

Supporting Information

Iodine Doped Anatase TiO₂ Photocatalyst with Ultra-long Visible Light Response Range: Correlation between Geometric/Electronic Structures and Mechanisms.

Gang Liu,^{†a,b} Chenghua Sun,^{† b,c} Xiaoxia Yan,^c Lina Cheng,^c Zhigang Chen,^a Xuwen Wang,^a Lianzhou Wang,^b Sean C. Smith,^{*c} Gao Qing (Max) Lu^{*b} and Hui-Ming Cheng^{*a}

^aShenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua RD, Shenyang 110016, P. R. China
E-mail: cheng@imr.ac.cn (H. M. Cheng)

^bARC Centre of Excellence for Functional Nanomaterials, The University of Queensland Qld. 4072, Australia
E-mail: maxlu@uq.edu.au (G. Q. Max Lu)

^cCentre for Computational Molecular Science, Australia Institute for Bioengineering and Nanotechnology, The University of Queensland, Qld. 4072, Australia
E-mail: s.smith@uq.edu.au (S. C. Smith)

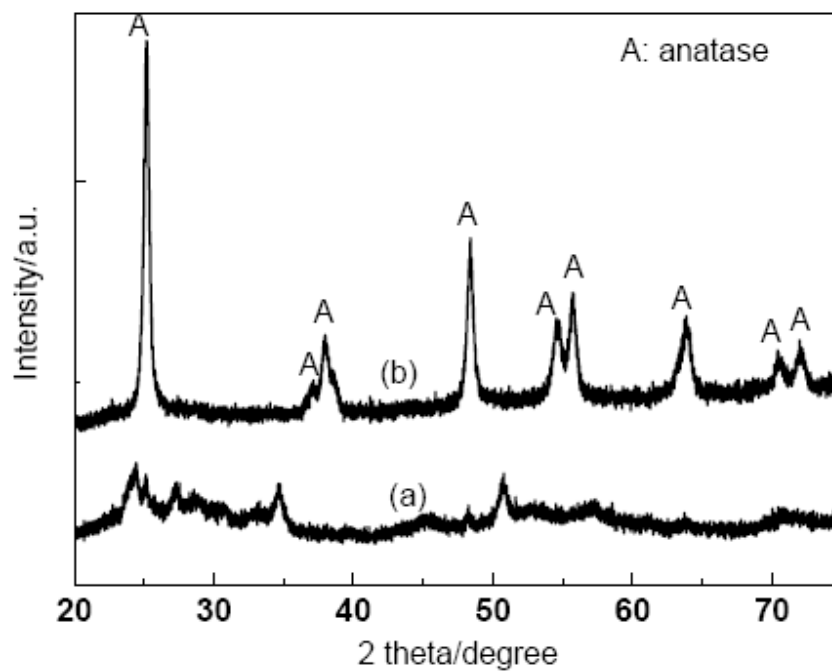
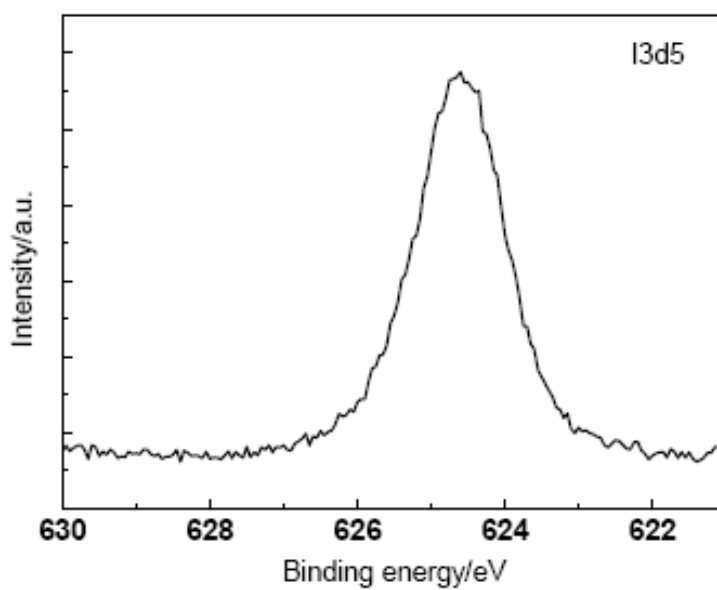
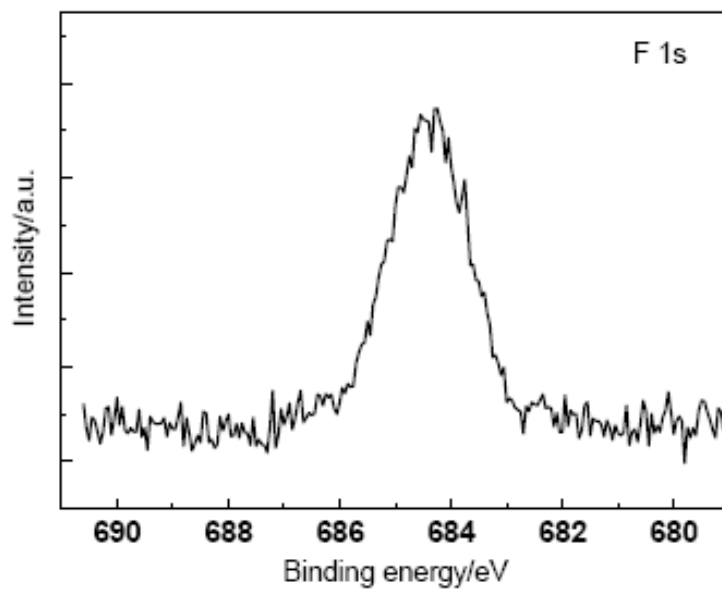


Fig. S1 XRD patterns of the intermediate compound (a) directly collected after hydrothermal process and the resultant iodine doped TiO₂ (b) by calcining (a) in air at 400 °C for 2 hrs.



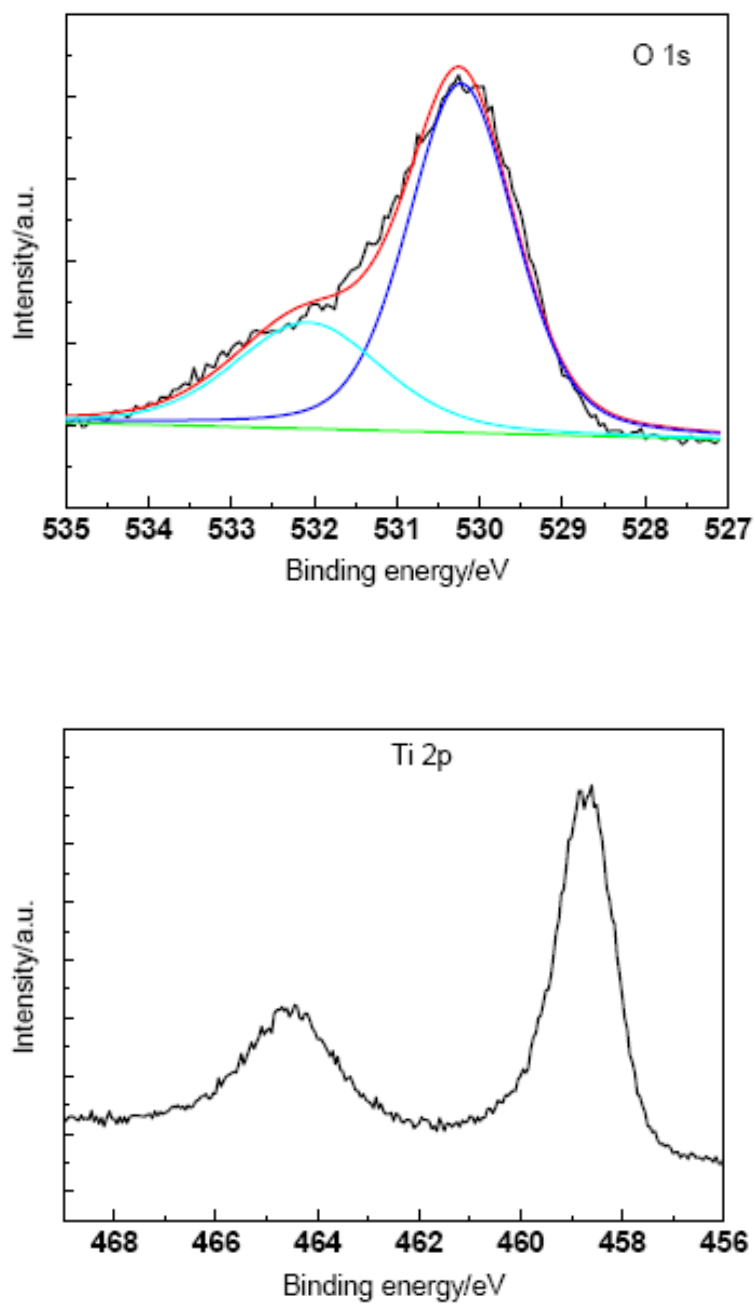


Fig. S2. High resolution XPS spectra of F 1s, I 3d₅, Ti 2p and O 1s of the intermediate compound.

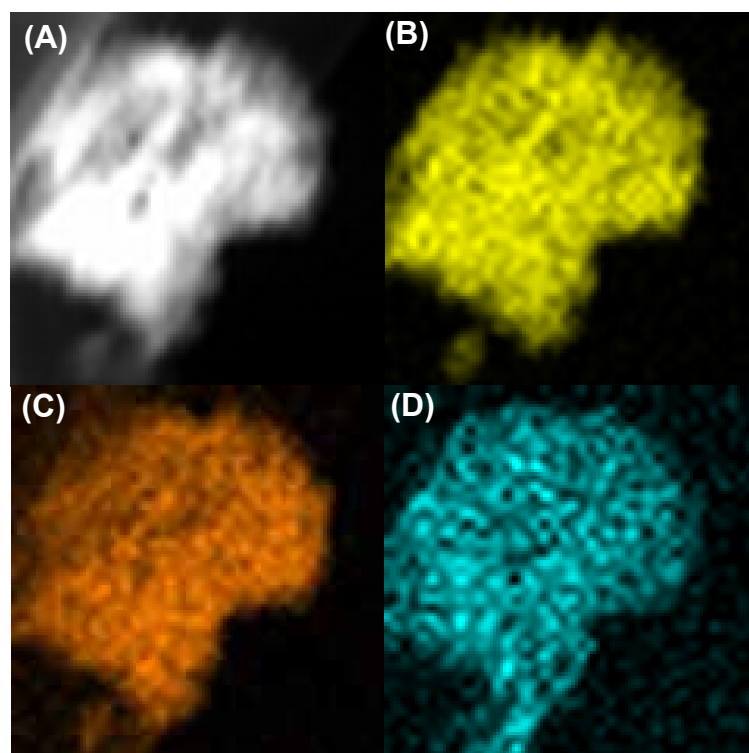


Fig. S3 Energy filtered TEM images of general morphologies (A), Ti (B), O (C) and I (D) elemental maps of the iodine doped titania prepared.

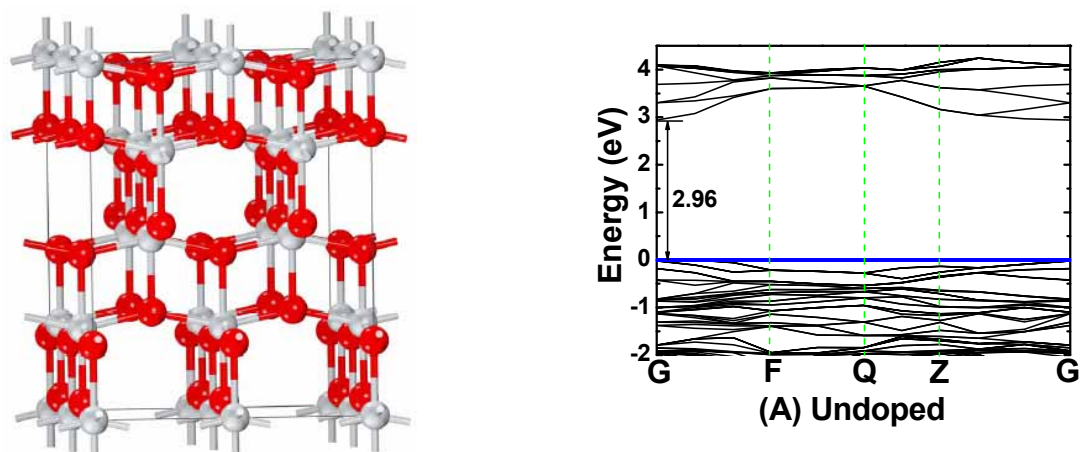


Fig. S4 Structural models and calculated energy band structure (A) for the supercell $\text{Ti}_{16}\text{O}_{32}$. Oxygen and titanium are indicated by red and white, respectively.

To investigate the effect resulted by surface doping, undoped (101) was studied firstly as the reference. From the optimized structure shown in Fig. S5-(A), no significant structural distortion is found, suggesting that the clean (101) is very stable, consistent with early experimental and theoretical reports. [42,43] As to electronic structures, except that the band gap increases from 2.96 eV to 3.09 eV due to the blue shift, no essential difference from the bulk case is found according to the calculated energy band structures and DOS of undoped (101), as shown in Fig. S5-(B). In particular, no interband state is shown between VB and CB for the undoped (101), and the position of the VB does not shift either upwards or downwards. Based on the local DOS, it is clear that both VB and CB are contributed by mixed Ti_{3d} and O_{2p} , which is also similar to the bulk structure. Therefore, the cleavage of the (101) surface does not result in obvious changes with respect to the bulk TiO_2 .

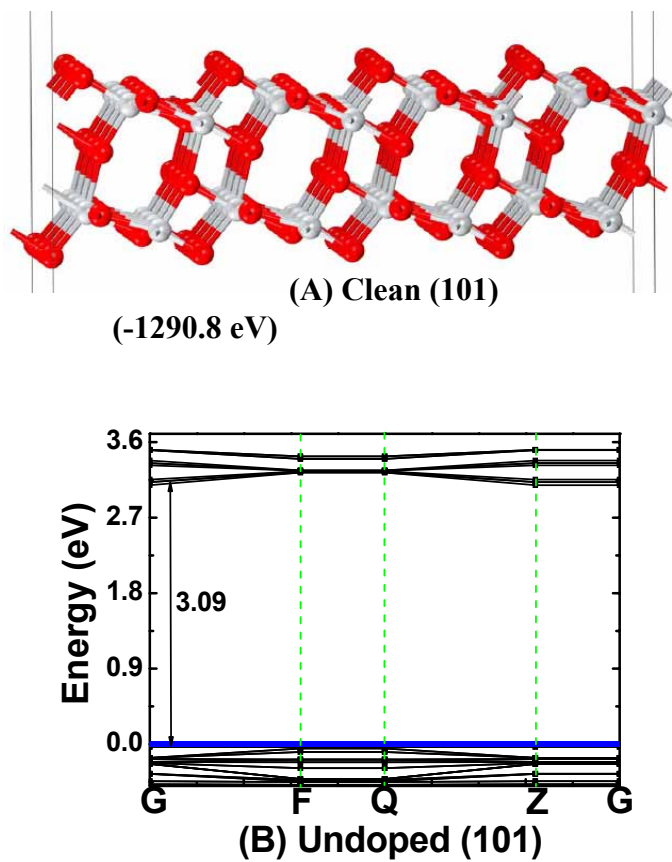


Fig. S5 Structural models (A) and calculated energy band structures (B) of undoped (101) TiO₂ surface. Oxygen and titanium atoms are indicated by red and grey spheres, respectively. The numbers listed in the parentheses are the calculated binding energies.