2.17		
Average	2.24	0	2.10	Average	2.24	0	0
Au/N-Surf	M-O	M-Zr	M-N	**Au/N-SubSurf**	M-O	M-Zr	M-N
Distances	2.19	3.14	1.94	Distances	2.02	2.91	0
		3.11			2.21		
		3.04			2.12		
Average	2.19	3.10	1.94	Average	2.12	2.91	0

1.6 Nb-doped Zirconia

1.6.1 Atoms

Ag/Nb-Surf	M-O	M-Zr	M-Nb	**Ag/Nb-SubSurf**	M-O	M-Zr	M-Nb
Distances	2.61	0	2.82	Distances	3.08	0	0
	2.61				2.80		
					2.80		
Average	2.61	0	2.82	Average	2.89	0	0
Au/Nb-Surf	M-O	M-Zr	M-Nb	**Au/Nb-SubSurf**	M-O	M-Zr	M-Nb
Distances	2.62	0	2.69	Distances	2.61	2.79	0
	2.62				2.61		
Average	2.62	0	2.69	Average	2.61	2.79	0

1.6.2 Tetramers

Ag/Nb-Surf	M-O	M-Zr	M-Nb	**Ag/Nb-SubSurf**	M-O	M-Zr	M-Nb

Distances	2.13	2.98	3.01	Distances	2.54	3.16	0
	3.06				2.95	3.17	
	2.40				2.19		
	3.07				2.91		
Average	2.67	2.98	3.01	Average	2.65	3.17	0
Au/Nb-Surf	M-O	M-Zr	M-Nb	**Au/Nb-SubSurf**	M-O	M-Zr	M-Nb
Distances	2.13	2.90	2.88	Distances	2.04	3.16	0
	2.05		2.89		2.12	3.06	
	2.59					3.02	
Average	2.26	2.90	2.89	Average	2.08	3.08	0

2. Deposition of Au and Ag Pentamers. Perspective Pictures and Projected DOS

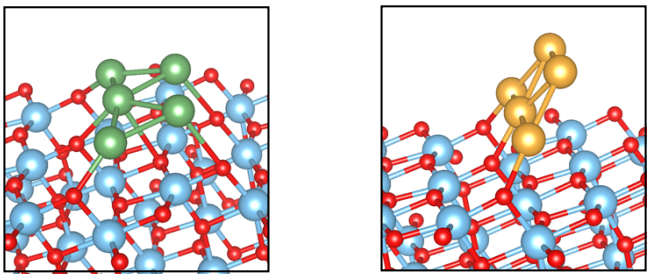

Fig 1. Perspective view of Ag (left) and Au (right) pentamers deposited on titania, corresponding to the structures reported in Figs. 19 (a-h). The structures are equivalent for the stoichiometric titania substrate and for those containing an O vacancy, a N-dopant or a Nb-dopant.

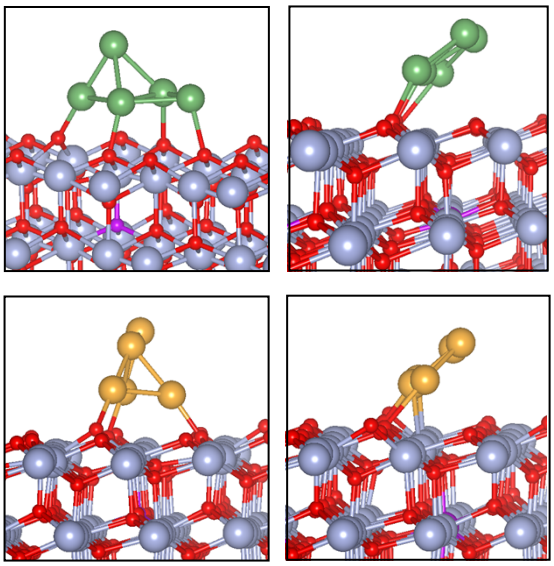

Fig. 2: Perspective view of Ag (top) and Au (bottom) pentamers deposited on N-doped zirconia at sub-surface (left) and Nb-doped zirconia at sub-surface (right). The structures correspond to Figs. 19(k,l) for the Ag pentamer and Figs. 19(o,p) for the Au pentamer.

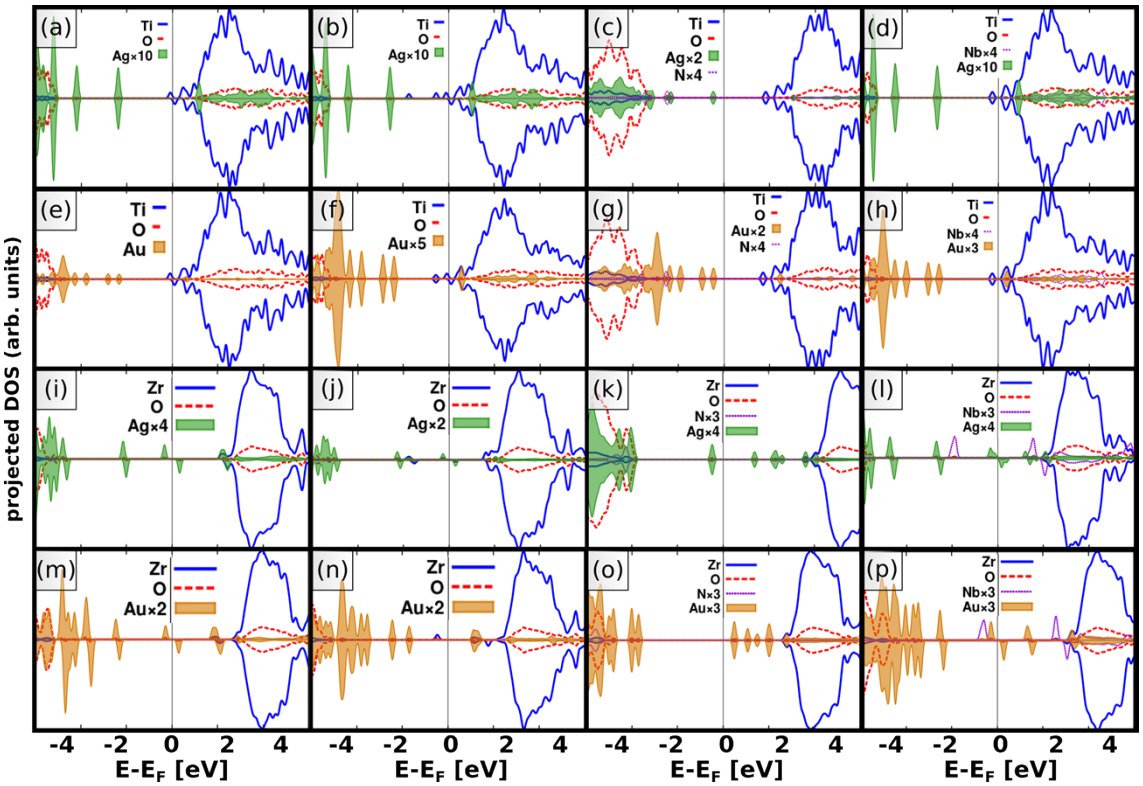

Fig. 3: Projected DOS of Ag and Au pentamers on titania (a-h) and zirconia (i-p) surfaces exhibiting different defects. (a) Ag_5 on stoichiometric TiO_2 surface, (b) Ag_5 on TiO_2 with a sub-surface O vacancy, (c) Ag_5 on TiO_2 N-doped at sub-surface, (d) Ag_5 on TiO_2 Nb-doped at sub-

surface. (e) Au_5 on stoichiometric TiO_2 surface, (f) Au_5 on TiO_2 with a sub-surface O vacancy, (g) Au_5 on TiO_2 N-doped at sub-surface, (h) Au_5 on TiO_2 Nb-doped at sub-surface. (i) Ag_5 on stoichiometric ZrO_2 surface, (j) Ag_5 on ZrO_2 with a sub-surface O vacancy, (k) Ag_5 on ZrO_2 N-doped at sub-surface, (l) Ag_5 on ZrO_2 Nb-doped at sub-surface. (m) Au_5 on stoichiometric ZrO_2 surface, (n) Au_5 on ZrO_2 with a sub-surface O vacancy, (o) Au_5 on ZrO_2 N-doped at sub-surface, (p) Au_5 on ZrO_2 Nb-doped at sub-surface. The 0 eV corresponds to the Fermi level.

3. Discussion of the distribution of the effective Bader charge on atoms in clusters.

Here, we report the charge distribution on the different clusters (Ag and Au tetramers and pentamers), deposited on defect-free and defective/doped titania anatase (101) and tetragonal zirconia (101) surfaces.

3.1 Tetramers

(a) Ag_4/TiO_2. Considering the effective Bader charges on the cluster, we detect a charge close to 0.00 |e| for all atoms of the Ag cluster, only the atom that is coordinated by 2 O atoms exhibits a charge of +0.35 |e|, which supports the thesis that there is orbital mixing, as it is found in the DOS (Fig. 8 (a)).

(b) Ag_4/ZrO_2. Some charge polarization can be detected considering the Bader charges for this cluster. The atoms that are part of the triangle are slightly positively charged and the atom which is not part of the triangle is partly negatively charged.

(c) Ag_4/Vo, surf, titania. The effective Bader charges of the Ag atoms of the tetramer on the surface vacancy are positive and only the atom in the centre of the cluster (the one coordinated by 3 other Ag atoms) has an effective Bader charge of around -0.16 |e|. The electronic response of the cluster upon interaction with the oxygen vacancy is polarization: Atoms in direct contact to the vacancy exhibit a positive partial charge, whereas the central atom of the cluster becomes slightly negatively charged.

(d) Ag_4/Vo, sub, titania. Also the Bader charge distribution is very similar to that of the cluster on the stoichiometric surface.

(e) Ag_4 and Au_4 on oxygen vacancies on ZrO_2: For both metals, when the vacancy is at the surface, the effective Bader charge is more negative on those atoms directly coordinated to the surface, since the electron density of the vacancy is partly delocalized or distributed on these atoms. When the vacancy is located at

the sub-surface position, the electric charge distribution is similar to the stoichiometric case.

(f) Au_4/TiO_2. The effective Bader charge on Au atoms of the tetramer are all close to 0.00 |e|, only the atom which is at the edge of the "triangle", in contact with the surface, exhibits a Bader charge of around +0.26 |e|.

(g) Au_4/ZrO_2. The Bader charge distribution for the atoms of the Au_4 cluster on stoichiometric zirconia is not uniform. All atoms exhibit effective Bader charges of around +0.1 |e|, only the Au atom in the centre of the chain shows an effective Bader charge of around -0.3 |e|. This atom is not the one with the largest distance to the support.

(h) Au_4/Vo, surf, titania. For the cluster on the surface oxygen vacancy, all atoms exhibit a slightly negative Bader charge, with the largest modulus being -0.48 |e| on the atom which is inside the vacancy.

(i) Au_4/Vo, sub, titania. Is the gold cluster deposited on a subsurface oxygen vacancy, the charge distribution is similar to that of the cluster on the stoichiometric surface.

(j) Ag_4/N-doped titania surfaces. For Ag_4 on the N-doped titania surfaces, the positive charge is distributed over the cluster, for the surface dopant and the sub-surface dopant, respectively. Only the central atom always remains neutral.

(k) Ag_4/N-doped ziconia surfaces. Considering the Bader charges on the atoms of the silver and gold tetramers on N-doped zirconia, a relatively uniform distribution of the positive charge can be observed. For the silver tetramer on N-doped zirconia, effective Bader charges on Ag atoms are around +0.1 |e|, but the atom in the middle of the cluster, which is closest to the support has the largest modulus in charge (around +0.2 |e| in both cases, surface and sub-surface N-dopant).

(l) Au_4/N-doped titania surfaces. A different charge distribution can be observed for the gold tetramers. When the N-dopant is on the surface, all atoms exhibit an effective Bader charge of around +0.1 |e| and only the Au atoms that has 1 Au neighbour has a larger positive charge.

(m) Au_4/N-doped zirconia surfaces. For the Au tetramers, a different behaviour can be observed. Is the N-dopant on the surface, only the Au atom in direct contact with the N-atom is partly positively charged. All others exhibit values close to 0

|e| or even slightly negative (-0.13 |e|). Is the N-dopant at the subsurface, a more uniformly distributed positive charge is observed.

(n) Ag_4/Nb-doped titania surfaces. For both cases, surface and sub-surface Nb-dopant, the Bader charge distribution is similar to that of the cluster on the stoichiometric surface. This indicates the absence of charge transfer.

(o) Au_4/Nb-doped titania surfaces . The Bader charge distribution of the Au clusters is again similar to that of the Au tetramer on the stoichiometric surface, just as in the case of the silver tetramers.

(p) Ag and Au tetramers on Nb-doped zirconia surfaces: The charge density is more or less uniformly distributed within the clusters, as in the stoichiometric surface.

3.2 Pentamers on titania

The charge distribution on the pentamers on the investigated titania surfaces are all quite similar, because the pentamers are always positively charged. The distribution of the positive charge on the clusters according to the Bader charge analysis is as follows: For Au, the three atoms directly attached to the titania surfaces (defective or not) exhibit all a more or less uniform effective Bader charge of around +0.2 to +0.3 |e| and the others are more or less neutral. This distribution pattern can also be found in the trapeze form of the Ag pentamers, independently of the present and type of dopants.

3.3 Pentamers on zirconia

Considering the Bader charge distribution of the pentamers on the stoichiometric zirconia surface, we observe that for both, silver and gold, there is no significant polarization. The effective Bader charge is more or less 0 |e| for all atoms. For the pentamers deposited on the sub-surface vacancies, a marginal polarization of the silver pentamer can be observed: The atoms that point to the vacuum are slightly negatively charged (around -0.1 |e|) and the atoms in direct contact to the surface are slightly positively charged (less than +0.1 |e|). For the gold pentamer on the sub-surface vacancy, all atoms are slightly negatively charged, whereby the two atoms pointing to the vacuum exhibit a larger modulus in effective Bader charge (around -0.2 |e|). On N-doped zirconia, the pentamers become positively charged (see Table 8). The positive charge accumulates on the atoms that are in direct contact to the support. For Nb-doped zirconia, the pentamers exhibit a similar charge distribution as those on the

stoichiometric zirconia. Generally, atoms attached to the surface exhibit a more positive effective Bader charges as those pointing to the vacuum.