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**Bandgap narrowing of TiO<sub>2</sub> via codoping for enhanced photocatalytic reactions<sup>1</sup>**

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We investigated the growth of Cr–N codoped single-crystal anatase TiO<sub>2</sub>(001) (A-TiO<sub>2</sub>) thin films using pulsed laser deposition with a target of Cr<sub>2</sub>O<sub>3</sub> and TiN mixture. N concentrations were finely tuned under different growth temperatures and oxygen pressures, and high quality films with atomically flat terraces were obtained. UV–Vis absorption measurements showed that the band-gap of the codoped A-TiO<sub>2</sub> film is significantly narrowed in comparison with the undoped and mono-element doped films. We further systematically investigated the structures and the activity of the oxidized and reduced (1 × 4) reconstructed surfaces of A-TiO<sub>2</sub> epitaxially grown on SrTiO<sub>3</sub> using scanning tunneling microscopy/spectroscopy, X-ray/ultraviolet photoemission spectroscopy and first-principles calculations. Quite unexpectedly, it is found that the perfect (1 × 4) surface of A-TiO<sub>2</sub> is not even active for H<sub>2</sub>O and O<sub>2</sub> adsorption at room temperature. Two types of intrinsic point defects are identified, among which only the Ti<sup>3+</sup> defect site on the reduced surface demonstrates considerable activity for H<sub>2</sub>O and O<sub>2</sub> adsorption. The perfect surface itself should be fully oxidized, but shows no obvious activity. We thus propose an oxidized ridge model for the reconstructed (1 × 4) surface, where the Ti atoms at the normal ridge sites are sixfold coordinated. The Ti-rich point defects on reduced surface are fourfold-coordinated. This model provides consistent explanations for our experimental observations. We have compared the results with those from rutile TiO<sub>2</sub>(001)-(1 × 1) surface in our investigations. Our findings suggest that the activity of the A-TiO<sub>2</sub> surface should depend on its reduction status, similar to that of rutile TiO<sub>2</sub> surfaces.

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