

## Electronic Supplementary Information (ESI)

# Three-Dimensional Ruthenium-Doped TiO<sub>2</sub> Sea Urchins for Enhanced Visible-Light-Responsive H<sub>2</sub> Production†

Thuy-Duong Nguyen Phan,<sup>a</sup> Si Luo,<sup>a,b</sup> Dimitriy Vovchok,<sup>a,b</sup> Jordi Llorca,<sup>c</sup> Shawn Sallis,<sup>d</sup> Shyam Kattel,<sup>a</sup> Wenqian Xu,<sup>e</sup> Louis F. J. Piper,<sup>d</sup> Dmitry E. Polyansky,<sup>a</sup> Sanjaya D. Senanayake,<sup>a</sup> Dario J. Stacchiola<sup>a\*</sup> and José A.

Rodriguez<sup>a,b\*</sup>

<sup>a</sup> Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, US

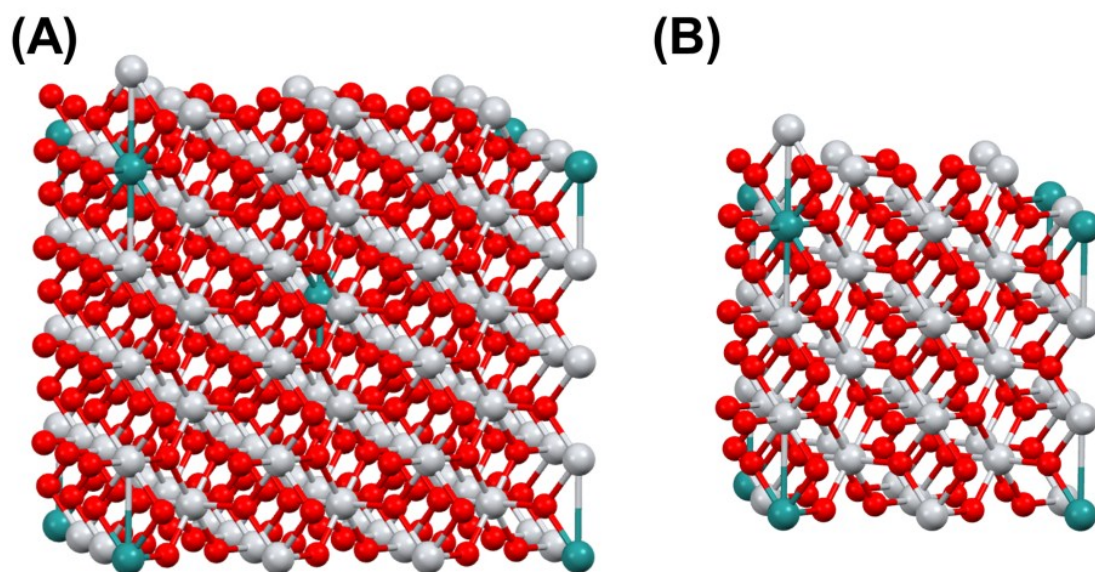
<sup>b</sup> Department of Chemistry, Stony Brook University, Stony Brook, NY 11790, US

<sup>c</sup> Institute of Energy Technologies and Centre for Research in NanoEngineering, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

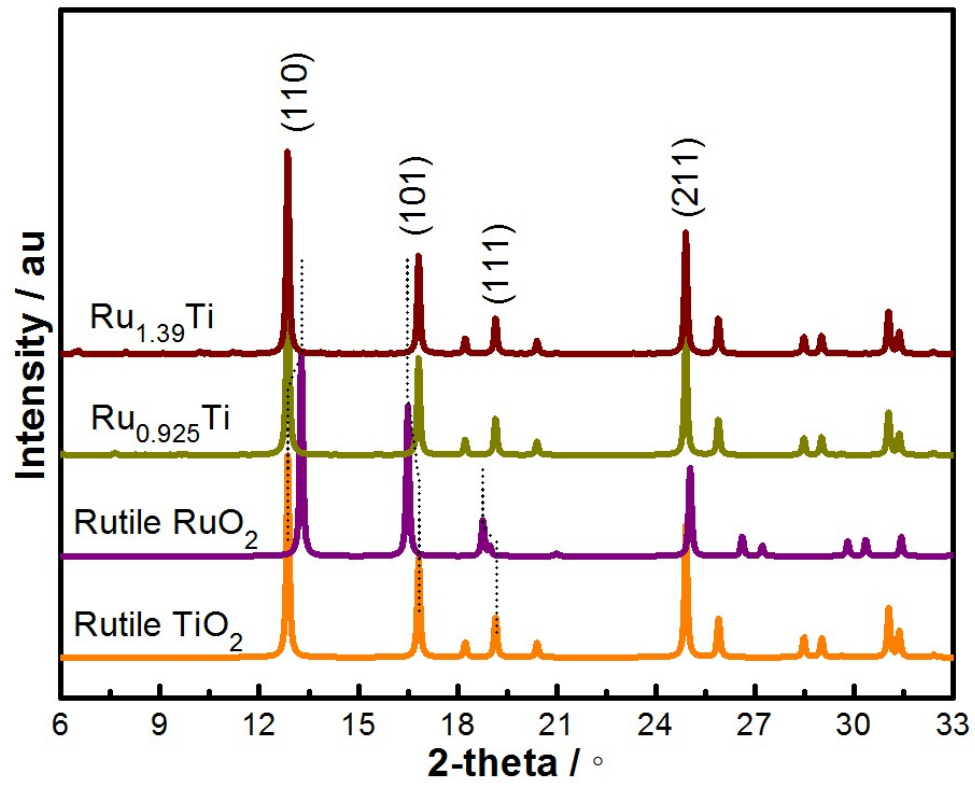
<sup>d</sup> Materials Science & Engineering, Binghamton University, Binghamton, NY 13902, US

<sup>e</sup> X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, US

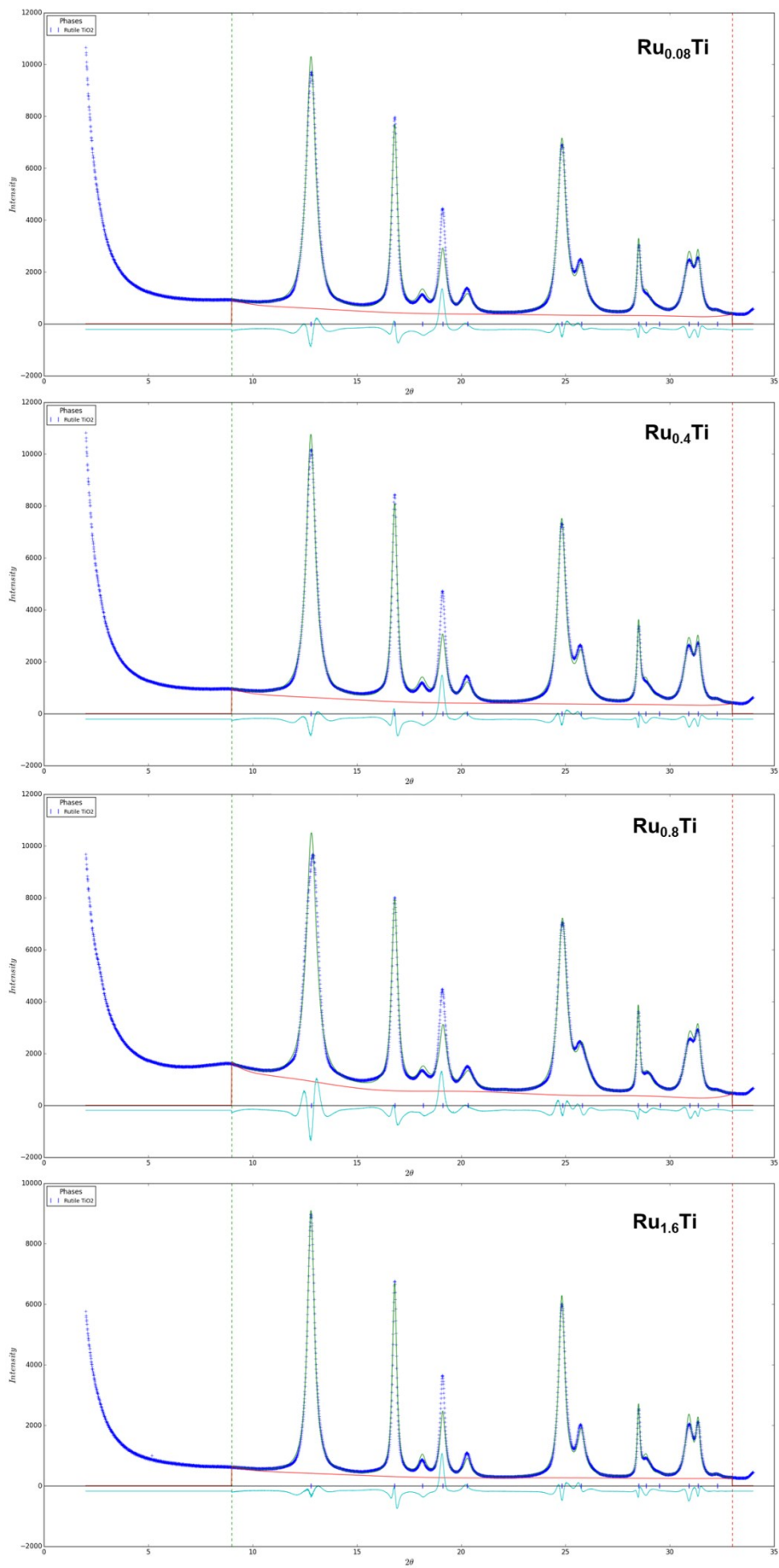
## Supplementary figures



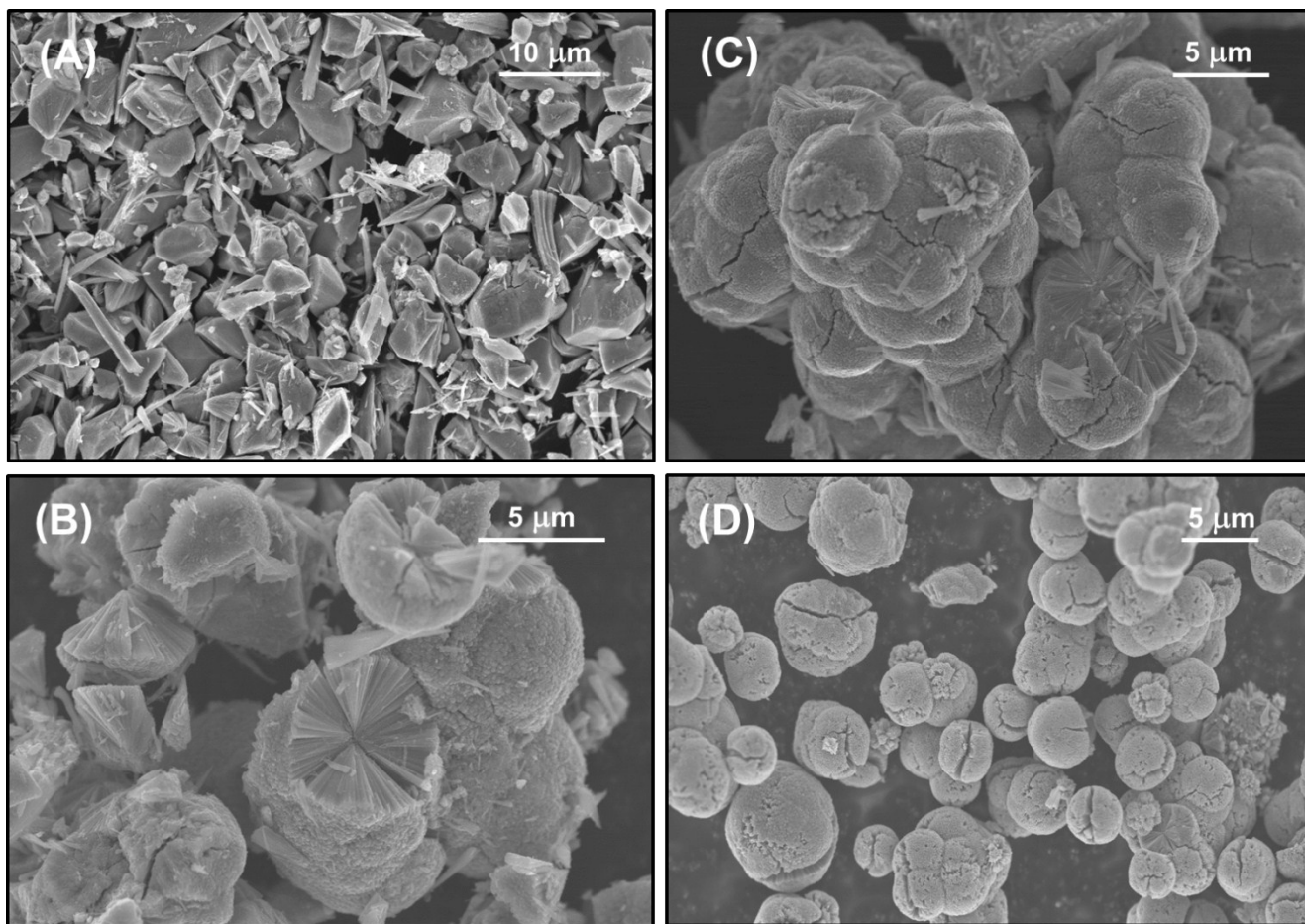
**Figure S1.** Model considered for Ru-doped rutile  $\text{TiO}_2$  supercells: (A) 0.925% Ru; and (B) 1.39% Ru. The Ru ions on random positions in rutile cells are shown as cyan spheres while Ti ions and oxygen ions are shown in gray and red spheres, respectively.



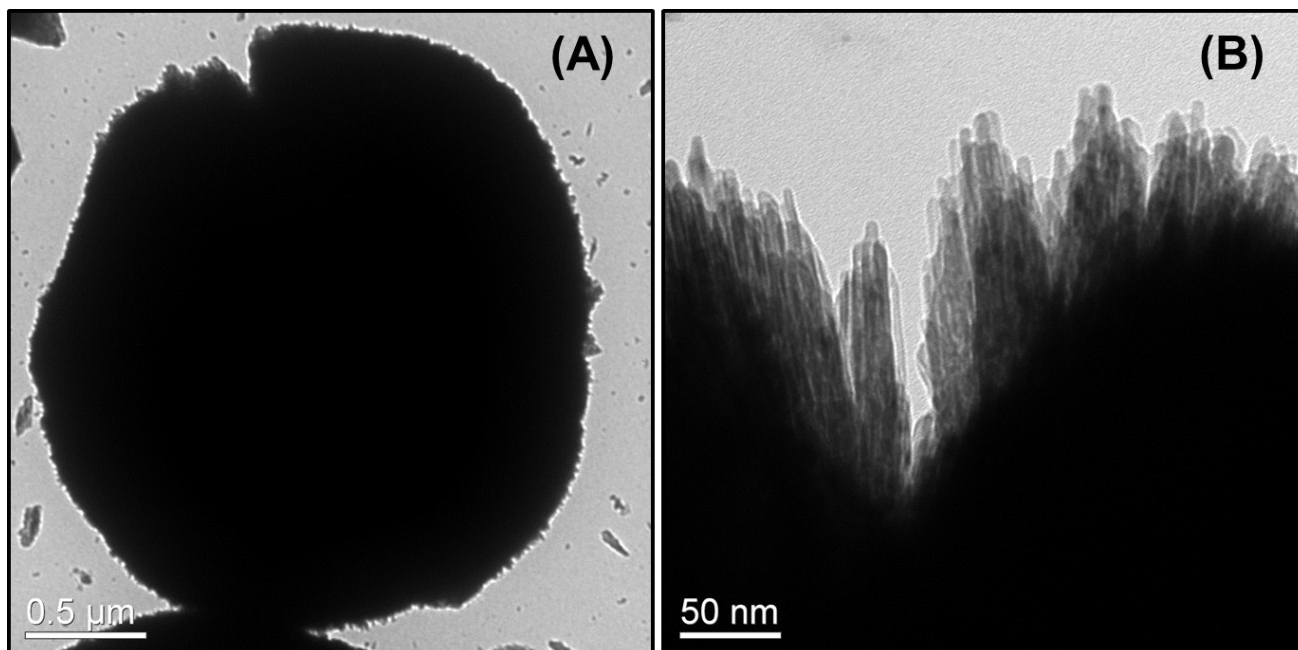
**Figure S2.** Simulated XRD patterns of bulk rutile TiO<sub>2</sub>, rutile RuO<sub>2</sub>, 0.925 mol% and 1.39 mol% Ru-doped rutile TiO<sub>2</sub>.



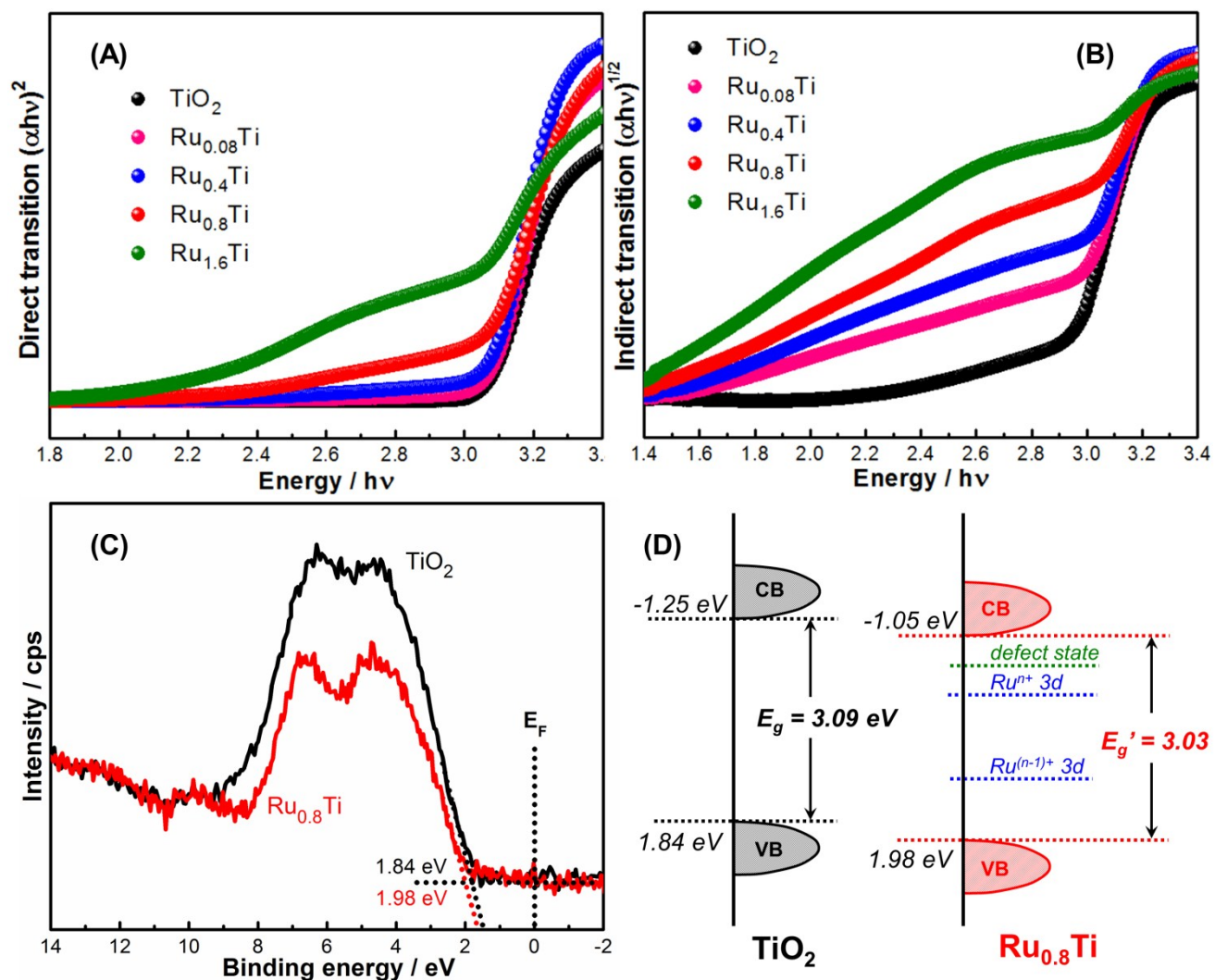
**Figure S3.** Rietveld refinement of Ru-doped TiO<sub>2</sub> series.



**Figure S4.** SEM images of: (A) undoped TiO<sub>2</sub>, (B) Ru<sub>0.08</sub>Ti, (C) Ru<sub>0.4</sub>Ti, and (D) Ru<sub>1.6</sub>Ti.



**Figure S5.** Low-magnification TEM images of Ru<sub>0.8</sub>Ti sample.



**Figure S6.** (A, B) Tauc's plot derived from UV-Vis diffused absorption spectra of Ru<sub>x</sub>Ti series for band gap determination: (A) direct transition and (B) indirect transition; (C) XPS valence band; and (D) estimated band structure of representative Ru<sub>0.8</sub>Ti photocatalyst.

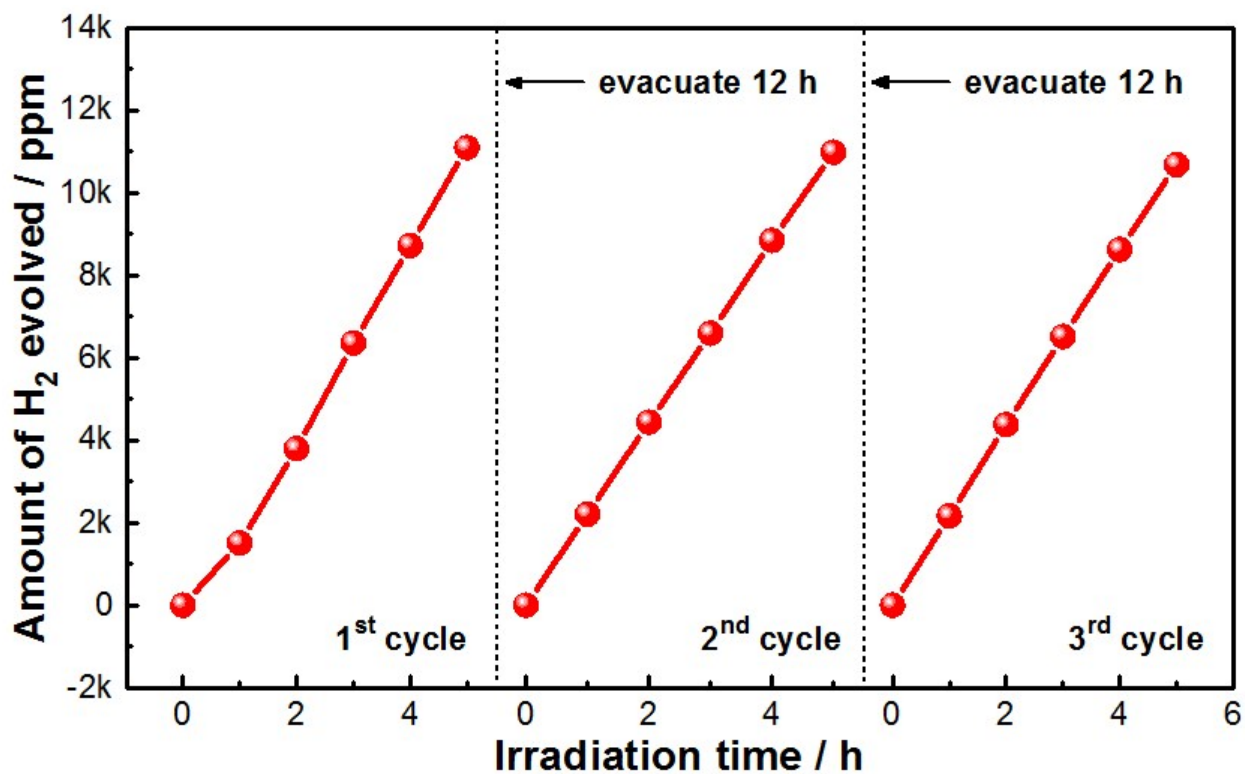
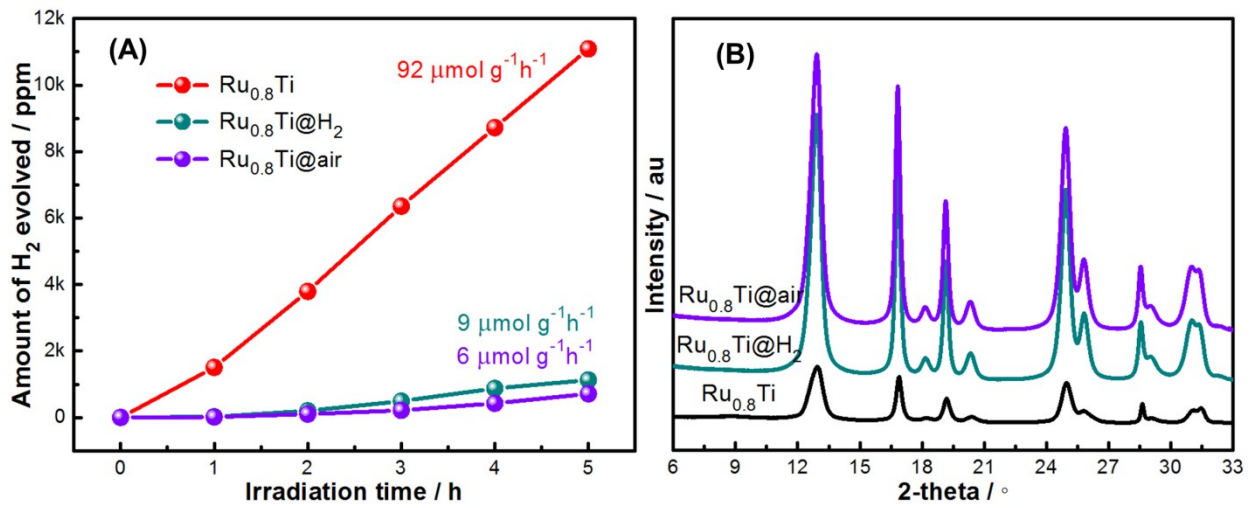


Figure S7. Photostability of Ru<sub>0.8</sub>Ti sample.





**Figure S8.** Influence of post treatment atmosphere over 0.8% Ru-doped TiO<sub>2</sub>: (A) H<sub>2</sub> production; and (B) crystallographic structure by XRD.