Supplementary information

Efficient full-spectrum driven ammonia synthesis over heterostructured TiO₂

nanosheet arrays

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1. Experiment Section

1.1 Synthesis of ST, HST, OST, AST and Ru@HST.

All the chemical reagents used in the experiment are high-purity without any nitrogen element. The Ti foil was ultrasonically cleaned in acetone and ethanol for 30 minutes, then rinsed with deionized water, and finally dried in a nitrogen flow.

Ti foil (2.0×1.0×0.02 cm) was put into the Teflon-lined stainless steel autoclave with 50 mL of NaOH aqueous solution (5.0 M), followed by heating at 453 K for 10 h under the autogenous pressure. The resulting product was washed with anhydrous ethanol several times and dried at room temperature in a vacuum drying oven. The finally obtained sample was designated as ST. The as-prepared ST was annealed in H2, air and argon at 923 K for 2 h to obtain HST, OST and AST, respectively.

The synthesis of metallic Ru decorated samples was carried out by the impregnation of HST (or other substrates) with a certain amount of ruthenium carbonyl ($Ru_3(CO)_{12}$) in tetrahydrofuran (THF) solution. After evaporating the THF solvent, $Ru_3(CO)_{12}$ was deposited evenly on the HST surface followed by the thermal decomposition at high temperature in vacuum, leading to the formation of metallic ruthenium species. The as-synthesized material was designated as Ru@HST. The content of Ru in the as-synthesized sample was measured based on the ICP results.

1.2 Photocatalytic ammonia synthesis testing

The as-prepared photocatalyst (2 mg) was placed at the bottom of an airtight quartz reactor, and then the activation was conducted in vacuum (P < 0.1 Pa) at 473 K.

After cooling to room temperature, 600 μ mol of mixture (450 μ mol H₂ and 150 μ mol N₂) gases were introduced into the quartz reactor, followed by the photocatalytic tests under visible light from a xenon lamp equipped with cutoff filters. The reaction temperature was kept at 293 K during the photocatalytic process with a cooling system. The produced ammonia was identified by gas chromatography-mass spectrometry and quantified by ion chromatography.

2. General Characterizations

The powder X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2550 diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å) at 200 mA and 50 kV. X-ray photoelectron spectroscopy (XPS) and XPS valance band were collected on an ESCALAB 250 spectrometer with a monochromatic Al K α X-ray (h υ = 1486.6 eV) as the excitation source. UV-Vis spectra were measured on a Perkin-Elmer Lambda 20 UV/Vis spectrometer with BaSO₄ as a reference. Infrared spectroscopy (IR) spectra were carried out using a Bruker IFS 66 v/s Fourier-transform spectrometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on a Philips-FEI Tecnai G2S-Twin with a field emission gun operated at 200 KV. Energy-dispersive X-ray spectroscopy (EDS) element analyses were taken on a Tecnai F20 electron microscope. The electron paramagnetic resonance (EPR) spectra were recorded on a JES-FA 200 EPR spectrometer. Electrochemical impedance spectroscopy (EIS) analyses were performed on a Solartron 1260 + 1287 apparatus. N₂-TPD and H₂-TPD was performed on an Autochem II 2920 apparatus (Micromeritics, USA). Generally,

20 mg of samples were loaded and pre-treated in a He flow at 500 °C for 1 h. The samples were saturated with a flow of 25 mL/min 10% N₂ (or H₂)/He for 60 min. After being purged with pure Ar for 1 h, the samples were heated from 50 °C to 550 °C with a heating rate of 10 °C min⁻¹ under Ar atmosphere, and the desorbed N₂ (or H₂) was determined using a thermal conductivity detector.



Figure S1. SEM images of ST, HST, OST and AST.



Figure S2. Powder XRD patterns of ST, HST and Ru@HST.



Figure S3. High-resolution TEM image of the ruthenium nanoparticle supported on the surface of HST.



Figure S4. XPS spectra of Ru 3d for Ru@HST.



Figure S5. XPS spectra of Ti 2p for ST, HST and Ru@HST.



Figure S6. Mott-Schottky profiles of anatase TiO₂, ZnO, CeO₂ and OST.



Figure S7. Powder XRD patterns of OST and AST.



Figure S8. Ammonia synthesis rates of various Ru@HST with different Ru loading.



Figure S9. (a) X-band EPR spectra of the HST samples after annealing in H_2 at different temperatures (from 723 K to 1023 K). (b) Ammonia synthesis rates of various HST with different surface oxygen vacancies (O_V) concentrations.



Figure S10. N₂-TPD and H₂-TPD profiles of ST, HST and Ru@HST.



Figure S11. Illustration of the energy bands for Ru@HST and the photocatalytic N_2 activation.