Supporting Information

From Titanium Oxydifluoride ($TiOF_2$) to Titania (TiO_2): Phase Transition and Non-metal Doping with Enhanced Photocatalytic Hydrogen (H_2) Evolution Properties

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Experimental Section

Synthesis of $TiOF_2$ and TiO_2

Titanium(IV) tetrafluoride (TiF_4, Sigma-Aldrich), hydrofluoric acid (HF, Sigma-Aldrich, 48%, ACS reagent) and n-butanol (Shanghai Lingfeng Chemical reagent) were used as the precursors and reaction medium, respectively. In a typical experiment, 0.45 g of TiF_4 was weighed in a 50 mL Teflon container and 20 mL of n-butanol was poured into the container subsequently (It should be pointed out that TiF_4 was not dissolved absolutely in this step). Then 0.2 mL of HF acid was added and finally the Teflon container was put into a stainless steel autoclave and hydrothermally treated at 200℃ for 6 h. After reaction, the final $TiOF_2$ product was harvested by centrifugation and washed with ethanol for 3 times.

The as-synthesized $TiOF_2$ was then calcinated under different reaction conditions, including mosit argon at 300℃ and 600℃ for 4 h, pure argon at 800℃ for 4 h, and H_2S at 800℃ for 4 h, respectively.

Co-catalyst loading for hydrogen evolution test

The as-obtained $TiOF_2$ and TiO_2 products were loaded with 1 wt % Pt and calcinated at 200 °C for 2 h. Then 22 mg of the Pt loaded powder was dispersed in 100 mL of aqueous solution containing 10% methanol in volume. A 300 W Xe lamp was used as a light source and the amount of H_2 evolved was determined using a gas chromatography (TECHCOMP, 7890Ⅱ).

Materials characterization

Crystallographic information of $TiOF_2$ and TiO_2 was obtained with X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu KR radiation, 40 kV). The morphology and structure of the samples were characterized by transmission electron microscopy and selected area electron diffraction (TEM/SAED, JEM-2100), and field emission scanning electron microscopy (FESEM, HITACHI S4800). Moreover，the crystal structure of the samples was determined by Raman spectroscopy (Renishaw, inVia+Reflex). Chemical compositions and surface bonding states of $TiOF_2$ and TiO_2 were analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Al Kα exciting radiation). All binding energies were referenced to the C1s peak (284.6 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Prior peak deconvolution, X-ray satellites, and inelastic background (Shirley-type) were subtracted for all spectra. Samples were centrifuged and washed with ethanol for three times and then redispersed in ethanol and dropped on a conductive SEM sample holder or a carbon-coated copper grid with irregular holes for TEM analysis. Samples for XPS were prepared by drying the sedimented particles overnight at 60 °C.

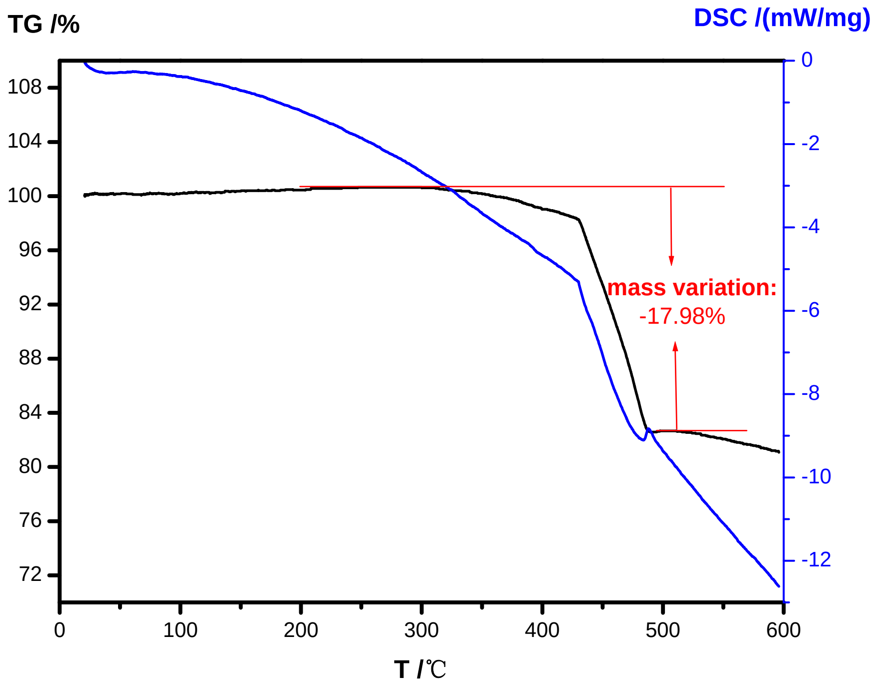
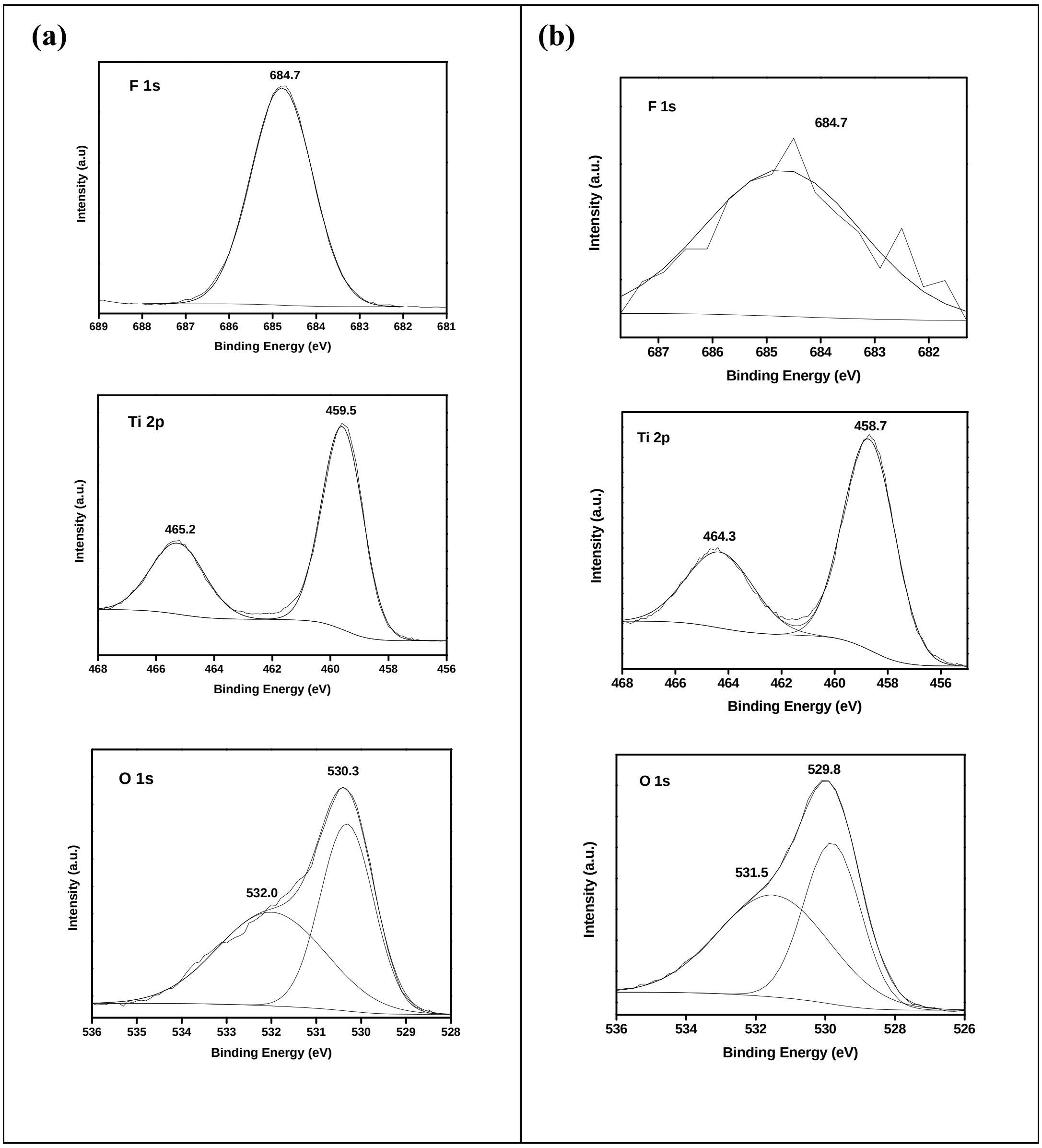


Figure S1. TG and DSC spectra of the as-synthesized $TiOF_2$.


(a)
F 1s
684.7
Intensity (a.u)
689 688 687 686 685 684 683 682 681
Binding Energy (eV)
Ti 2p
459.5
465.2
Intensity (a.u.)
468 466 464 462 460 458 456
Binding Energy (eV)
O 1s
530.3
532.0
Intensity (a.u.)
536 535 534 533 532 531 530 529 528
Binding Energy (eV)
(b)
F 1s
684.7
Intensity (a.u.)
687 686 685 684 683 682
Binding Energy (eV)
Ti 2p
458.7
464.3
Intensity (a.u.)
468 466 464 462 460 458 456
Binding Energy (eV)
O 1s
529.8
531.5
Intensity (a.u.)
536 534 532 530 528 526
Binding Energy (eV)

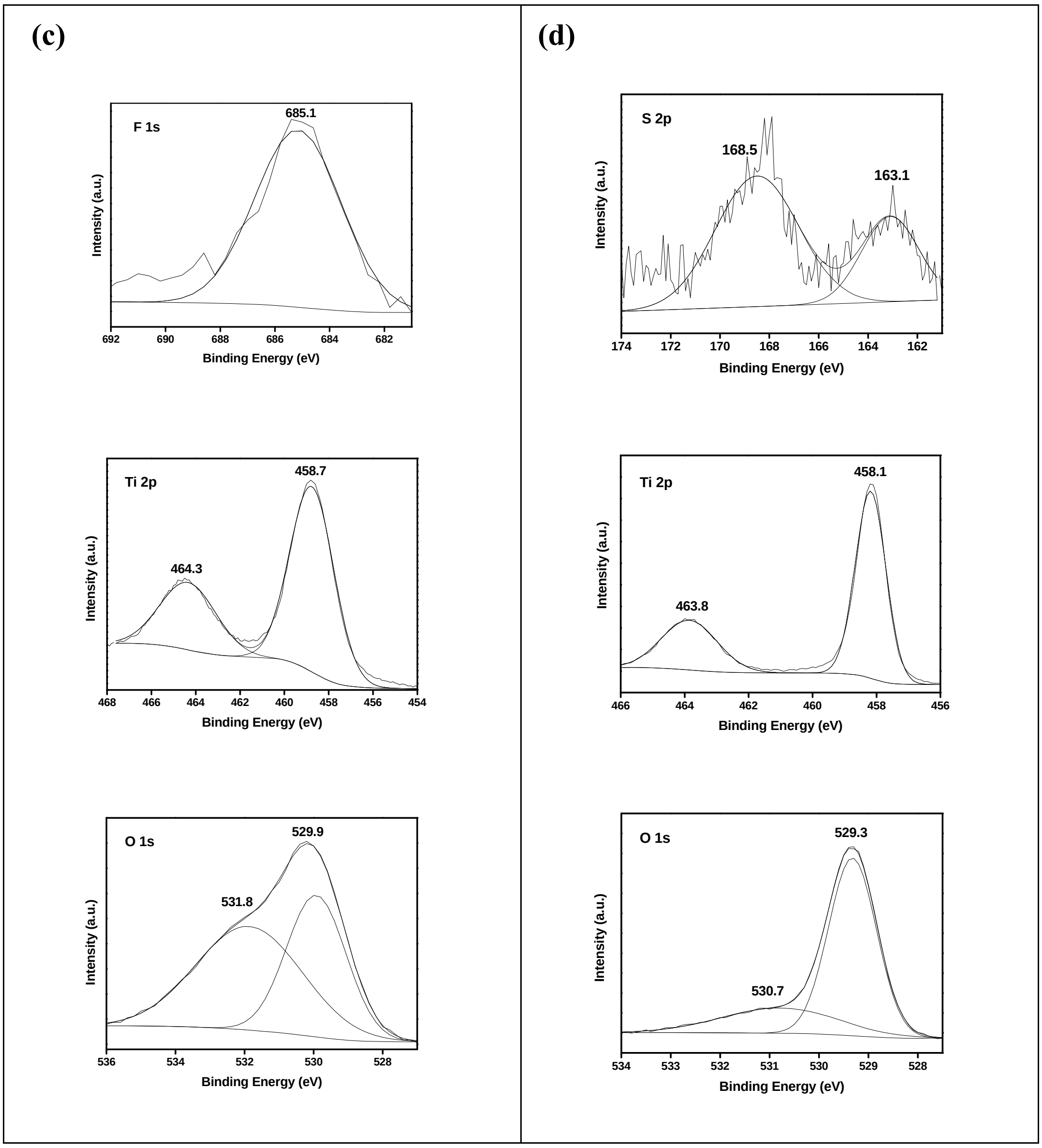


Figure S2. (a-d) XPS spectra of untreated $TiOF_2$, the samples derived through heat-treating the original $TiOF_2$ crystals under moist argon at 300℃ and 600℃ for 4 h, and the sample derived through heat-treating the original $TiOF_2$ crystals under H_2S at 800℃ for 4 h, respectively.

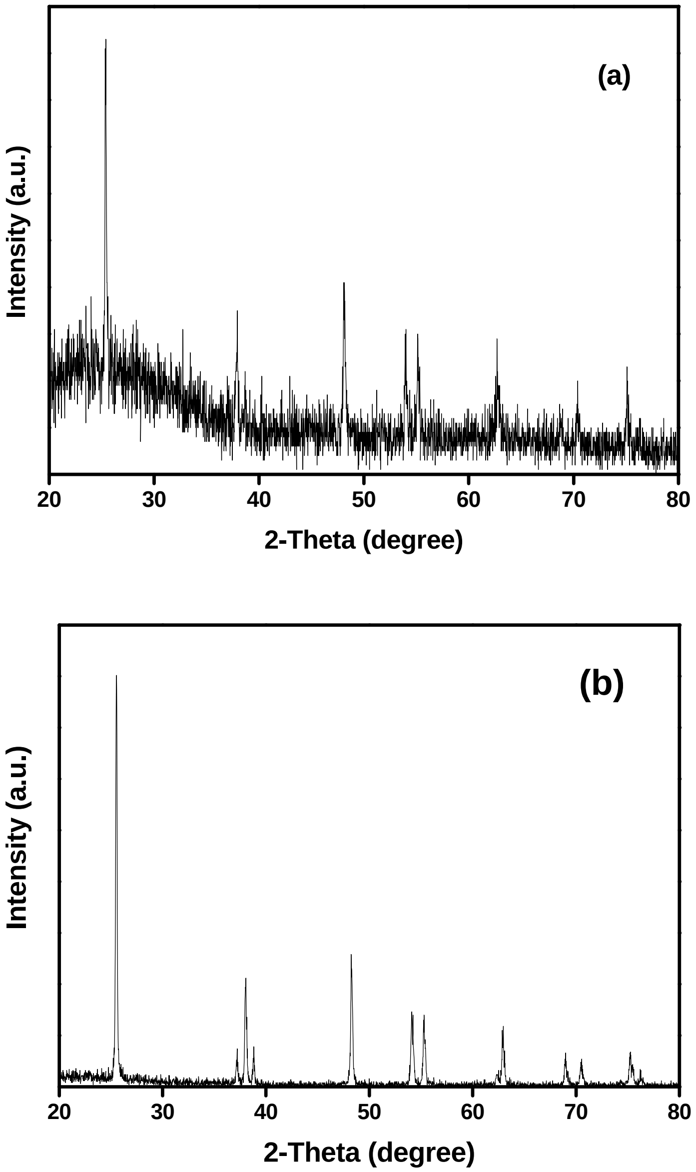


Figure S3. a-b) XRD patterns of the products derived through heat-treating the original $TiOF_2$ crystals under pure argon and H_2S, respectively.

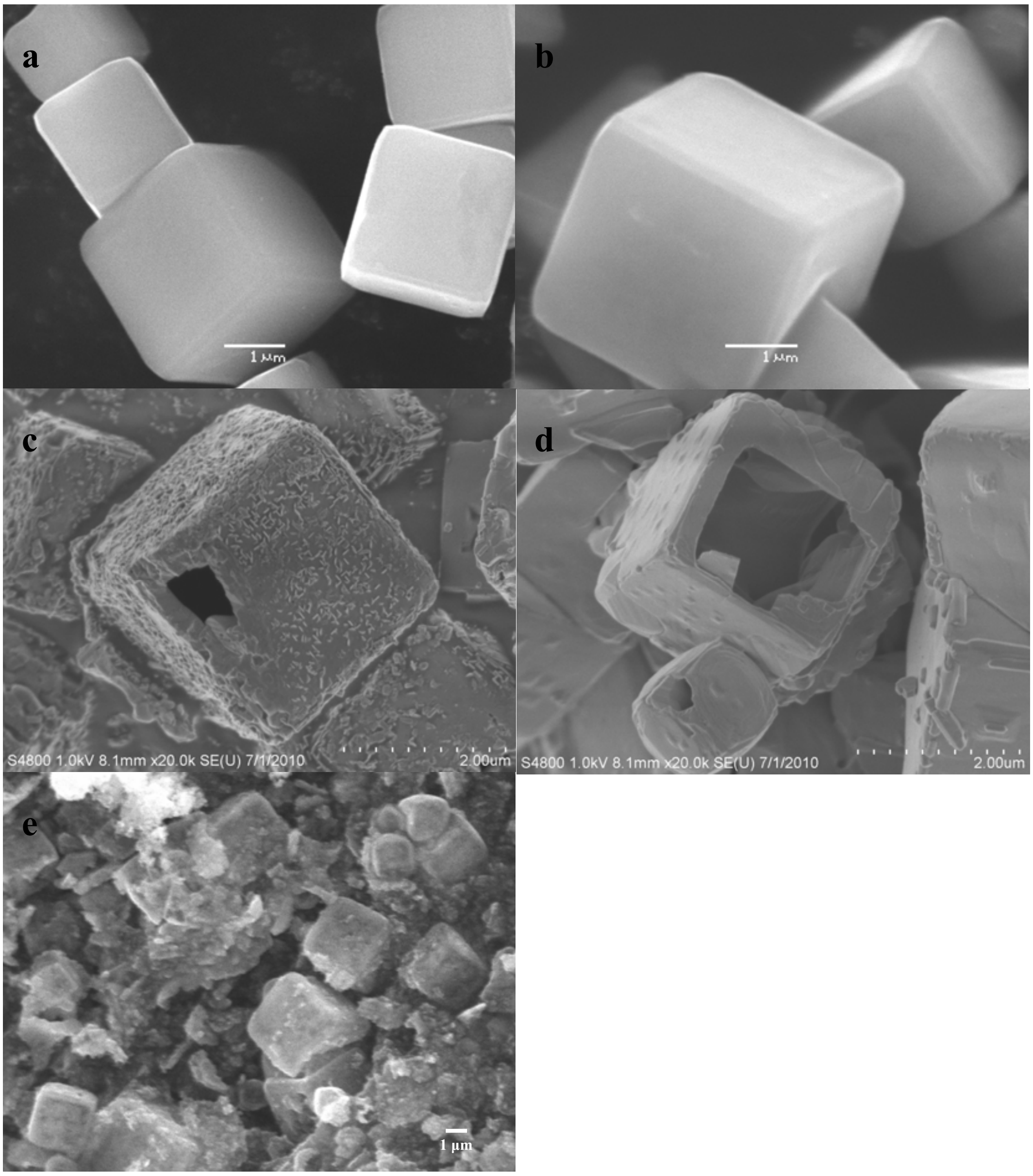


Figure S4. a-e) SEM images of the products derived through heat-treating the original $TiOF_2$ crystals under pure argon atmosphere at 600℃, 700℃, 800℃, 900℃ and 1000℃ for 4 h, respectively.