Supplementary Information for

Theoretical Design of Highly Active $SrTiO_3$–based Photocatalysts from Co-doping Scheme toward Solar Energy Utilization for Hydrogen Production

A. Experimental details

1. Sample synthesis

The codoped $SrTiO_3$ samples were synthesized by a solid-state reaction. The starting materials TiO_2 (99.9%), $SrCO_3$ (99.9%), Cr_2O_3 (99.9%), La_2O_3 (99.99%), Y_2O_3 (99.9%), Sb_2O_5 (99.9%), Nb_2O_5 (99.9%) were weighed according to the stoichiometric ratio of $Sr_{0.95}La_{0.05}Ti_{0.95}Cr_{0.05}O_3$, $Sr_{0.95}Y_{0.05}Ti_{0.95}Cr_{0.05}O_3$, $Sr_{1.00}Ti_{0.90}Cr_{0.05}Sb_{0.05}O_3$, and $Sr_{1.00}Ti_{0.90}Cr_{0.05}Nb_{0.05}O_3$, and then ground for 0.5 h in mortar. After that, the mixtures were sintered at 1150 -1200 ℃ for 24 h. Finally, the sintered products were ground and ready for further characterizations.

2. Experiment details for the photocatalytic activity for H_2 evolution

To load Pt co-catalyst on the codoped $SrTiO_3$ samples, some amount of H_2PtCl_6 aqueous solution (equaling to 0.5 wt% of catalyst) was mixed with the codoped $SrTiO_3$ sample and the mixture was ground until becoming dry. Then the mixture was calcined at 400 ℃ for 2 h. After that, the photocatalytic H_2 evolution was carried out with 0.3 g photocatalyst suspending in 270 ml CH_3OH solution (50 ml CH_3OH and 220 ml H_2O) in a Pyrex glass reaction cell. The reaction cell was connected to a gas-closed system with a gas-circulated pump. A 300-W Xe arc lamp was employed for the light source of photocatalytic reaction. During the visible-light reaction, a L42 cutoff filter was used to remove UV light ($\lambda > 400$ nm). The evolved H_2 was analyzed by an online gas chromatograph (GC-8A; Shimadzu Corp., Japan) equipped with a thermal conductivity detector.

3. Experiment details for the X-ray photoelectron spectroscopy (XPS) and UV-visible absorption spectra measurements.

XPS experiments were performed in type Theta probe (Thermo Fisher) using monochromatized Al Kα at hυ = 1486.6 eV. Peak positions were internally referenced to the C_{1s} peak at 284.6 eV. The diffuse reflectance spectra of the samples were recorded on a UV-visible spectrophotometer (UV-2500PC; Shimadzu Corp., Japan) with barium sulfate as the reference. Then the absorption spectra were obtained from the reflectance spectra by means of Kubelka–Munk transformations.

B. Optical absorption of the codoped $SrTiO_3$ samples

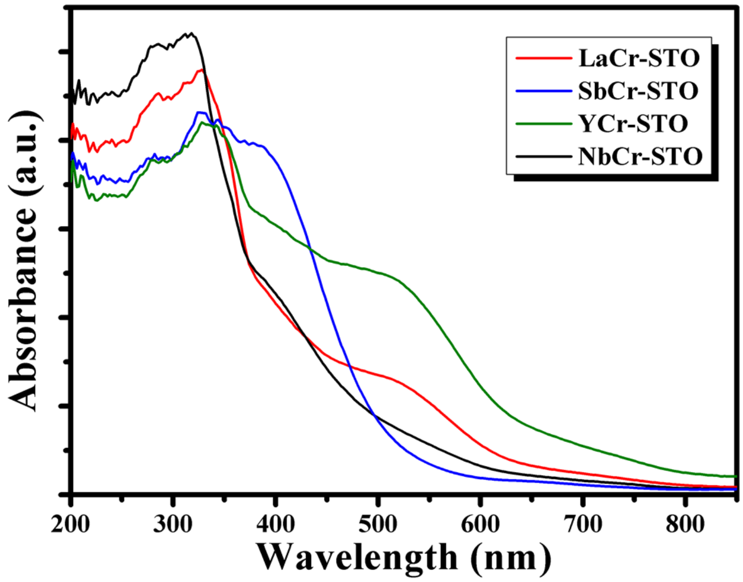

Figure S1 UV-visible absorption spectra of as-prepared samples. All samples showed visible light absorption.

C. The density of states (DOS) obtained by hybrid-density functional calculations

1. Density of states of Cr_{Ti} in the negatively charged state

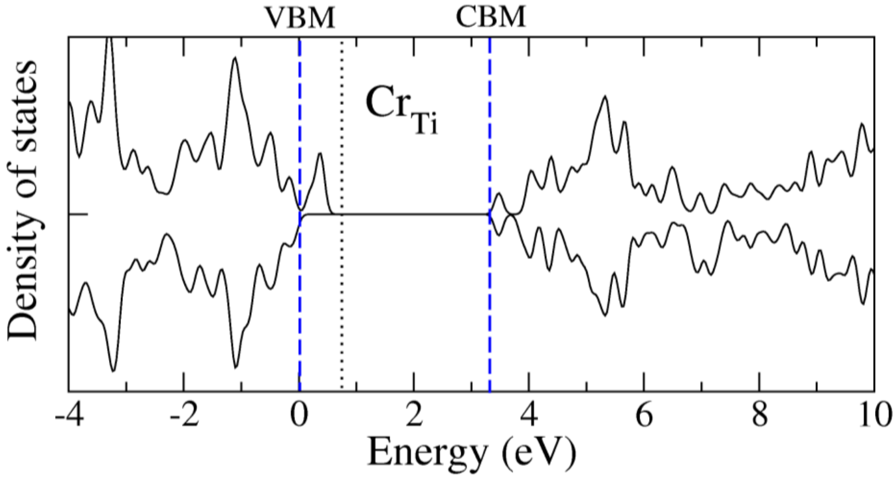

Figure S2 Spin-polarized total density of states for $SrTiO_3$ 40-atom supercell with a Cr substituted for Ti in the negative charge state. The DOS of supercell with Cr defect is aligned with that of defect-free supercell using the position of Sr 4*s* which is localized in the valence band. The vertical broken lines corresponds to the valence band maximum (VBM) and the conduction band minimum (CBM) of the defect-free supercell. The highest occupied state of the electron is shown as the vertical dotted line.

2. Density of states of the codopant donor-type defect in the positive charged state

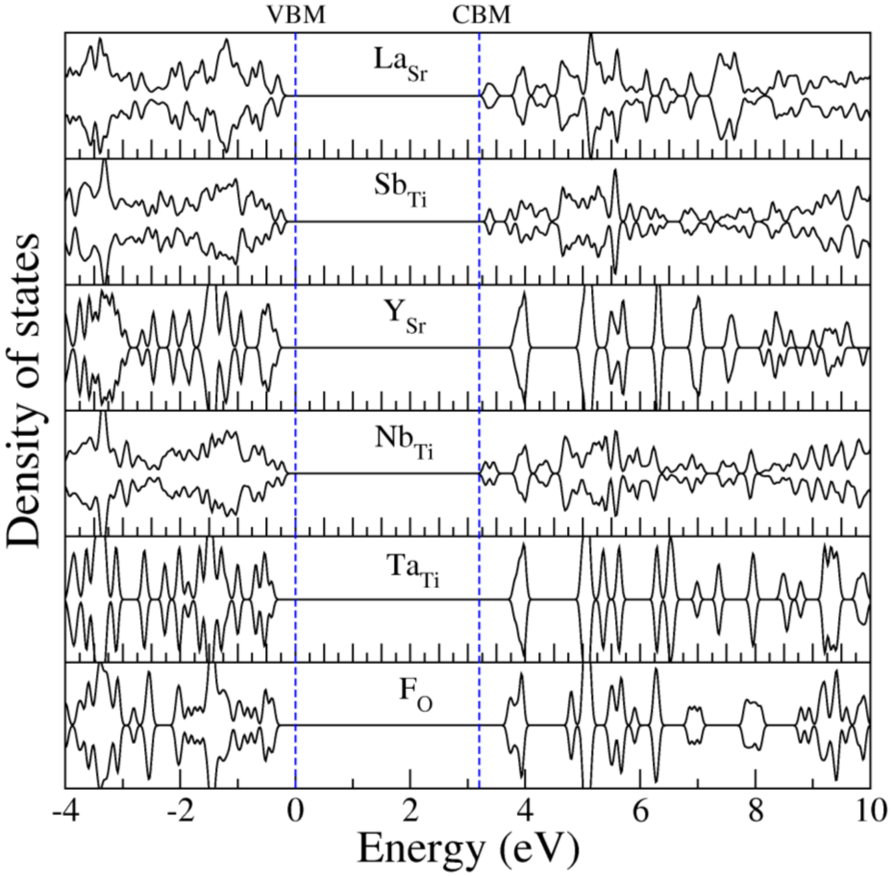

Figure S3 Spin-polarized total density of states for $SrTiO_3$ 40-atom supercell with a donor-type codopant defect in the positive charge state. The DOS of supercell with a donor-type codopant defect is aligned with that of defect-free supercell using the position of Sr 4*s* which is localized in the valence band. The top to the bottom panels show the DOS for La_{Sr}, Sb_{Ti}, Y_{Sr}, Nb_{Ti}, Ta_{Ti}, and F_O respectively. The vertical broken lines corresponds to the valence band maximum (VBM) and the conduction band minimum (CBM) of the defect-free supercell. The highest occupied state is at the VBM. This shows that the codopant does not induce any defect levels in the band gap of codoped $SrTiO_3$.