Supporting information: Presence of gap states at Cu/TiO_2 anatase surfaces: consequences for the photocatalytic activity.

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Supporting information.

In the Supporting Information, further details of the atomic structures and the electronic density of states of the copper clusters supported on titania are shown.

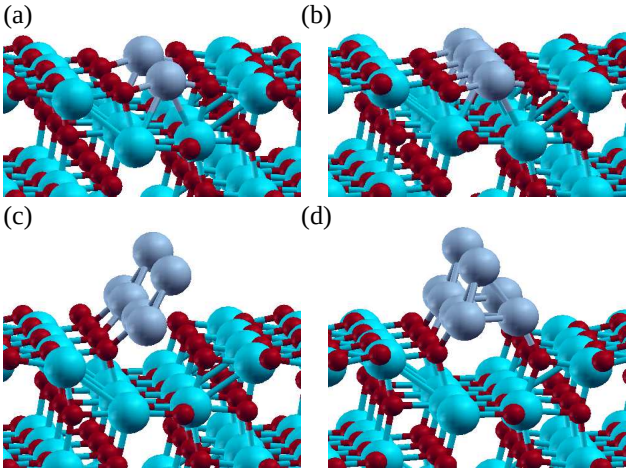

Figure 1: Atomic structure of the stable clusters with 1-4 Cu atoms on the defect-free surface of anatase TiO_2(100). Blue balls: titanium; red balls: oxygen; grey balls: copper.

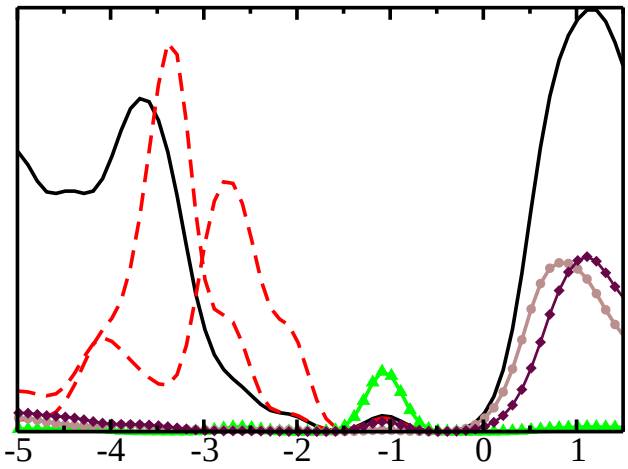

Figure 2: Density of states (DOS) for the majority spins of the stable cluster with 2 Cu atoms on the surface of anatase TiO_2(101), calculated with DFT+U. Solid line: total DOS; red dashed line: Cu-3d states; green solid line with triangles: 4s states of the Cu atom with a Cu-Ti bond; brown solid line with circles: Ti3d states of a six-fold coordinated Ti atom in the vicinity if the Cu cluster (see text); dark brown solid line with diamonds: Ti3d states of a five-fold coordinated Ti atom with a direct Cu-Ti bond. The projections on the single states have been multiplied by 10 to put them on the same scale as the total DOS. The zero of energy has been set to the Fermi energy.

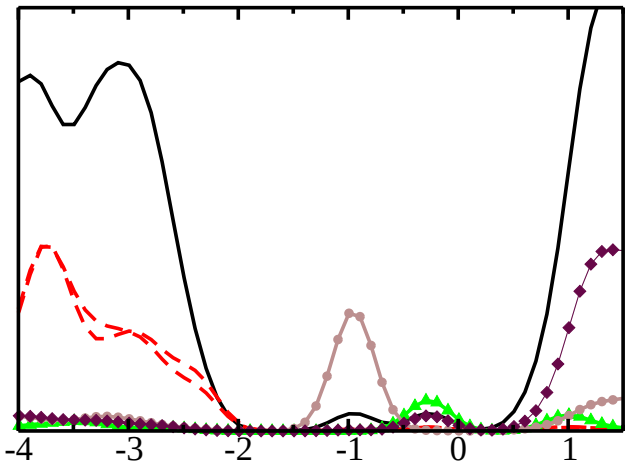

Figure 3: Density of states (DOS) for the majority spins of the stable cluster with 4 Cu atoms on the surface of anatase TiO_2(101), calculated with DFT+U. Solid line: total DOS; red dashed line: Cu-3d states; green solid line with triangles: 4s states of the Cu atom with a Cu-Ti bond; brown solid line with circles: Ti-3d states of a six-fold coordinated Ti atom in the vicinity if the Cu cluster (see text); dark brown solid line with diamonds: Ti-3d states of a five-fold coordinated Ti atom with a direct Cu-Ti bond. The projections on the single states have been multiplied by 10 to put them on the same scale as the total DOS. The zero of energy has been set to the Fermi energy.

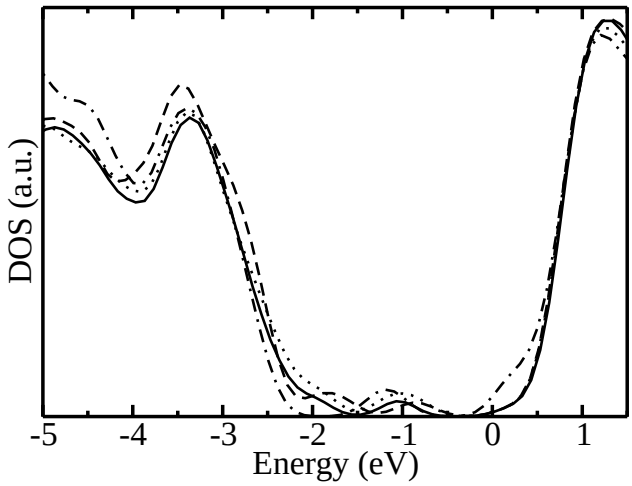

Figure 4: Density of states for the majority spin of the stable clusters with 1-4 Cu atoms on the surface of anatase $TiO_2(100)$, calculated with DFT+U. Solid line: adatom; dotted line: dimer; dashed line: trimer; dot-dashed line: tetramer. The zero of energy has been set to the Fermi energy.