Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Materials

A novel Z-scheme Bi-Bi_2O_3/$KTa_{0.5}Nb_{0.5}O_3$ heterojunction for efficient photocatalytic conversion of N_2 to NH_3

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1. Photocatalytic N_2 fixation reaction

The photocatalytic nitrogen fixation experiments were also performed in the self-build photochemical reactor. A 300W Xe lamp (PLS-SXE300C, Beijing ProfectLight Co. Ltd., China) was used as the simulated sunlight sources. Before light irradiation, 0.05 g of solid catalyst was added into a 100 mL methanol solution (containing 5 mL methanol and 95 mL deionized water) and stirred for 1 h in the dark to ensure an adsorption–desorption equilibrium. When the light is on, 3 mL portion of liquid was taken out from the solution every one-hour intervals for ammonia detection. The sample solution was centrifuged to obtain a supernatant. Then, 20 μL of sodium tartrate and 30 μl of Nessler's reagent were added dropwise successively. After 12 min of reaction, the ammonia concentration was analyzed by the absorbance at 420 nm measured by a UV-vis spectrophotometer. The photocatalytc N_2 fixation in the presence of different scavengers was performed in a similar way. Only the scavenger is changed. For the reaction in the presence of N_2, the bubbling N_2 flow rate was controlled to 50 mL/min. For the reaction under vacuum, the reactor was replaced with a closed quartz reactor. After the reaction solution and catalyst were added, the air in the reactor is evacuated. The relative pressure to the outside world is -97kPa (the real pressure is about 4.3 kPa). In order to make the result reliable, all the activity testing experiments were repeated three times, and the error limits are presented in the figures as error bars at each data point.

2. Characterizations of Bi-Bi_2O_3/KTN photocatalysts

The Bi content in the Bi-Bi_2O_3/KTN composite was analyzed by inductively coupled

plasma-optical emission spectrometer (ICP-OES) (Thermo Scientific, iCAP 7400). X-ray diffraction (XRD) analysis was performed on a D8 Advance (BRUKER AXS GMBH, Germany) X-ray diffractometer using Cu Kα radiation (40 kV/40 mA). The Raman spectra of the Bi-BiO_x/KTN catalysts were recorded on a RM1000 spectrometer (Renishaw) via an excitation source of an Ar ion laser (514.5 nm). Brunner−Emmet−Teller (BET) surface area analysis was performed by N_2 adsorption at 77 K on a 3H-2000PS2 apparatus (Beishide Instrument). Scanning electron microscopy (SEM) was carried out on a Field emission scanning electron microscope (Hitachi S-4800) with the accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was employed on a JEM-2010F transmission electron microscope via the accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were obtained via using a Thermo Scientific ESCALAB 250Xi Microprobe instrument using Al-Kα as a ray source. The C 1s signal was adjusted in the location of 284.6 eV. UV-visible diffuse reflection spectroscopy (DRS) was actualized on a UV-visible spectrophotometer (Agilent Cary5000) and the reference sample was $BaSO_4$. A CHI 660E electrochemical workstation with a standard three-electrode cell was employed to perform the photocurrent (PC) responses, electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and Mott-Schottky measurements. The test was operated at room temperature. The photocatalyst, Ag/AgCl (saturated KCl), and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. The coated area of the photocatalyst on the ITO glass was 1×1 cm and Na_2SO_4 (0.5 M) aqueous solution was used as the electrolyte. For PC measurement, a 300 W Xe lamp was served as the light source.

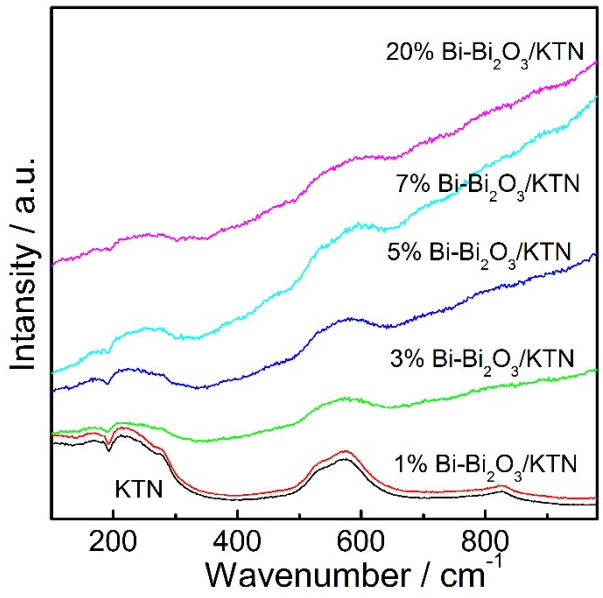

Figure S1 Raman spectra of KTN and Bi-Bi_2O_3/KTN composites

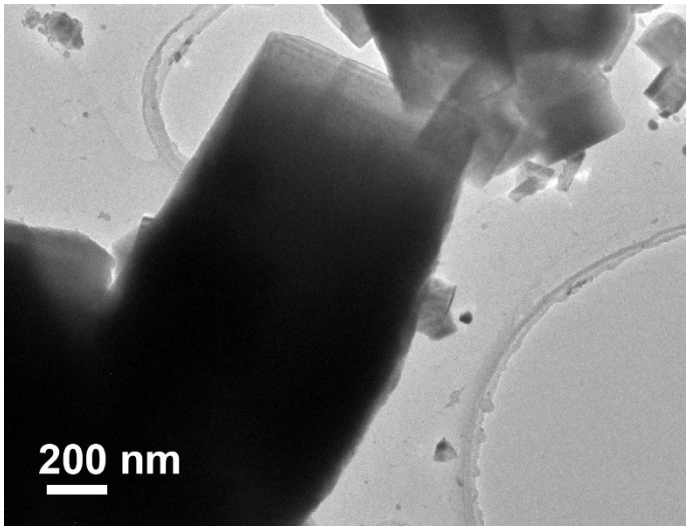

Figure S2 TEM image of 20% Bi-Bi_2O_3/KTN composite

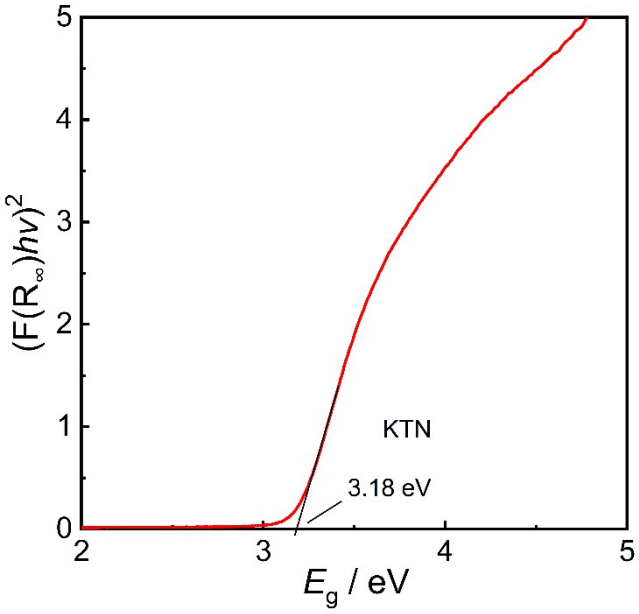

Figure S3 Estimated band gap of KTN based on the DRS spectrum.

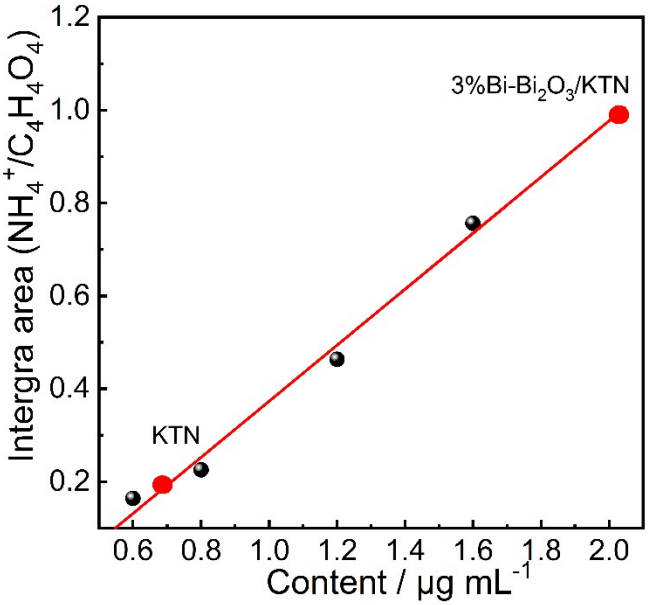

Figure S4 Standard curve line obtained via the external standards method based on the ^{1}H NMR spectra.

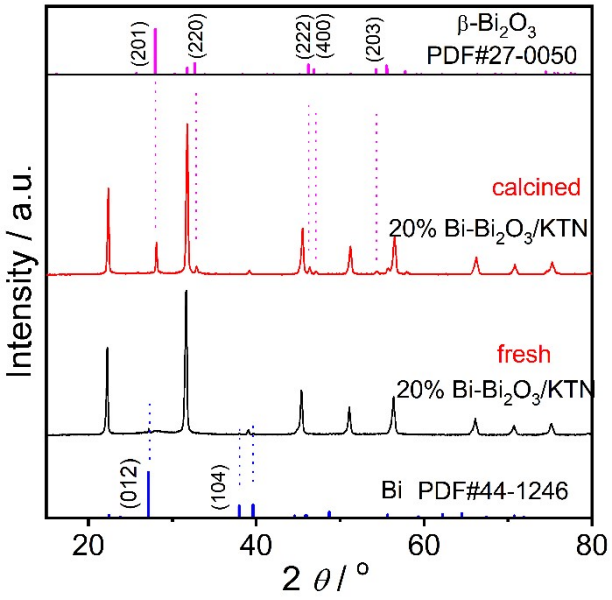

Figure S5 XRD patters of 20% Bi-Bi_2O_3/KTN sample before and after heating at 500 °C for two hours

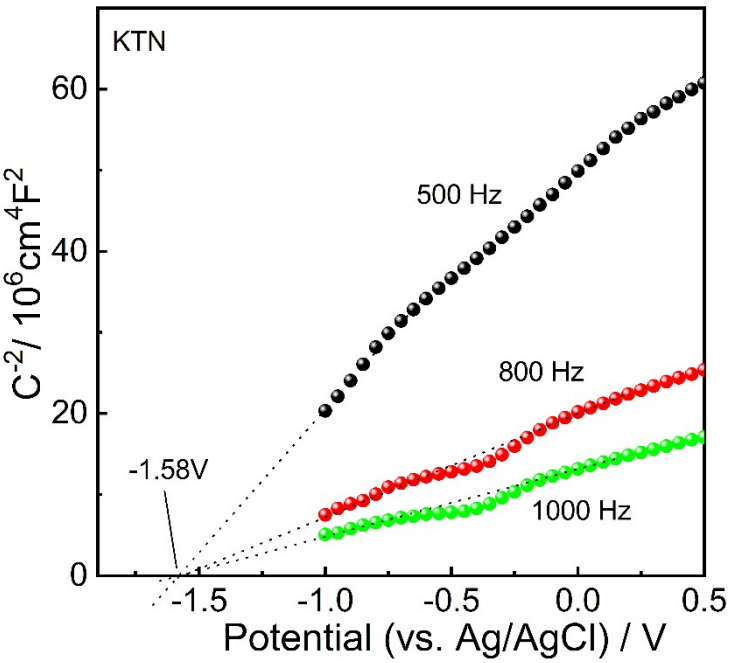

Figure S6 Mott-Schottky plots of KTN sample.