Supporting Information for Publication

The Origin of Enhanced Photocatalytic Activities of Hydrogenated TiO_2 nanoparticles

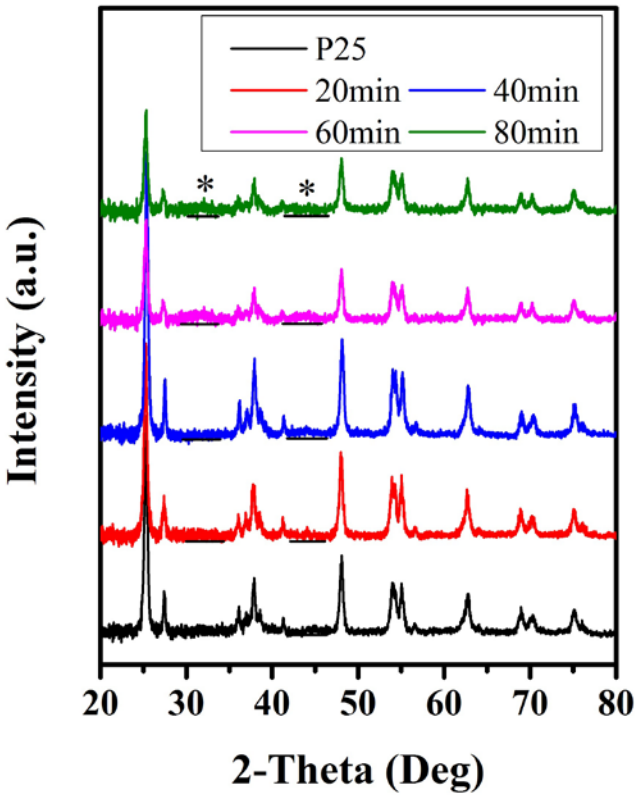

Figure. S1 XRD patterns of the pristine P25 TiO_2 and hydrogenated TiO_2 treated at 300 ^oC for 20 min, 40 min, 60 min and 80 min, respectively.

X-ray diffraction (XRD) patterns were recorded on a diffractometer (Bruker AXS D8 Focus) using Cu Ka radiation at 45 kV and 250 mA and scan rate of $0.15°s^{-1}$. The pattern exhibits intense diffraction peaks at 2θ=25.22°, 27.32°, 36.2°, 37.9°, 47.80°, and so on, most peaks are in good agreement with the standard spectrum of TiO_2 (JCPDS 21-1272 and JCPDS 21-1276), corresponding to the diffractions from the (101), (004), (200) crystal planes of anatase TiO_2 and (110), (101) crystal planes of rutile TiO_2， respectively. As the peak intensity weakens and half-maximum (FWHM)

broadens, the nanocrystal size and crystalline degree of both the anatase and rutile decrease with the hydrogenated time extension.

And two new peaks (marked with * in Fig. S1) are also observed for longer reaction time, indicating that a new crystalline phase may have been formed. These new diffraction peaks cannot be matched to a known phase in the Powder Diffraction File (PDF) database. We agree with Sun et al.[1] that these new peaks could be attributed to a mixture of several reduced titanium oxides such as Ti_9O_{17}, Ti_8O_{15}, Ti_3O_5, which means that oxygen vacancy was produced on the surface of TiO_2 nanocrystals through the chemical reduction treatment.

Fig. S2

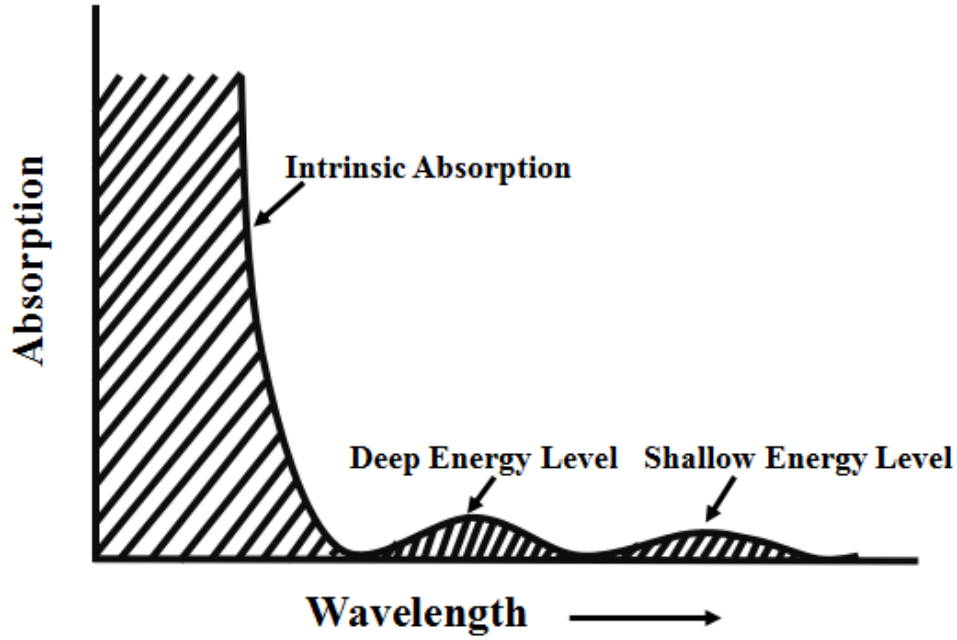

Figure. S2 Schematic diagram of impurity absorption.[2]

Impurity absorption is caused by the deep and shallow energy levels in the midgap of semiconductor, which can raise the visible light absorption intensity. Generally, they do not narrow the bandgap or shift the absorption edge.

Fig. S3

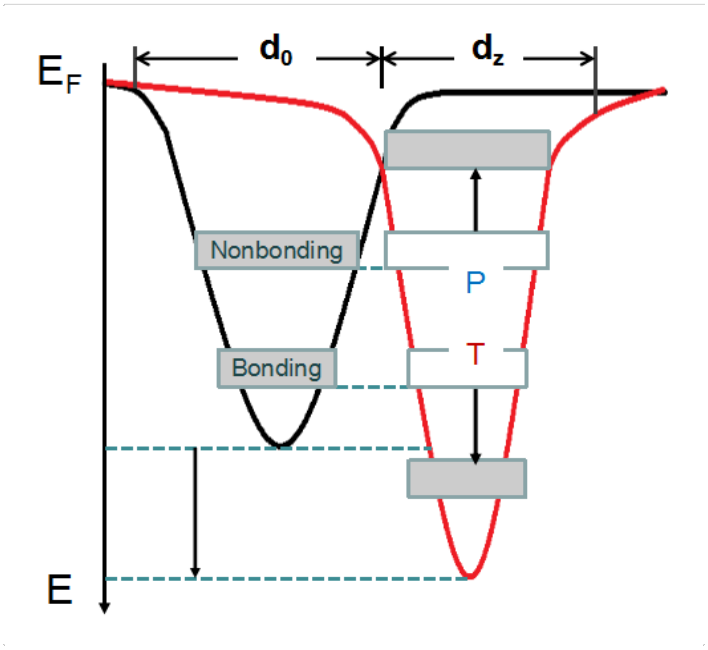

Figure. S3 Schematic diamatic of BOLS-NEP notation.

BOLS-NEP notation indicates that atomic undercoordination shortens the local bond ($d_z < d_0$) and deepens the local potential well that densifies and entraps the bonding electrons (T). The densely entrapped electrons polarize the nonbonding electrons to form the polarized states (P) shifting up. The polarized states will screen and split the local potential, which will add polarized states to the core band unless the core band is too deep to be sensitive to the polarization.[3]

References

1 H. Tan, Z. Zhao, M. Niu, C. Mao, D. Cao, D. Cheng, P. Feng and Z. Sun, *Nanoscale*, 2014, 6(17), 10216-10223.

2 K. Huang and X. Xie, (1958), *Semiconductor Physics* (1st ed.). Beijing: Science Press P349.

3 L. Li, H. W. Tian, F. L. Meng, X. Y. Hu, W. T. Zheng and C. Q. Sun, *Applied Surface Science*, 2014, 317, 568-572.