## Selective Formation of Disordered Layer in Single Titanium Dioxide Nanoparticle: Novel Metal-free Photocatalysis

Despite longstanding controversy, TiO2 polymorphs heterojunction composed of anatase

and rutile outperform the individual ones because of the energetic type-II band alignment at the heterojunction interface. However, localization of the disordered layer within conventional  $\text{TiO}_2$  nanoparticles with heterojunction has remained a big challenge.

Here we report a selective positioning of a disordered layer with different thickness ranges in between the anatase and rutile phases by a conceptually different synthetic route for highly efficient novel metal-free photocatalytic H2 production. The multiple heterojunction in DE-P25 single nanoparticle with the disordered layer of 2~3 nm could be synthesized which is confirmed by high resolution-TEM, electron energy loss spectroscopy (EELS) and electron holography mapping for the first time.

This multiple heterojunction in single  $\text{TiO}_2$  nanoparticles composed of crystalline anatase/disordered rutile/rutile demonstrate not only superior interfacial charge separation efficiency, but also novel-metal free surface reactivity, which synergistically yields ~140 times higher H<sub>2</sub> production rate than conventional heterojunction system.