Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Materials

Preparation of $NiO/KNbO_3$ nanocomposite via photodeposition method and its superior performance in photocatalytic N_2 fixation

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Preparation of $KNbO_3$ and NiO

$KNbO_3$ nanorods were synthesized though a hydrothermal method at 250 ^oC. In brief, 1.222g (4.6mmol) Nb_2O_5 was added into 4M KOH solution and stirred for 1h. Subsequently the obtained mixture was transferred into a 100mL para-polyphenylene (PPL) reactor, which was heated at 250 ^oC for 18 hours. After the reactor had cooled down to room temperature, the white precipitate was separated by centrifugation, washed with water and ethanol for several times. Finally, the precipitate was dried at 60 ^oC for 12 hours for further application. NiO was synthesized as follows. 3.00g (0.05 mol) urea and 4.42g (0.025mol) nickel acetate were dissolved in 70 ml deionized water and stirred for 1 h. Then, the clear solution was moved to 100 ml Teflon reactor and heated at 140 ^oC for 6 h. After that, green precipitate ($Ni(OH)_2$) was obtained by centrifugation, washed with water for several times, and dried at 60 ^oC for 12 h. Finally, the $Ni(OH)_2$ precursor was heated at 550 ^oC for 3 h to obtain black NiO powders.

Photocatalytic test

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, 0.1 g of solid catalyst was added into a 100 mL ethanol solution (containing 10 mL ethanol and 90 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.

Characterizations of NiO/$KNbO_3$ photocatalysts

Brunner−Emmet−Teller (BET) surface area analysis was performed by N_2 adsorption at 77 K on a 3H-2000PS2 apparatus (Beishide Instrument). The crystalline phases and chemical constitution of the samples were examined by powder X-ray diffraction (XRD) analysis, which were performed on a Philips PW3040/60 X-ray diffractometer with Cu Kα radiation (40 kV/40 mA). The morphologies of the as-prepared samples were observed by field-emission scanning electron microscopy (SEM, Hitachi S-4800). Transmission electron microscopy (TEM) images were obtained from a JEM-2010F field-emission transmission electron microscope at an acceleration voltage of 200 kV. UV–visible diffuse reflection spectroscopy (DRS) was actualized on a UV–visible spectrophotometer (PerkinElmer Lambda900) and $BaSO_4$ was used as a reflectance standard. The Raman spectra of the catalysts were recorded on a RM1000 spectrometer (Renishaw). The excitation laser wavelength is 785 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Quantum 2000 Scanning ESCA Microprobe instrument using g AlKa. The C 1s signal was adjusted in the position of 284.6 eV. Using a CHI660E electrochemical workstation with a standard three-electrode cell to further evaluate the electrochemical impedance spectroscopy (EIS), transient photocurrent (PC), Mott-Schottky analysis, and linear sweep voltammetry (LSV) of the samples. The photocatalyst was coated on the ITO glass and Na_2SO_4 (0.5 M) aqueous solution was used as the electrolyte,

Ag/AgCl, and Pt electrodes were acted as the working, the reference and the counter electrodes, respectively.

To determine the nickel content in the $NiO/KNbO_3$ composite, metals were extracted by treatment with HNO_3 (14.5 M) at room temperatue K for 6 h. Afterwards, the solution was analyzed by Atomic Absorption Spectroscopy (ICP-AES, NexION 300X)

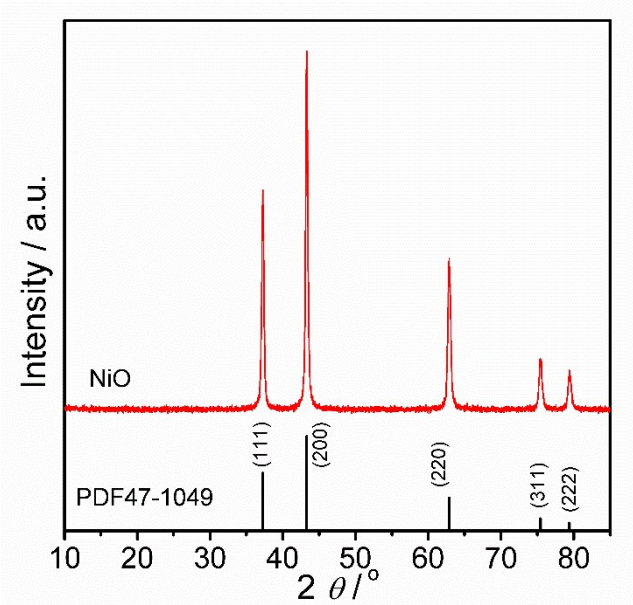

Fig. S1 XRD pattern of NiO

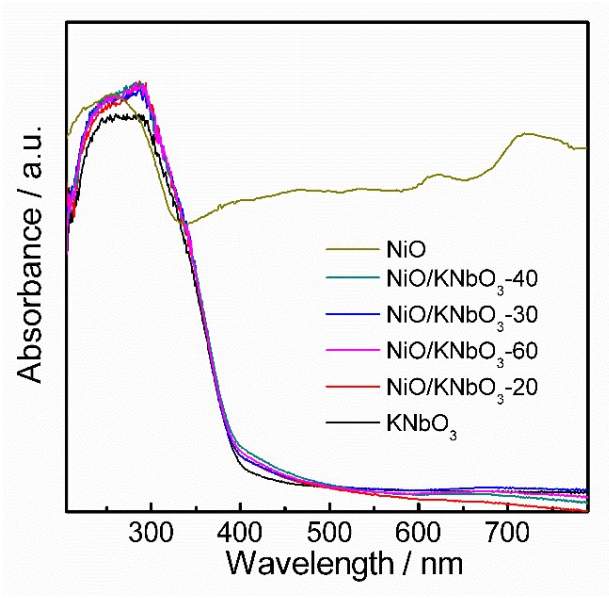

Fig. S2 DRS spectra of $KNbO_3$, NiO, and NiO/$KNbO_3$ composites.

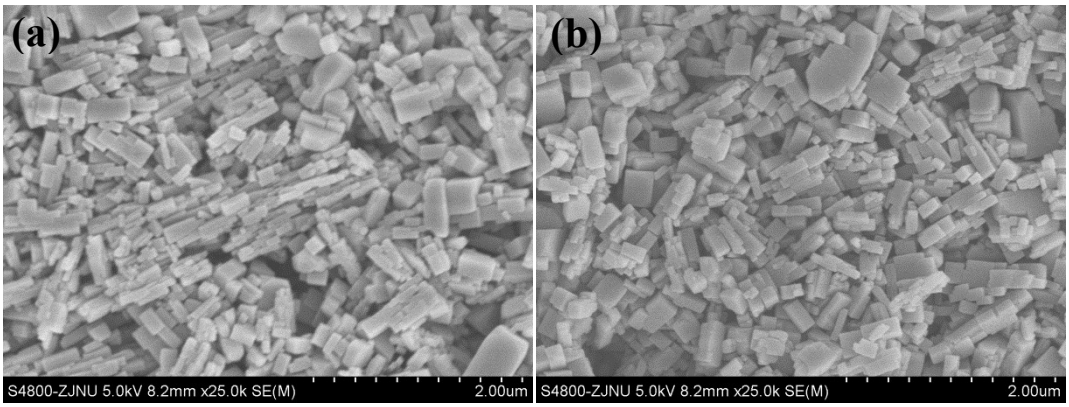

Fig. S3 SEM images of $KNbO_3$ (a) and NiO/$KNbO_3$-30 (b) photocatalysts

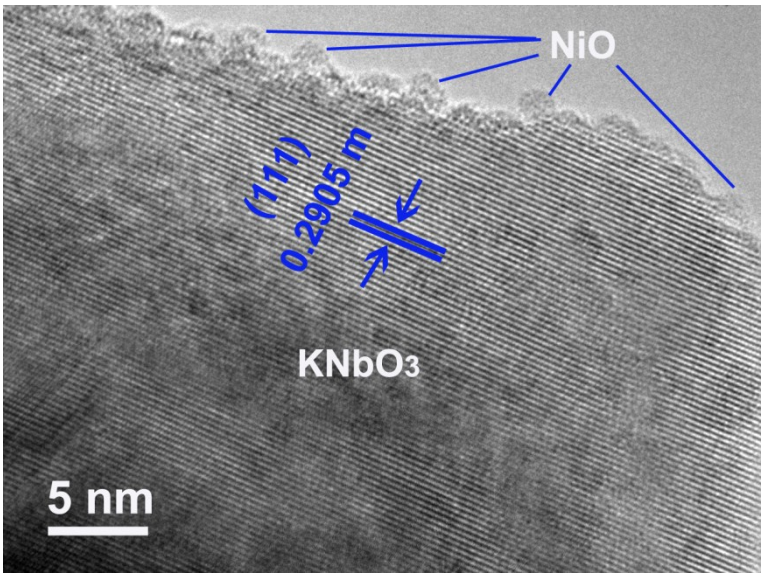

Fig. S4 HR-TEM image of NiO/$KNbO_3$-30 photocatalyst

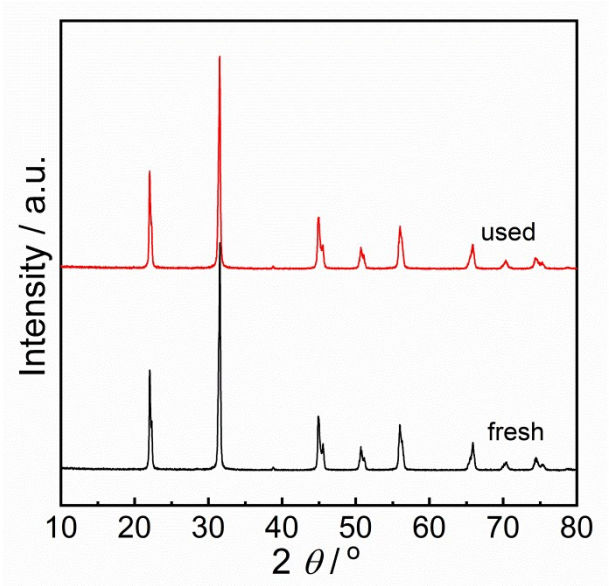

Fig. S5 XRD patterns of NiO/$KNbO_3$-30 sample before and after photocatalytic reaction.

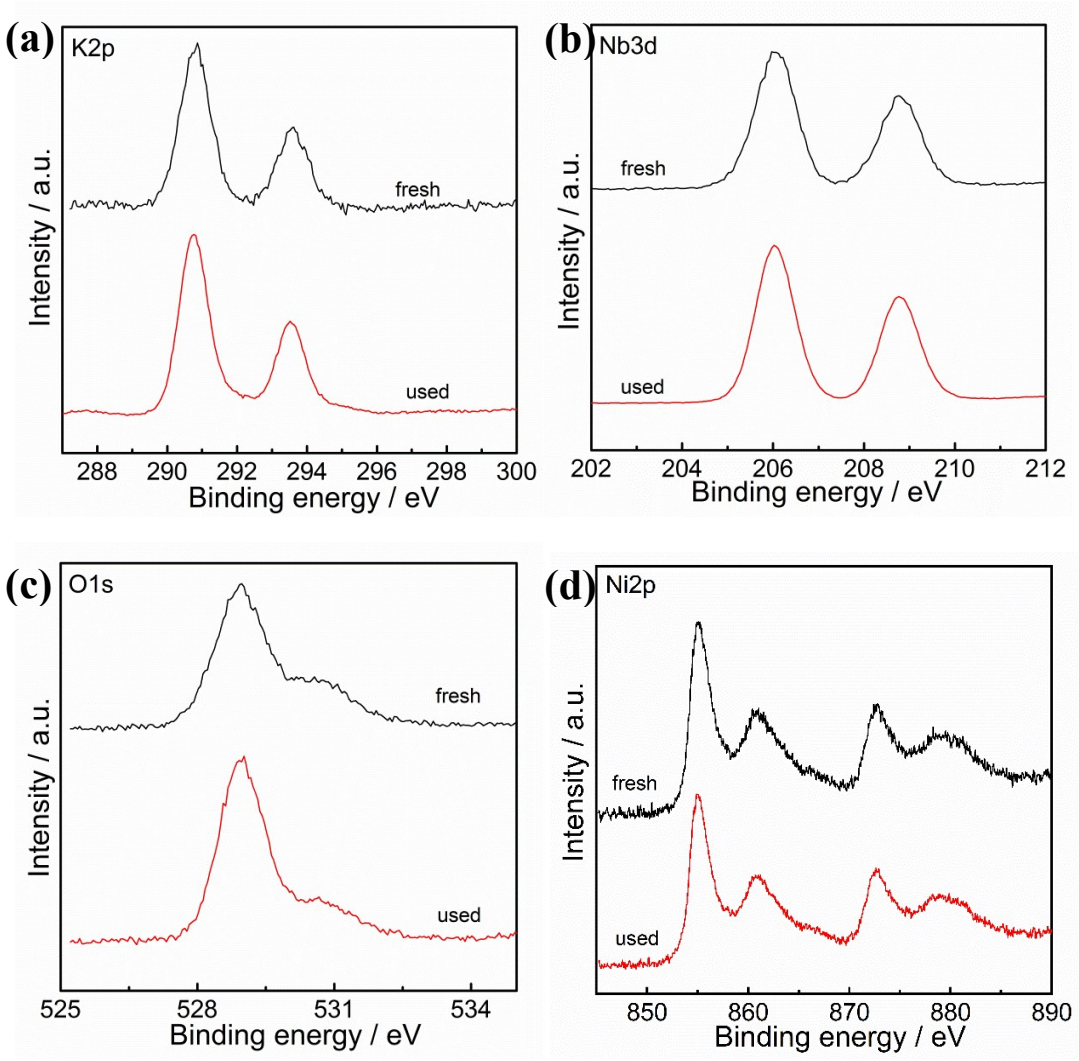

Fig. S6 XPS spectra of NiO/$KNbO_3$-30 sample before and after photocatalytic reaction. (a) K2p; (b) Nb3d; (c) O1s, (d) Ni2p

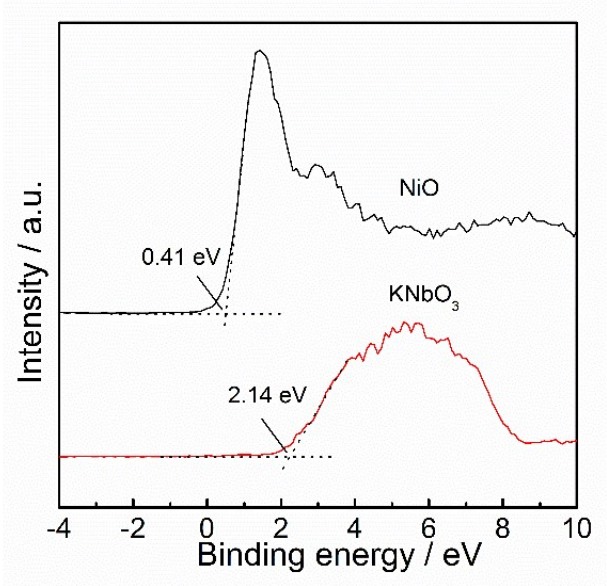

Fig. S7 Valence band XPS spectra of NiO and $KNbO_3$ samples.

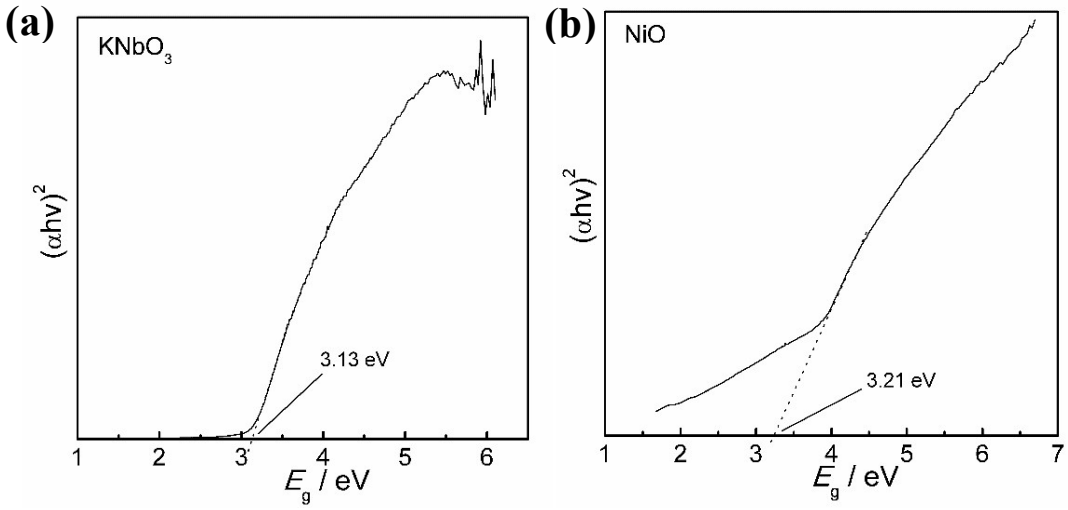

Fig. S8 Band gap energies of $KNbO_3$ and NiO via K-M method.

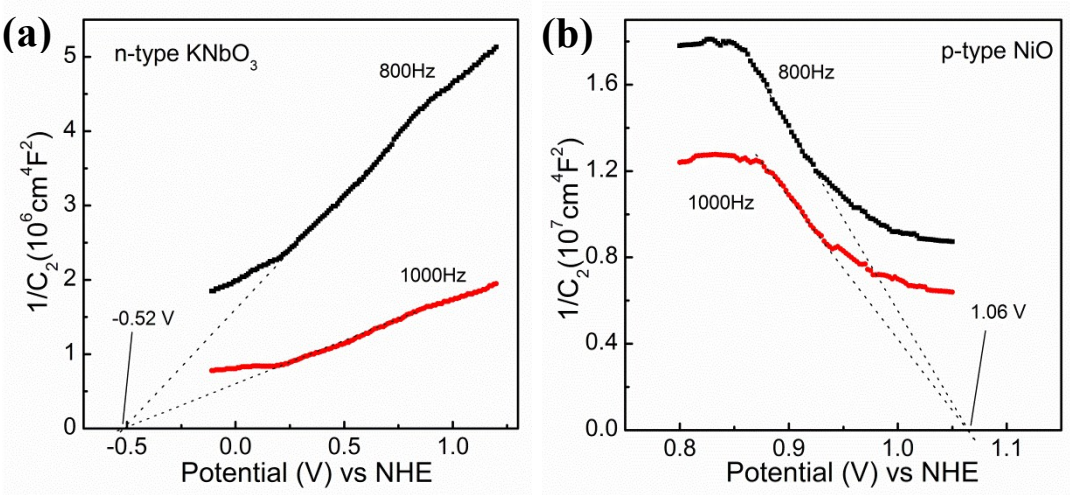

Fig. S9 Mott-Schottky plots of $KNbO_3$ (a) and NiO (b) electrodes.