Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplemental Materials

Understanding Electronic and Optical Properties of Anatase TiO_2 Photocatalysts co-doped with Nitrogen and Transition Metals

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Table S1 Determination of Hubbard U parameters* used in the GGA+U method.

Metal	Metal oxides	Band gap (experimental)	Band gap (calculated)	Hubbard *U*
Sc	Sc_2O_3	5.9 eV	5.95	5.0
Ti	TiO_2	3.2 eV	3.30	8.2
V	V_2O_5	2.8 eV	2.85	4.5
Cr	Cr_2O_3	3.5 eV	3.46	12.0
Mn	MnO_2	0.25 eV	0.27	9.0
Fe	Fe_2O_3	2.2 eV	2.17	6.8
Co	CoO	2.6 eV	2.57	10.1
Ni	NiO	3.5 eV	3.49	10.0
Cu	CuO	1.7 eV	1.64	6.7
Zn	ZnO	3.2 eV	3.22	8.0[1]
Y	Y_2O_3	5.6 eV	5.58	6.7
Nb	Nb_2O_5	3.4 eV	3.44	8.0
Zr	ZrO_2	5.0 eV	5.00	8.8
Mo	MoO_3	3.8 eV	3.77	7.5
Cd	CdO	2.2 eV	2.28	2.0[1]

*The band gap of metal oxides of the corresponding doped transition metals were calculated by using different U value ranging from 1eV~15 eV.

Table S2 Spin states of doped transition metals in the calculations

Systems \ Spin / Energy* (eV)	Singlet	Doublet	Triplet	Quadruplet	Quintet
Sc, N	0.338		0.000		
V, N	0.000		0.000		
Cr, N		0.000		0.000	
Mn, N	0.000		0.004		0.001
Fe, N		0.000		0.001	
Co, N	0.000		0.358		
Ni, N		0.000		0.226	
Cu, N	0.000		0.000		
Zn, N		0.000		10.139	
Y, N	0.000		0.030		
Zr, N		0.000		0.000	
Nb, N	0.000		0.020		
Mo, N		0.000		0.003	
Cd, N	0.338		0.000		

*The lowest energy was set as zero in each co-doped system.

Table S3 Ionic radius (pm) of transition metal considered in this work.[2]

Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{3+}	Mn^{4+}	Fe^{3+}	Co^{2+}	Ni^{4+}	Cu^{2+}	Zn^{2+}	Zn^{2+}
88.5	74.5	72	75.5	67	69	79	62	87	74*	88**
Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{3+}	#Mn^{4+}	#Fe^{3+}	#Co^{2+}			Cd^{2+}	Cd^{2+}
104	86	78	83	78.5	78.5	88.5			92*	109**

*The radius of the 4-coordinated Zn (Cd) atom.

**This radius of the 6-coordinated Zn (Cd) atom.

#Ionic radius (pm) of doped transition metal with high spin state.

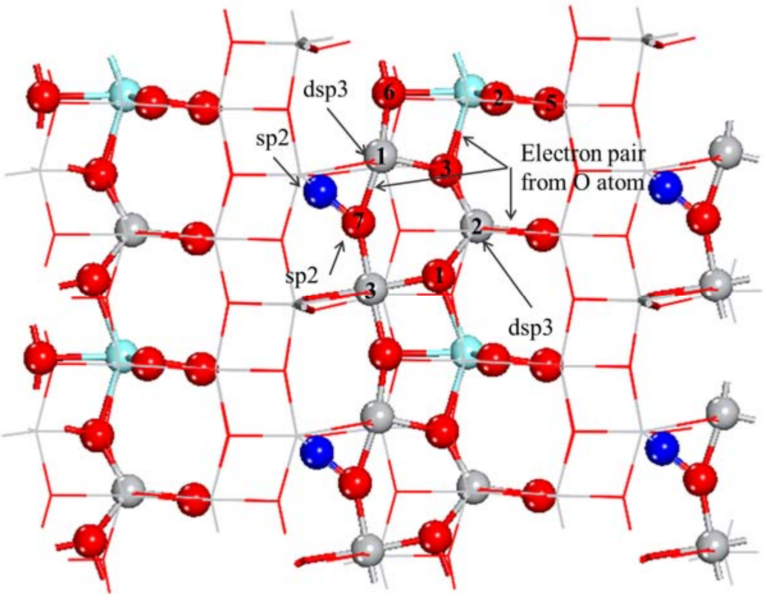

Fig. S1 Local electronic structure of (Y, N) co-doped TiO_2, the nattier blue ball is Y atom.

Compare with (Sc, N) co-doped system, no IELs were found in the gap region of (Y, N) system. Mulliken population analysis indicates that the population of N-Ti_1 bond that connects the O-Y bond has decreased from 0.27 (in the N-doped system) to 0.02, indicating the cleavage of this N-Ti_1 bond. Different from the (Sc, N) co-doped system; the N atom is in a planar triangle structure with the two N-Ti bonds and one newly formed N-O_7 bond, indicating a *sp2* hybridization. In this N atom, 3 electrons fill in the bonding orbitals and the other 2 electrons fill in the non-bonding p_z orbitals. The O_7 atom also shows a sp^2 hybridization, two electrons filled in the N-O_7 and O_7-Ti_3 bonding orbitals, the other 2 electrons filled in the O_7-Ti_1 bonding orbital. Meanwhile, the Ti_1 atom is five coordinated, indicating a dsp^3 hybridization. As such, four electrons filled in four bonding orbitals with the last bonding orbitals being filled by the lone pair from the O_7 atom. The same situation was also observed in Ti_2 atom, with the electron pair from O_8 filled in the O_8-Ti_2 bonding orbital. In turn, the bonding orbital of O_3-Ti_1 and O_3-Ti_2 are filled by one Ti electron and one O electron, which means the O_3-Y bonding orbitals are filled by the electron pair that comes from O_3 atom. Thus, the situation of the six O-Y bonds surrounded the Y atoms is clarified, three of them are formed by electrons come from Y and O (Y-O_2, Y-O_4, Y-O_6; see Table 3); the other three are formed by electron pairs come from O atoms (Y-O_1, Y-O_3, and Y-O_5).

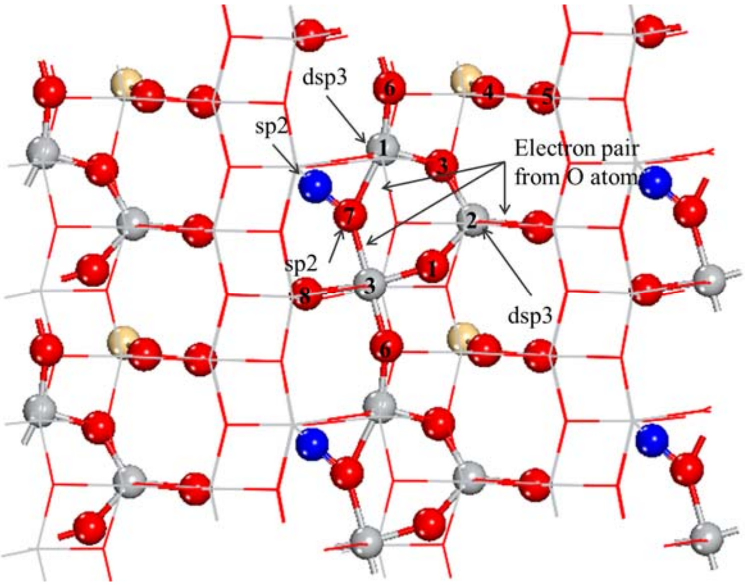

Fig. S2 Local electronic structure of (Cd, N) co-doped TiO_2, the gold ball is Cd atom.

For (Cd, N) co-doped TiO_2, the Mulliken population analysis indicates that Cd only binds the two O atoms (Cd-O_2 and Cd-O_4, Table 3) through a *sp* hybridization. Thus, the O_1, O_3, O_5 and O_6 atoms all show sp^2 hybridization, with two electrons filling in two O-Ti bonding orbitals. The other two electron pairs are retained on the atom, which can act as an electron donor.

Similar to the (Y, N) co-doped system, the Ti_1 atom is five coordinated, showing a dsp^3 hybridization, with 4 electrons filling in four bonding orbitals and the electron pair coming from the O_7 atom fill in the last bonding orbital. Meanwhile, the Ti_3 atom is six coordinated, 4 electrons filled in four bonding orbitals, and the last two bonding orbitals are filled by the electron pair that comes from the O_7 and O_8 atoms. Thus, the electrons for the N-O_7 bonding orbital are the lone electron pair from N atom. Consequently, we confirmed that the valence electrons of N atom in this structure show *sp2* hybridization, only one electron filled in the p_z orbital of N. Thus, in the orbital analysis, the IELs located in the gap region of (Cd, N) co-doped system shows N p_z feature (see Fig. 6).

Large version of the band structure, orbital analysis and DOS results of the co-doped TiO_2

(Sc, N)

Reference

(1) Bai, L. N.; Zheng, B. J.; Lian, J. S.; Jiang, Q. *Solid State Sci.* **2012**, *14*, 698.

(2) Winter, M. J.; The University of Sheffield and WebElements Ltd, UK: 1993-2012.