Mechanism of photocatalytic activities in Cr-doped $SrTiO_3$ under visible-light irradiation: an insight from hybrid density-functional calculations

(Supplementary information)

Pakpoom Reunchan,[a] Naoto Umezawa,*[a,b], Shuxin Ouyang,[a] and Jinhua Ye[a,c]

[a] *The Research Unit for Environmental Remediation Materials, National Institute for Materials Sciences, Ibaraki 305-0047, Japan*

[b] *PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*

[c] *International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Sciences, Ibaraki 305-0047, Japan*

Email: umezawa.naoto@nims.go.jp

A. Density of states (DOS) for Cr_{Ti}

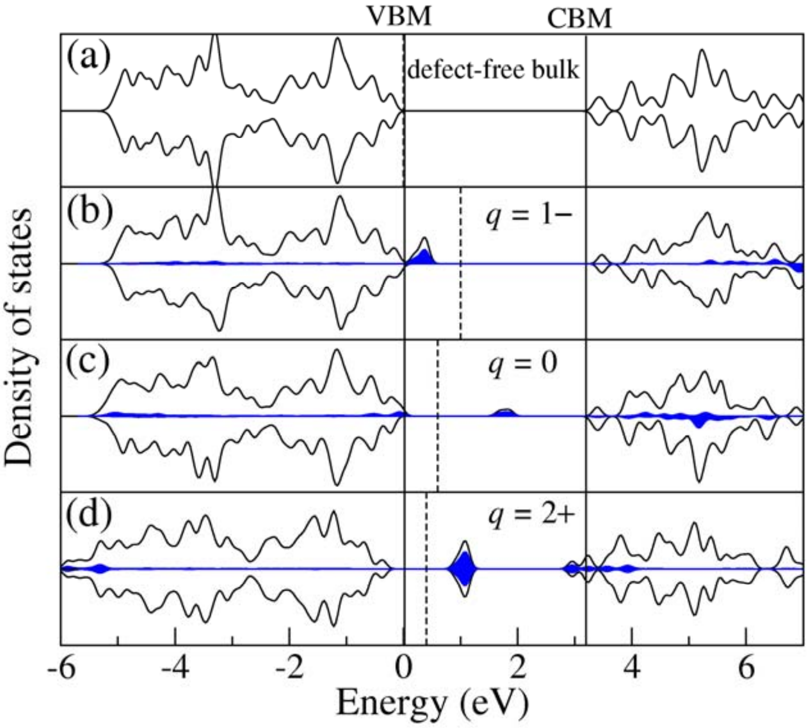

Figure S1. Spin-polarized DOS for $SrTiO_3$ 40-atom supercell with a Cr substituted Ti (Cr_{Ti}). The unfilled curve in each panel is the total DOS whereas the filled curve is the DOS projected to Cr *d* state using a sphere of radius of 1.164 Å. The DOS of supercell with a Cr defect is aligned with that of defect-free supercell using the position of Sr 4*s* state which is localized in the valence band. The top to the bottom panels are shown for (a) defect-free supercell, (b) Cr_{Ti}^{-}, (c) Cr_{Ti}^{0}, and (d) Cr_{Ti}^{2+}, respectively. The Fermi level for each charge state is shown as a dashed vertical line.

The in-gap states introduced by $\mathrm{Cr}_{\mathrm{Ti}}^{-}$ and $\mathrm{Cr}_{\mathrm{Ti}}^{0}$ are only found in the majority spin channel, associating with the high-spin state of $\mathrm{Cr}_{\mathrm{Ti}}$. The Cr *d* states split into lower-lying t_{2g}-derived states (t'_{2g}) and higher-lying e_g-derived states (e'_g) by the octahedral crystal field. In neutral charge state, the t'_{2g} states are occupied by two electrons and subsequently split into an empty state in the upper part in the gap (Figure S1(c)) and the two occupied states resonant in the valence band. In 1– charge state, an additional electron is added to the empty state, resulting in three-fold degenerate fully occupied t'_{2g} states located above the VBM (Figure S1(b)). Therefore, the three electrons can be removed from these states when the Fermi level lies near the VBM, resulting in $\mathrm{Cr}_{\mathrm{Ti}}^{2+}$ with the empty t'_{2g} states located in the lower part of the gap (Figure S1(d)).

B. Interstitial Chromium (Cr_i)

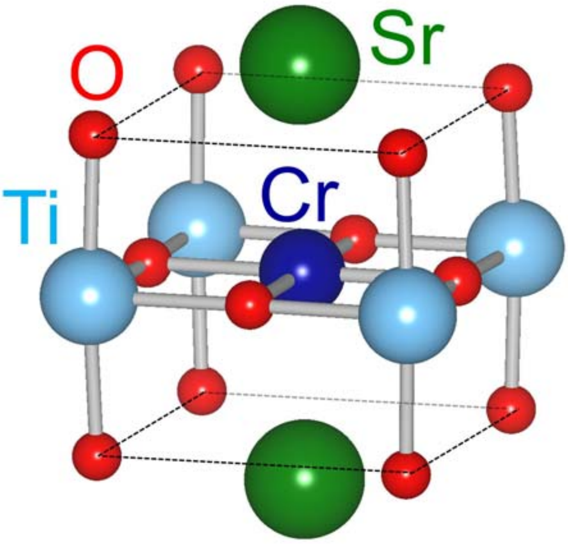

Figure S2. The relaxed local atomic structure for the Cr_i.

Based on calculated formation energy we find that Cr atom prefers to occupy the interstitial site located between the Sr-Sr neighboring atoms (Cr_i) (see Figure S2) rather than between the Sr-Ti neighboring. Cr_i is found to occur in 4+, 2+, 1+ and neutral charge state with the transition levels $\varepsilon(4+/2+) =$ 0.56 eV, $\varepsilon(2+/1+) =$ 2.78 eV, and $\varepsilon(2+/1+)$ = 2.96 eV. Hence, Cr_i is a donor defect which can also predominate in a *p*-type condition under the chemical potential either O-poor or $\mu = \mu_{\mathrm{Cr/Sr}}$ (Figure 3(a) and 3(b)). The importance of Cr_i lies in the fact that it becomes a compensating defect for $\mathrm{Cr}_{\mathrm{Ti}}^{-}$ when O vacancies (V_{O}) fail acting as a good donor for some reason. In such a case, charge balance occurs between Cr_i^{2+} and $\mathrm{Cr}_{\mathrm{Ti}}^{-}$, which results in the formation of Cr_i^{2+} as well as $\mathrm{Cr}_{\mathrm{Ti}}^{-}$ in the same order of concentration. We found that Cr_{i}^{2+} gives rise to occupied t_{2g} states comparable to those in $\mathrm{Cr}_{\mathrm{Ti}}^{-}$ and photoabsorption properties of these two defects are expected to be qualitatively similar. In fact, our calculated migration barrier for Cr_{i}^{2+} is about 1.7 eV, which is more than twice of that of neutral V_{O} reported in ref. S1. Thus, Cr_{i} is less mobile than V_{O}, indicating Cr_{i} can be a better donor in relatively higher temperature.

C. Transition initiated at $\mathrm{Cr}_{\mathrm{Ti}}^{0}$

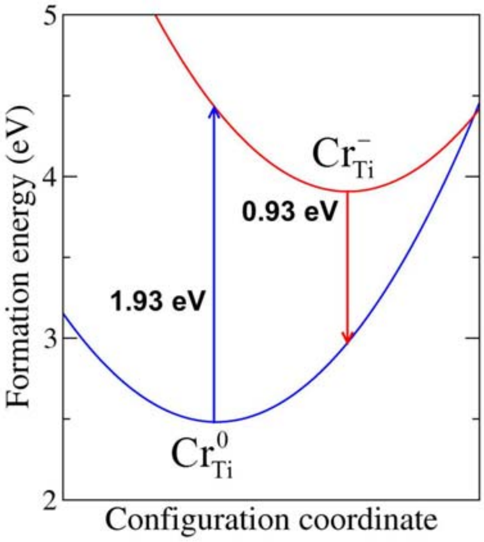

Figure S3. Configuration coordinate diagram for illustrating $\mathrm{Cr}_{\mathrm{Ti}}^{0} + h\nu \rightarrow \mathrm{Cr}_{\mathrm{Ti}}^{-} + h^{+}$ transition. The formation energy corresponds to the O-poor condition and to ε_F at the VBM.

The transition occurs through the absorption of a photon by $\mathrm{Cr}_{\mathrm{Ti}}^{0}$, converting to $\mathrm{Cr}_{\mathrm{Ti}}^{-}$ with a hole in the VB. The absorption energy, derived from $E^{f}(\mathrm{Cr}_{\mathrm{Ti}}^{-};\mathrm{Cr}_{\mathrm{Ti}}^{0}) - E^{f}(\mathrm{Cr}_{\mathrm{Ti}}^{0};\mathrm{Cr}_{\mathrm{Ti}}^{0})$, was found to be 1.93 eV which is in the visible region. The emission energy of 0.93 eV is derived from $E^{f}(\mathrm{Cr}_{\mathrm{Ti}}^{-};\mathrm{Cr}_{\mathrm{Ti}}^{-}) - E^{f}(\mathrm{Cr}_{\mathrm{Ti}}^{0};\mathrm{Cr}_{\mathrm{Ti}}^{-}) = 0.93$ eV.

References

S1. R. A. Evarestov, E. A. Kotomin and Y. F. Zhukovskii, Int. J. Quantum Chem. **106**, 2173 (2006).