

Supporting Information

Schottky Junction Effect Enhanced Plasmonic Photocatalysis by TaON@Ni NPs Heterostructures

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Experimental Section

Chemicals. Tantalum pentoxide (Ta₂O₅, 99.9%), nickel nitrate hexahydrate (NiCl₂·6H₂O, 98%), sodium hydroxide (NaOH, 99%) and sodium borohydride (NaBH₄ ≥ 98%) were purchased from Aladdin reagent (Shanghai) Co., Ltd. De-ionized (DI) water with a resistivity of 18 MΩ cm⁻² was used in experiments. All reagents were used without further purification.

Synthesis of TaON particles. TaON particles were synthesized according to previously reported method.^[1] Briefly, 0.5 g Ta₂O₅ powders were put in an alumina boat and then placed at the center of a horizontal alumina tube furnace (inner diameter = 50 mm), followed by heating at 1000 °C for 15 h in water-saturated NH₃ flow (1L min⁻¹). Finally, the furnace was naturally cooled down to room temperature, leading to TaON particles.

Synthesis of Ni(OH)₂ layer covering TaON particles (TaON@Ni(OH)₂). In a typical synthesis, 0.2 g TaON and a certain amount of NiCl₂·6H₂O were dissolved into 30 mL DI water to form a stable precursor solution. Under vigorous stirring, 4 mmol NaBH₄ reducing agent were quickly added to the mixed solution and stirred for up to 24 h. All of the above processes were performed in an ice bath at 0 °C. Subsequently, the product was collected and washed with DI water multiple times to remove residual ions. Finally, TaON@Ni(OH)₂ was obtained after drying at 70°C. The TaON@Ni(OH)₂ composites with a different covering of Ni(OH)₂ layer were synthesized by controlling the amount of NiCl₂·6H₂O (0.05, 0.1, and 0.2 mmol) under identical conditions. The resulting TaON@Ni(OH)₂ samples were noted as TaON@Ni(OH)₂-*x* samples (*x* = 0.05, 0.1, and 0.2 mmol, respectively, stands for the mole amount of the precursor NiCl₂·6H₂O).

Synthesis of TaON@Ni. First, 100 mg of as-synthesized TaON@Ni(OH)₂ powders were spread evenly and placed at the center of a fused quartz CVD tube (φ25.4×φ23.4×1000 mm) furnace. Then the furnace tube was evacuated and heated to 900 °C at a rate of ≈30 °C min⁻¹ with a flowing gas mixture of 500 sccm Ar and 150

sccm H₂. After 5 min of reaction period, the furnace was turned off and the tube was left to cool quickly to room temperature while H₂/Ar continues to flow. The resulting powders were collected and directly used for further characterization. Accordingly, the corresponding samples were noted as TaON@Ni-0.05, TaON@Ni-0.1 and TaON@Ni-0.2, respectively. For comparison, TaON was treated in parallel using the same procedures as that for TaON@Ni, except for the introduction of Ni(OH)₂, in which the product was labeled as TaON(H).

Electrochemical and photoelectrochemical measurements. Electrochemical and photoelectrochemical measurements were conducted in a standard three-electrode configuration with a CHI 660E (Chenhua, China) electrochemical workstation. Saturated Ag|AgCl and Pt foil were used as reference and counter electrodes, respectively. To prepare the working electrode, 40 mg of the as-prepared catalyst (TaON, TaON@Ni-0.1, etc.) and 10 mg iodine were dispersed in 50 mL acetone with the assistance of sonication to form a powder suspension, after which the catalyst particles were deposited on fluorine-doped tin oxide (FTO) conductive glass with an exposure area of 1 cm² by electrophoretic deposition at 15 V bias for 3 min. Linear sweep voltammetry with scan rate of 30 mV s⁻¹ was conducted in 1 M NaOH. The Mott-Schottky (M-S) curves were measured using an electrochemical analyzer (2273, Princeton Applied Research, AMETEK) by performing a potential scan in the anodic direction under frequency of 1 kHz and an AC amplitude of 15 mV in 1 M NaOH electrolyte.

General characterization. The powder XRD patterns were recorded on a Rigaku Ultima III X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The scanning electron microscope (SEM) images were obtained with a Nova NanoSEM 230 scanning electron microscope. The TEM images were obtained with a JEOL JEM-2100F microscope equipped with a field emission gun operating at 200 kV. The XPS was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a Thermo K-Alpha X-ray photoelectron spectrometer. The elemental spectra were all corrected with respect to C1s peaks at 284.6 eV. The UV-Vis absorption spectra of samples were recorded by a UV-Vis-NIR spectrophotometer (Lambda950).

Photocatalytic CO₂ reduction tests. The visible-light driven photocatalytic CO₂ reduction measurements were performed with 0.1 g powdered catalyst, which was placed on the bottom of a pyrex glass cell (230 mL). The reaction temperature was controlled at 20 °C by circulation of cooling water. Before starting the experiments, the closed circulation reactor system was vacuum-treated several times, and followed filled with high-purity CO₂ until ambient pressure was reached. Then, 0.4 mL of distilled water was injected into the reactor to generate a water vapor for 4 hours and establish an adsorption-desorption balance in the CO₂-H₂O atmosphere. A 300 W Xe lamp, with cut-off filter at 420 nm, was used for visible-light illumination. The gaseous product (1 mL) was continually taken from the reaction cell at given time intervals for qualitative analysis by gas chromatograph (GC-2014, Shimadzu Corp., Japan). For comparison, the noble metal Pt (0.1 mmol) modified TaON (0.2 g) were prepared by an in-situ photo deposition method using H₂PtCl₄ (0.1 mmol) as the

precursor, in which the product was labeled as TaON@Pt-0.1. To evaluate the stability of TaON@Ni-0.1, three consecutive photoreaction runs of 4 h in each run were conducted over TaON@Ni-0.1. The isotope labeling was carried out using $^{13}\text{CO}_2$ as the carbon source, and $^{13}\text{CH}_4$ was identified by GC-MS (Agilent 6890N/5973I, Agilent Corp., USA).

Finite-difference time-domain (FDTD) simulation. The electromagnetic fields distributed around plasmonic catalysts were calculated using FDTD solutions 8.7.1 (Lumerical Solutions). The 3D simulation model was designed based on experimental measurements that Ni nanoparticles were attached onto the surface of TaON. The Ni sizes and the Ni-Ni distances were 15 and 20 nm, respectively. The incident laser wavelength was set at 600 nm, with the polarization direction along the x-axis. A grid size of 0.5 nm was chosen in calculating the electric field intensity enhancements of TaON@Ni heterostructures. The refractive index of TaON was set to be 2.56.^[2]

Density functional theory (DFT) calculations. The charge transfers among TaON (111) and Ni (111) are investigated by the Vienna Ab-initio Simulation Package (VASP) using the Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA).^[3,4] The PAW pseudo-potential of Ta ($5p^6s^6d$), O ($2s^22p^4$), N ($2s^22p^3$), Ni ($3d^84s^2$) and C ($2s^22p^2$) potentials were used to describe the interaction between valence electrons and the ionic core. Considering the lattice matching, 4×4 , 5×5 and 5×5 supercells were used to the TaON (111) and Ni (111), respectively. A plane-wave basis with energy cutoff of 350 eV and an energy convergence of 1.0×10^{-4} eV are adopted to perform the geometry optimization.

Considering the computational cost, the geometry optimization calculations are only conducted at the gamma point.

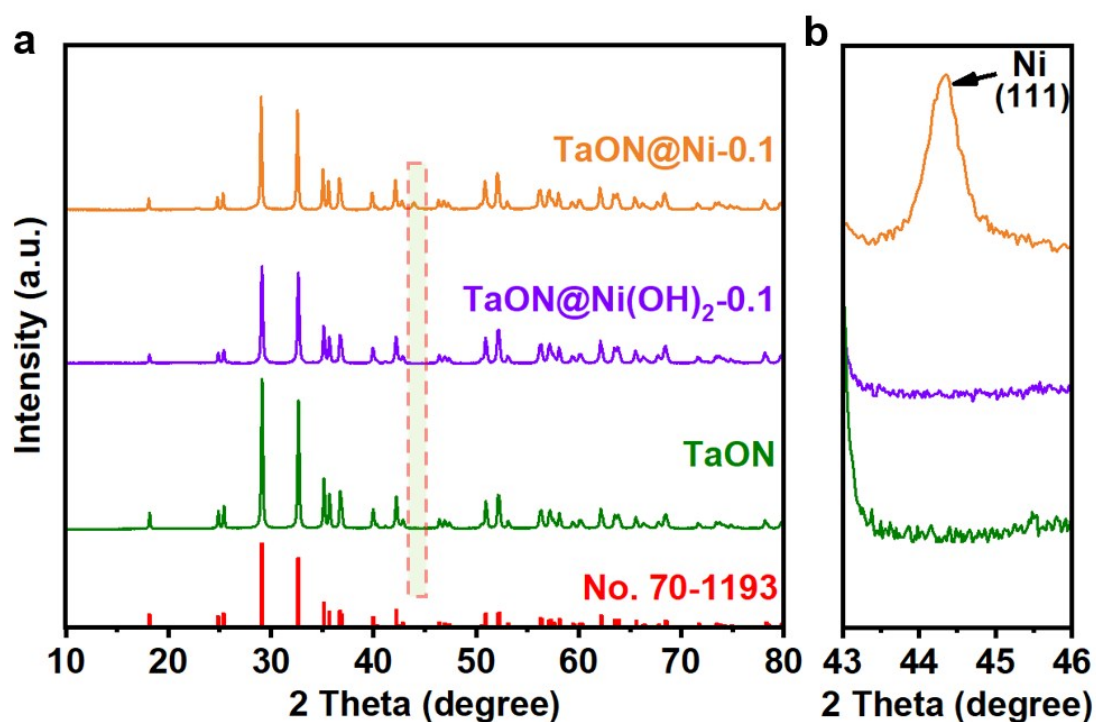


Fig. S1 (a) XRD patterns of the as-synthesized TaON, TaON@Ni(OH)₂-0.1, and TaON@Ni-0.1, respectively. (b) Magnified view of the XRD area marked by rectangle in (a). Notably, an obvious decrease in the intensity of diffraction peaks for TaON is observed after the coating of Ni(OH)₂ layers, likely due to the shading effect by the Ni(OH)₂.

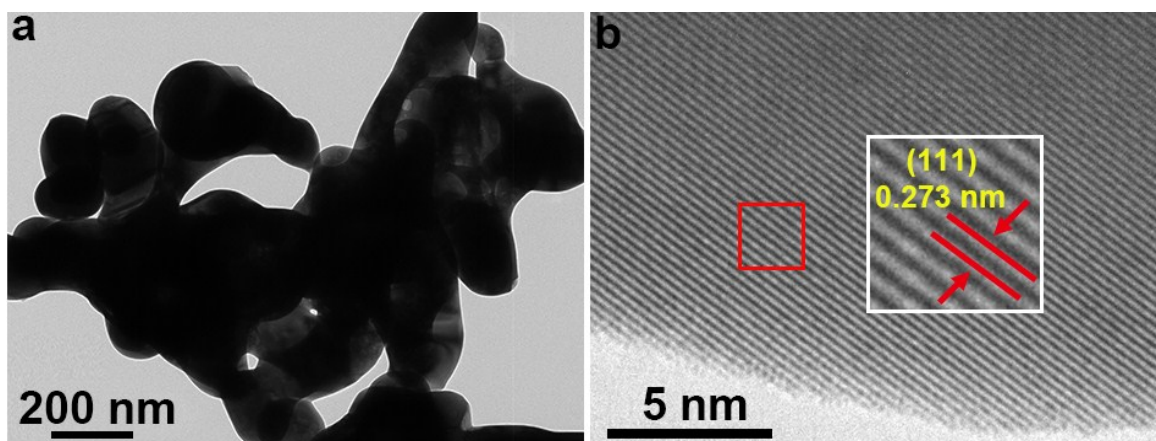


Fig. S2 The TEM (a) and HRTEM (b) images of as-synthesized TaON sample.

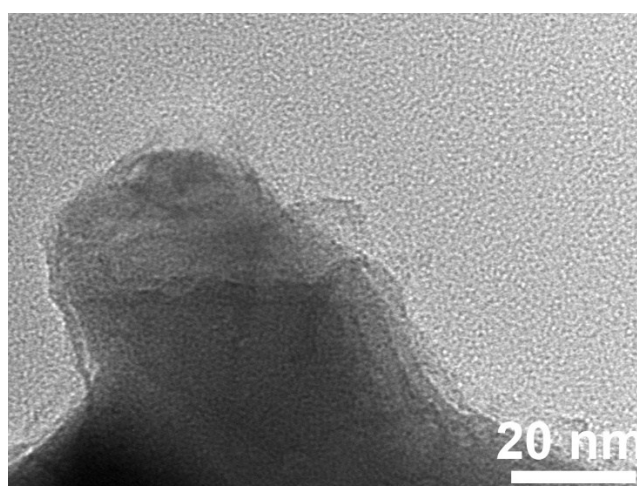


Fig. S3 The TEM image of Ni(OH)_2 taken from the $\text{TaON@Ni(OH)}_2\text{-0.1}$ hybrid in Fig.1c.

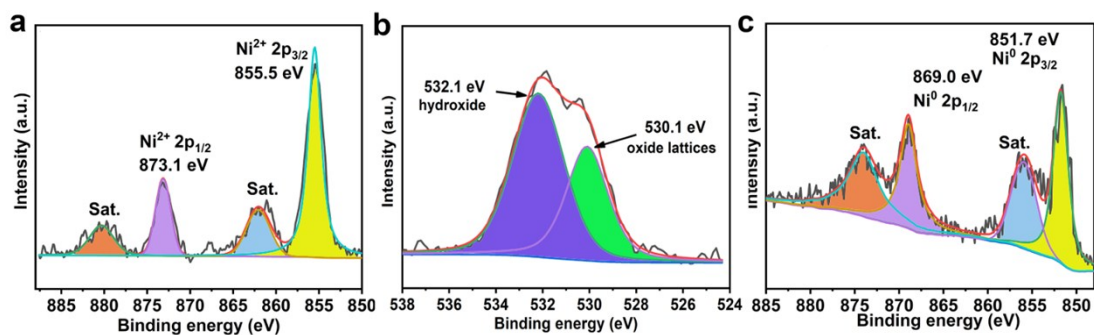


Fig. S4 (a) Ni 2p XPS spectra for TaON@Ni(OH)₂-0.1. (b) O 1s XPS spectra for TaON@Ni(OH)₂-0.1. (c) Ni 2p XPS spectra for TaON@Ni-0.1.

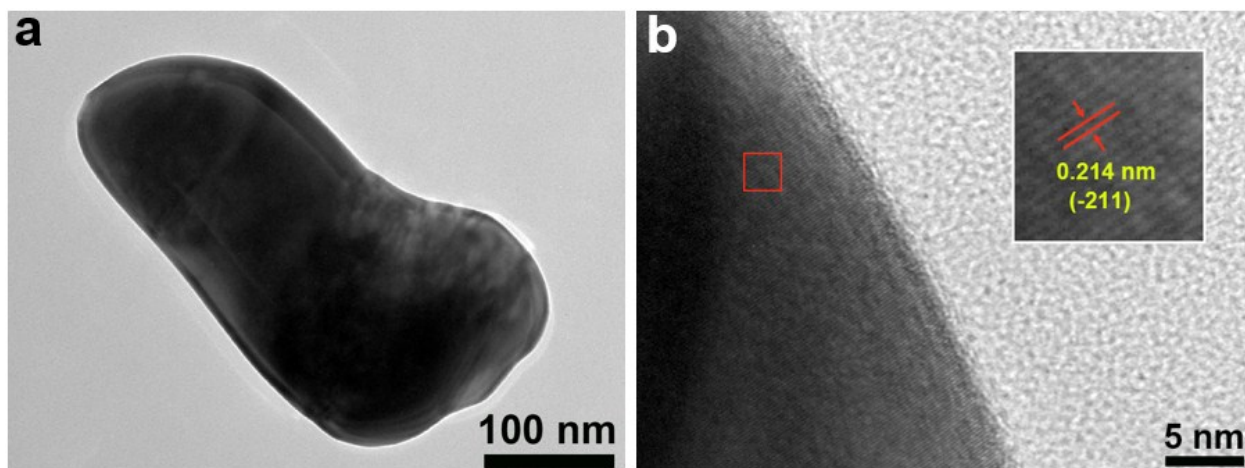


Fig. S5 The TEM (a) and HRTEM (b) images of as-synthesized TaON(H) sample.

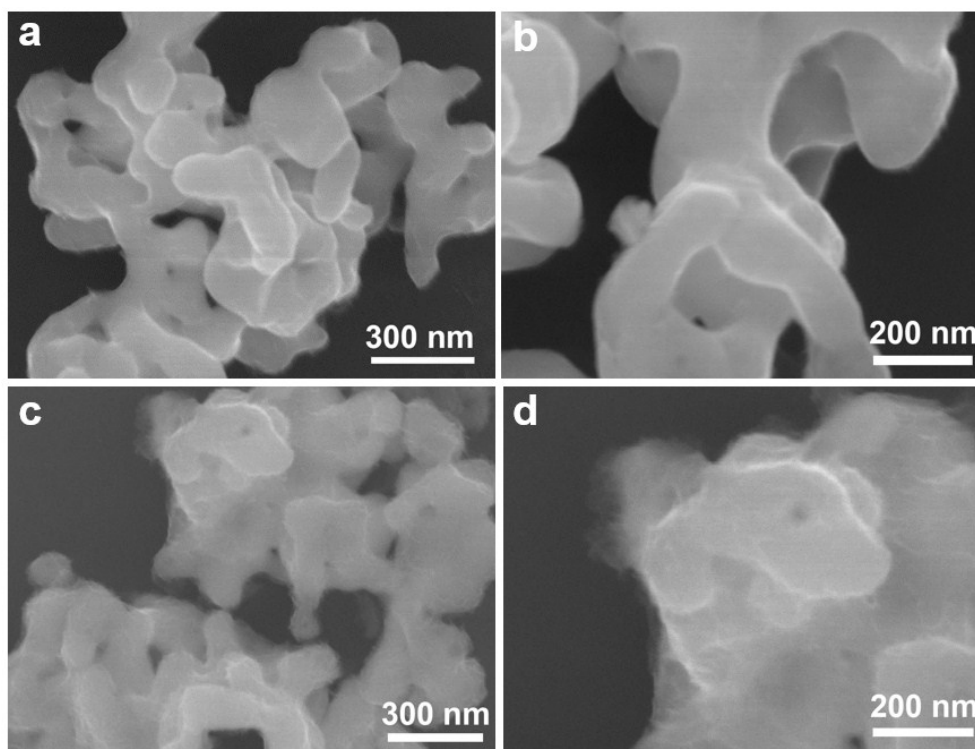


Fig. S6 (a, b) SEM images of TaON@Ni(OH)₂-0.05. (c, d) SEM images TaON@Ni(OH)₂-0.2.

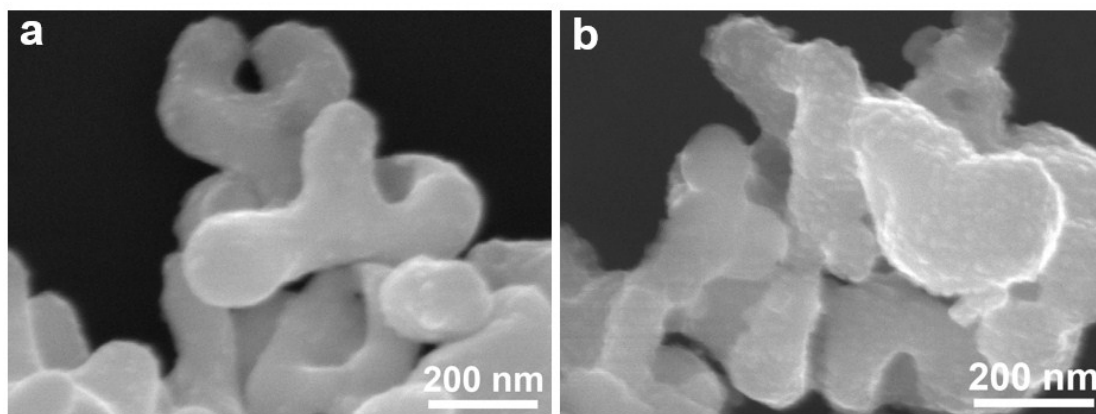


Fig. S7 SEM images of (a) TaON@Ni-0.05 and (b) TaON@Ni-0.2, respectively.

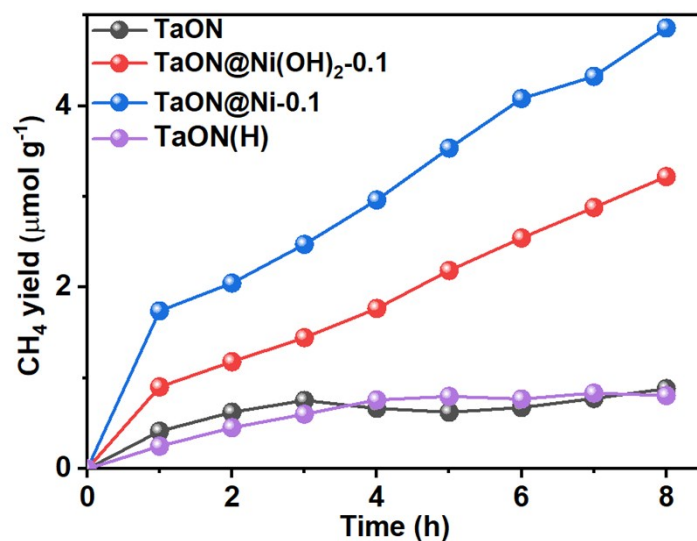


Fig. S8 CH₄ yields as a function of visible-light irradiation times ($\lambda > 420$ nm) of various TaON-based photocatalysts.

All the samples presented a relatively high CH₄ yield in the first hour and a stable CH₄ yield in the subsequent 7 h. In general, the fast CH₄ generation in the first hour probably resulted from the sufficient CO₂ adsorption on the fresh surface of the catalysts. Furthermore, the adsorption of intermediates formed on photocatalyst surface during the reaction process may also affect the reaction kinetics.

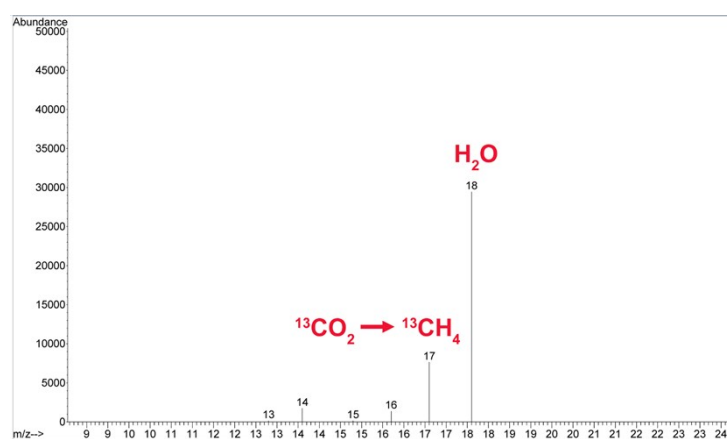


Fig. S9 GC-MS results of ¹³CH₄ produced over TaON@Ni-0.1 from ¹³CO₂ isotope experiment.

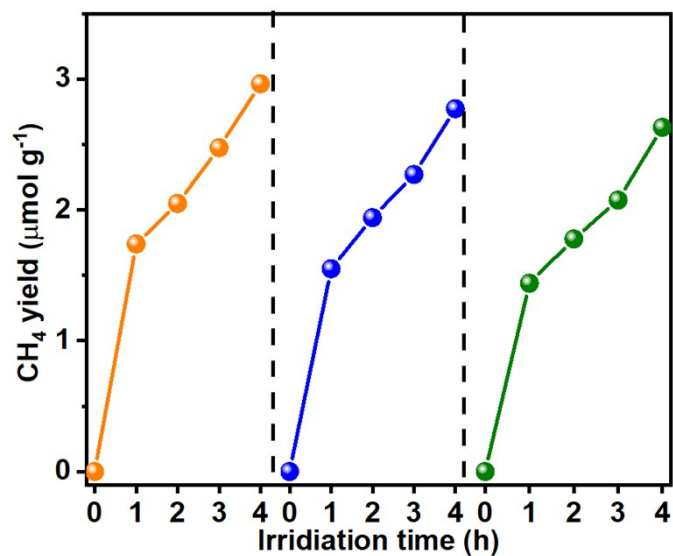


Fig. S10 Cycling curves for CH₄ production over TaON@Ni-0.1 hybrid.

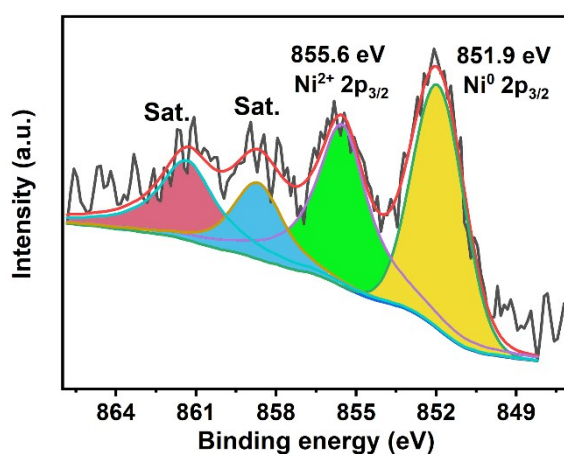


Fig. S11 Ni 2p XPS spectra for TaON@Ni-0.1 after photocatalytic reaction.



Fig. S12 The photographs of as-synthesized TaON, TaON@Ni(OH)₂-0.1, and TaON@Ni-0.1, respectively.

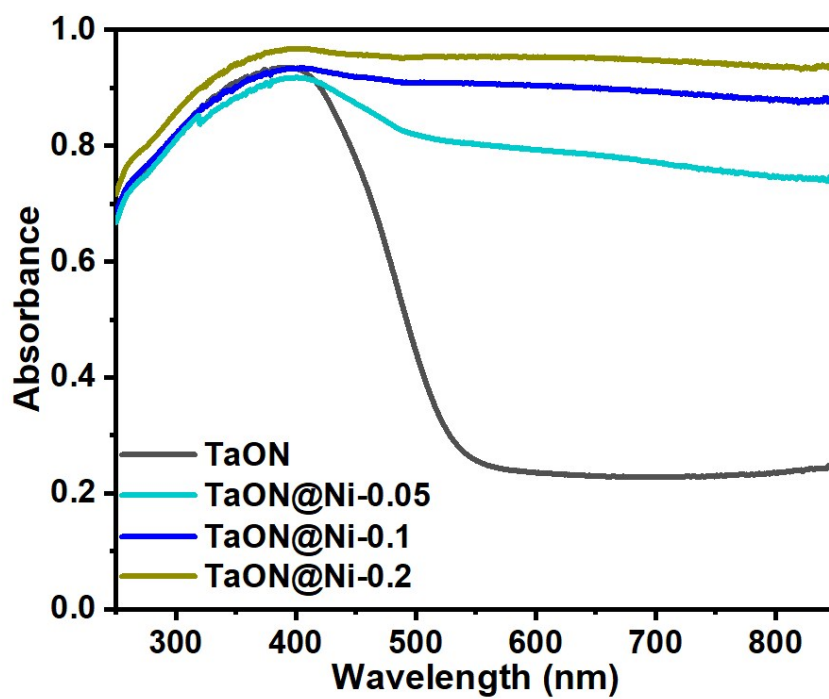


Fig. S13 UV-vis absorption spectra of the as-synthesized TaON, TaON@Ni-0.05, TaON@Ni-0.1, and TaON@Ni-0.2, respectively.

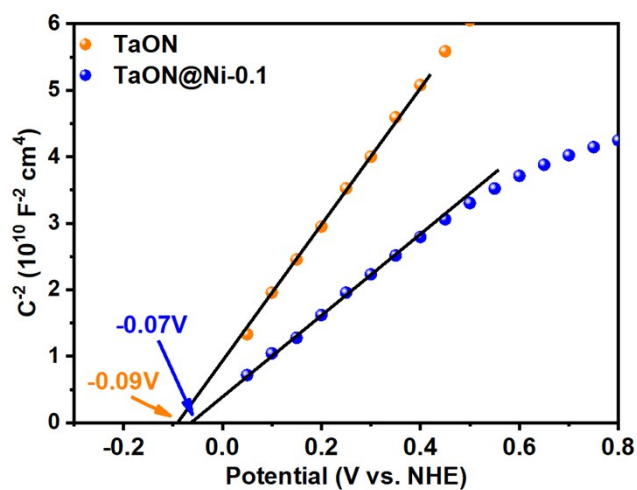


Fig. S14 M-S plots for TaON and TaON@Ni-0.1 photoelectrodes.

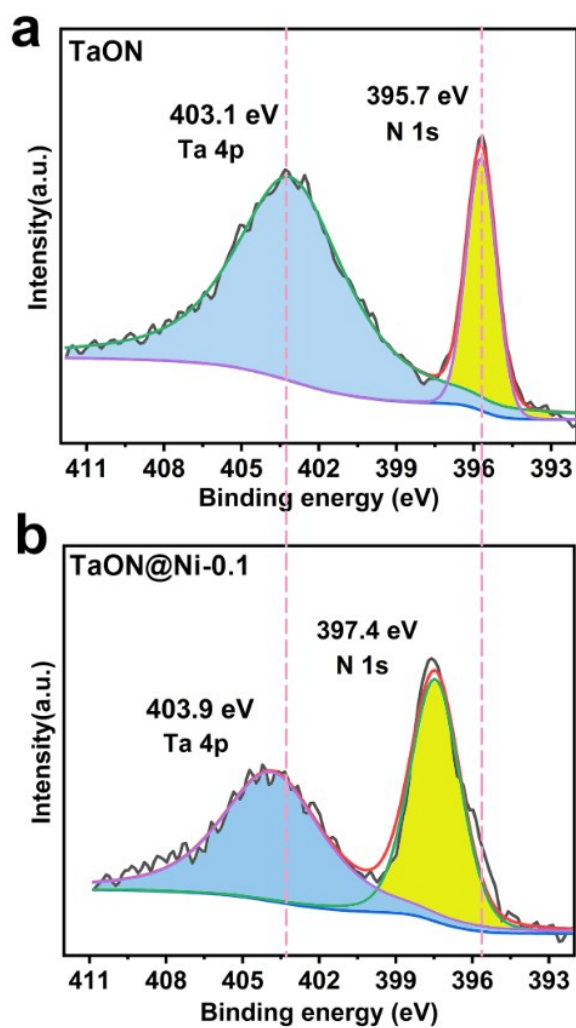


Fig. S15 High-resolution XPS spectra of N 1s and Ta 4p of (a) TaON and (b) TaON@Ni-0.1, respectively.

References

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