## **Supporting Information**

Exploitation of the synergistic effect between surface and bulk defects in ultra-small N-doped titanium suboxides for enhancing photocatalytic hydrogen evolution

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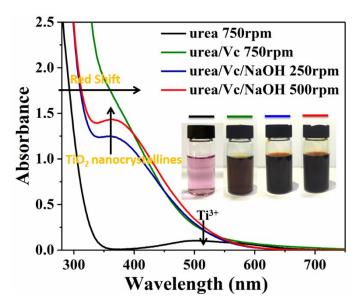


Figure S1. UV-Vis absorption spectra of titanium precursors modified with urea/ascorbic acid (The inset is the pictures of different precursors).

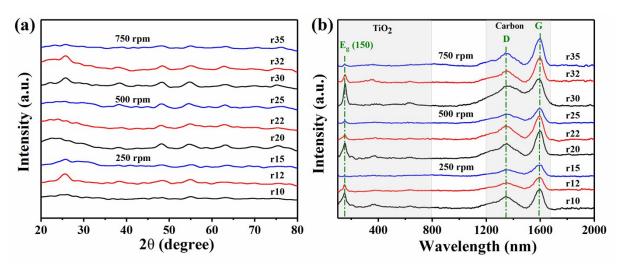


Figure S2. (a) XRD patterns and (b) Raman spectra of the samples calcinated under constant pressure (black line: 0 mg urea; red line: 20 mg urea; blue line: 50 mg urea).

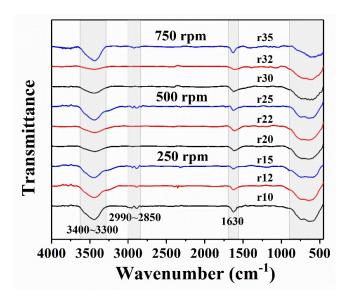


Figure S3. FT-IR spectra of the samples calcinated under constant pressure (black line: 0 mg urea; red line: 20 mg urea; blue line: 50 mg urea).

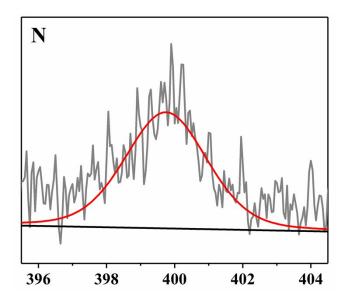


Figure S4. N 1s XPS high-resolution spectra of sample r22.

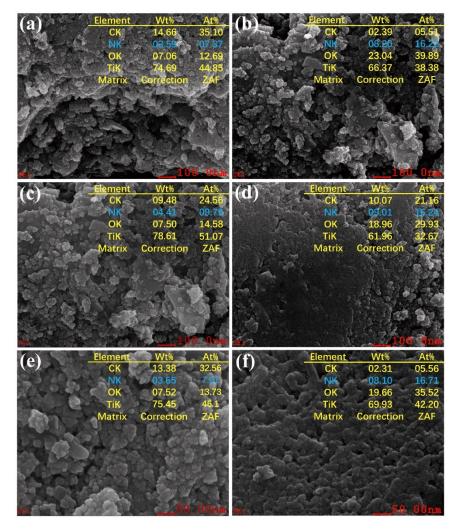


Figure S5. SEM and EDX analysis of (a) r12, (b) r15, (c) r22, (d) r25, (e) r32 and (f) r35.

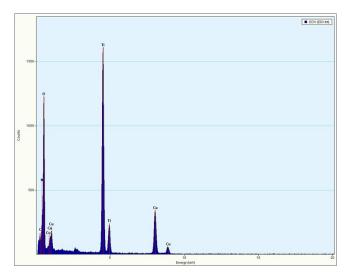


Figure S6. EDX analysis of the nanoparticles in sample r22 (Figure 2d).

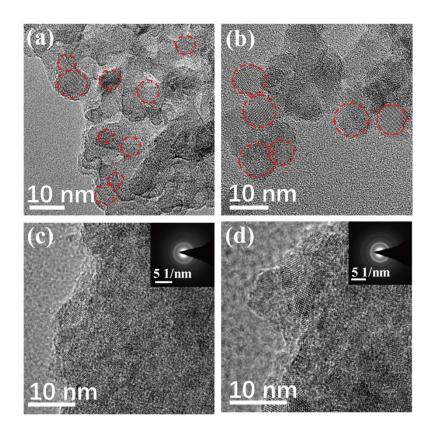


Figure S7. TEM images of the samples calcinated under vacuum (a) r12; (b) r32, (c) without calcination, (d) calcinated under constant pressure. The inset in (c) and (d) is the corresponding SAED pattern.

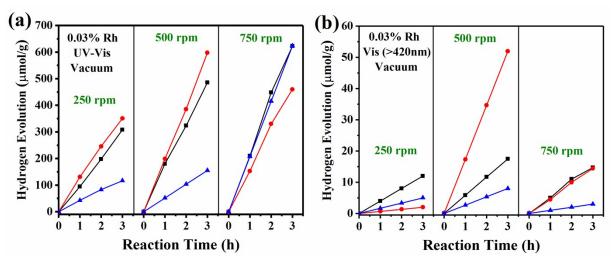


Figure S8. Hydrogen evolution of the samples calcinated under vacuum (a) without, (b) with a 420 nm long-pass filter (>420 nm) (black line: 0 mg urea; red line: 20 mg urea; blue line: 50 mg urea).

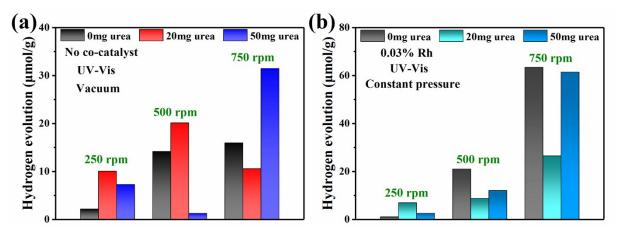


Figure S9. Hydrogen evolution of the samples under UV irradiation (a) calcinated under vacuum without co-catalyst, (b) calcinated under constant pressure with 0.03% Rh.