Electronic Supporting Information:

Crystallization-suppressed annealing preserves amorphous TiO_2 interfaces and strengthens Pt coupling for photocatalysis

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Materials

Preparation of NVCN

Dissolve 15 g of urea in an aqueous KOH solution (0.01 g KOH in 30 mL H_2O) under stirring for 30 min. Evaporate the resulting solution to dryness overnight in an oven at 80 °C. Calcine the dried solid in a muffle furnace at 500 °C for 3 h at a heating rate of 10 °C min^{-1}. After cooling the crucible to room temperature, wash the product three times with deionized water and dry at 60 °C overnight. Collect the obtained NVCN nanosheets for subsequent use.

Preparation of NVCN/Pt/aT_0

Disperse 0.2 g of freshly prepared NVCN nanosheets in 200 mL of ethanol and ultrasonicate for 1 h. Add $(NH_4)_2SO_4$ (0.33 g in 2.5 mL) and $H_2PtCl_6 \cdot 6H_2O$ (0.01 g in 1 mL), stir to mix thoroughly, and continue ultrasonication for another 1 h. Then add 0.9 mL of ammonia solution dropwise to the suspension and stir for 0.5 h. Next, inject 1.5 mL of Tetrabutyl Orthotitanate (TBOT) into the mixture, seal, and stir at 45 °C for 20 h, followed by natural cooling to room temperature. After washing, dry in a vacuum oven at 60 °C for 24 h.

Preparation of NVCN/Pt/aT

NVCN/Pt/aT_0 were treated in Ar at 450°C for 2.5 h.

Preparation of NVCN/Pt/TiO_2

NVCN/Pt/aT_0 were treated in air at 450°C for 2.5 h.

Characterizations

The morphology and microstructure was characterized by scanning electron microscope (SEM, Hitachi SU8010, Tokyo. Japan), transmission electron microscope (TEM, JEOL JEM-F200, JAPAN), X-ray diffraction (XRD, Empyrean, PANalytical B.V, Almelo, Netherlands), and X-ray photoelectron spectroscope (XPS, Thermo fisher Nexsa, Waltham, MA, USA).

Photocatalytic hydrogen evolution test

The hydrogen production experiments were performed on a Trace Gas Reaction Evaluation System (6A, Beijing Perfectlight). Typically, 5 mg of NVCN/Pt/aT was dispersed in 100 mL of an aqueous triethanolamine solution (10 vol%). The reaction was carried out under a 300 W xenon lamp (Zhongjiao Jinyuan) equipped with a 420 nm cutoff filter. Prior to irradiation, the system was evacuated for 30 min. Hydrogen was quantified/analyzed using a gas chromatograph (GC-9790, Fuli) equipped with a thermal conductivity detector (TCD) and a molecular sieve column.

Photoelectrochemical measurements

Electrochemical impedance spectroscopy (EIS) and transient photocurrent responses were recorded in

0.2 M Na_2SO_4 using a platinum Sheet as the counter electrode and fluorine-doped tin oxide (FTO) as the working electrode. The working electrode was prepared by ultrasonically dispersing 20 mg of the sample in 200 μL ethanol and 20 μL Nafion to form a suspension, drop-casting it onto an FTO glass substrate, and drying overnight.

Computational details

Based on spin-polarized density functional theory (DFT), calculations were performed using the Vienna Ab initio Simulation Package (VASP). The ion-electron interactions and the exchange-correlation energy were described by the projector augmented-wave (PAW) method and the generalized gradient approximation (GGA), respectively. A 30Å vacuum layer was introduced along the c axis. For surface optimization, the plane-wave energy cutoff was set to 500 eV, and a k-point mesh of 3 × 3 × 1 was used. The convergence thresholds for total energy and forces were 1×10^{-5} eV and 0.02 eV $Å^{-1}$, respectively. van der Waals (vdW) interactions were included at the DFT-D3 level. Molecular adsorption on the surface was calculated using the same settings as those for optimizing the corresponding bare surface.

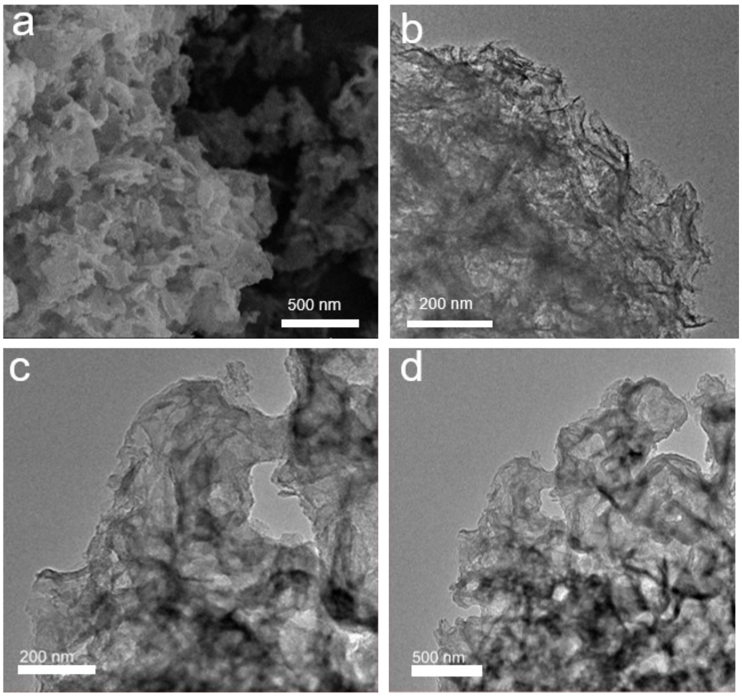

Figure S1. The (a) SEM and (b)TEM of NVCN/Pt/aT. (c,d)The TEM of NVCN/Pt/aT_0.

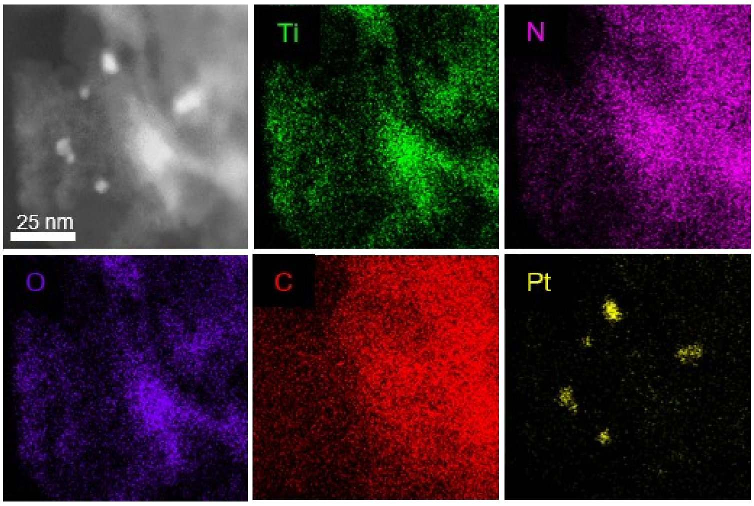

Figure S2. The TEM and EDS of NVCN/Pt/aT.

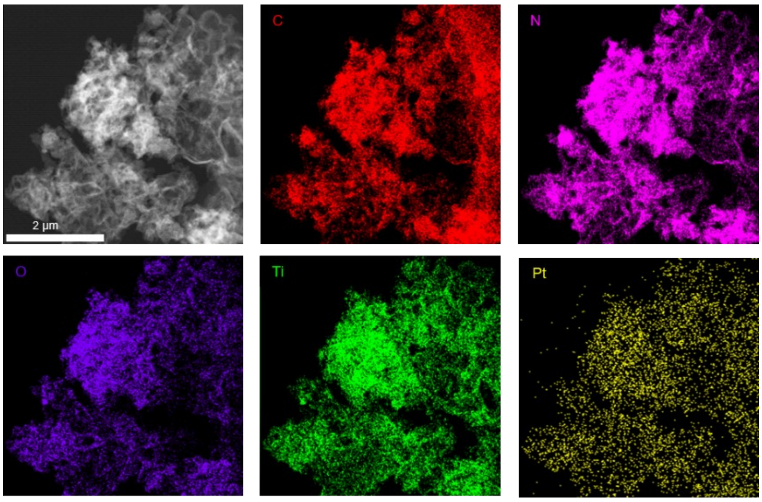

Figure S3. The TEM and EDS of NVCN/Pt/aT_0.

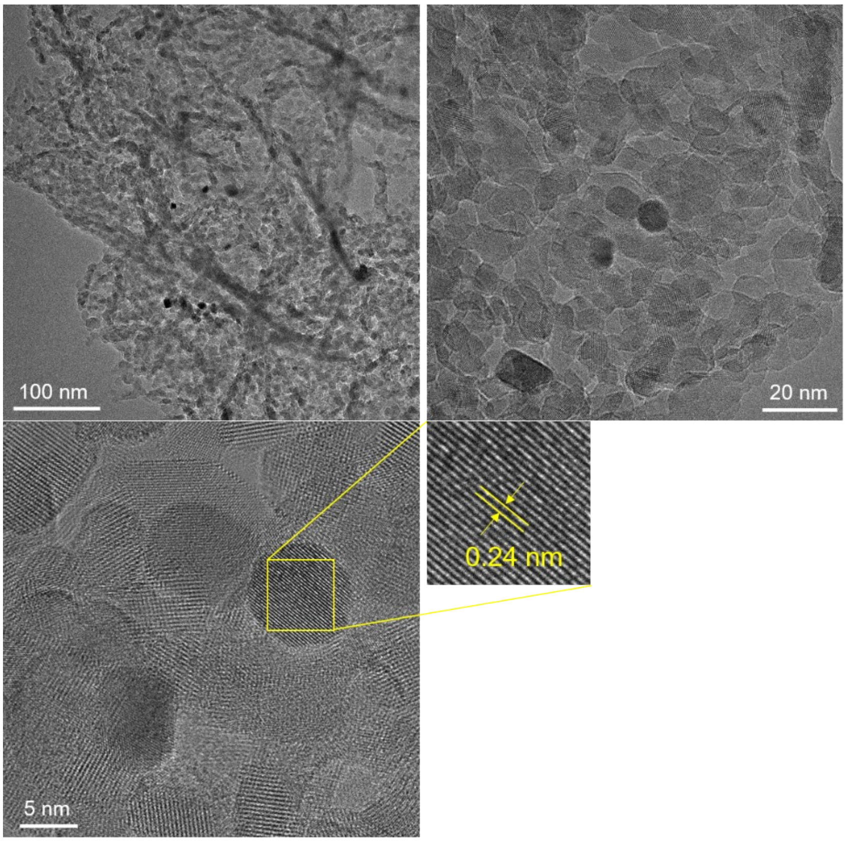

Figure S4. The (a,b) TEM and (c)HRTEM of NVCN/Pt/TiO$_2$.

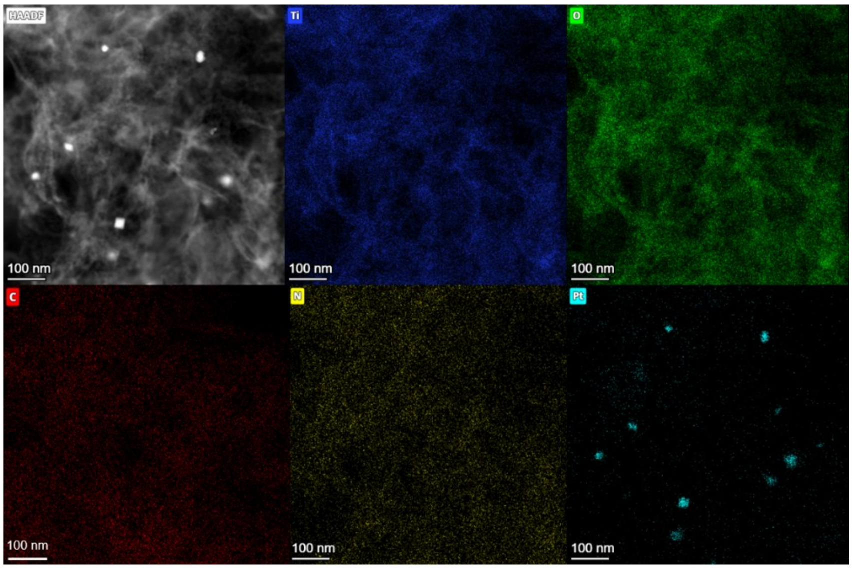

Figure S5. The EDS of NVCN/Pt/TiO$_2$.

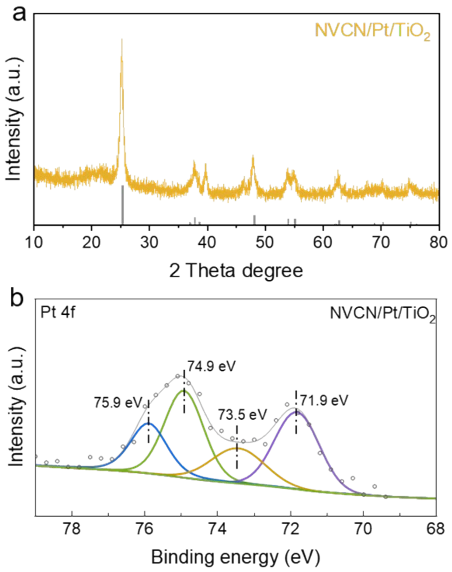

Figure S6. (a) The XRD and (b) Pt 4f XPS spectrum of NVCN/Pt/TiO_2.

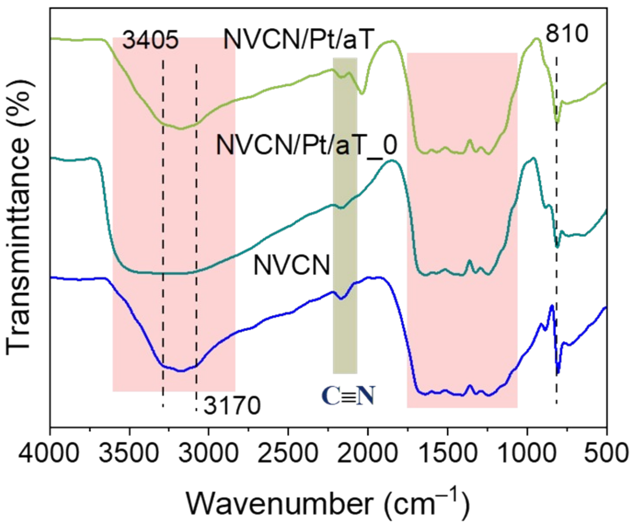

Figure S7. FTIR patterns of NVCN, NVCN/Pt/aT_0 and NVCN/Pt/aT catalysts..

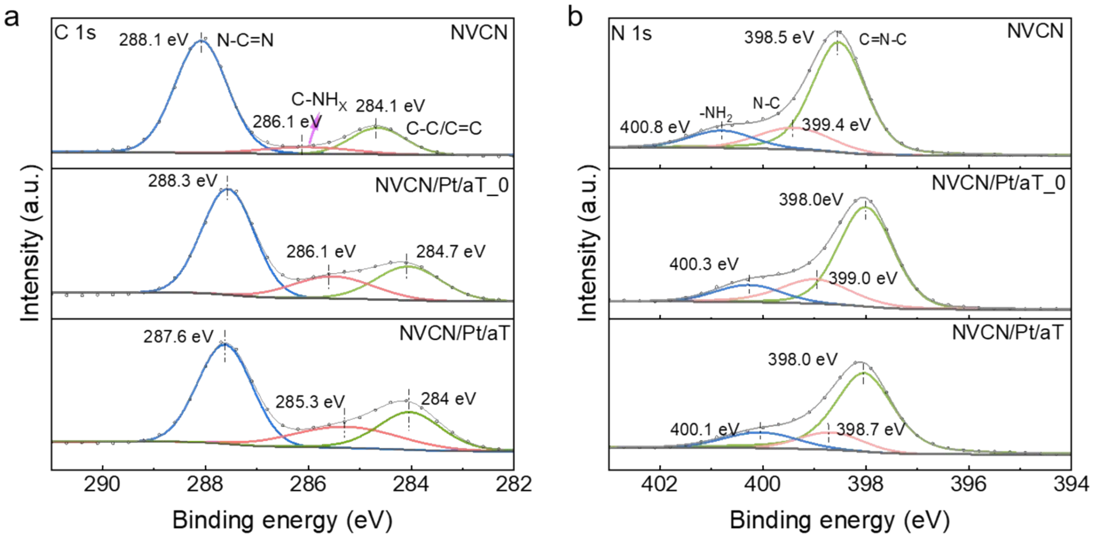

Figure S8. XPS spectra of NVCN, NVCN/Pt/aT_0 and NVCN/Pt/aT. (a) C1s and (b) N1s.

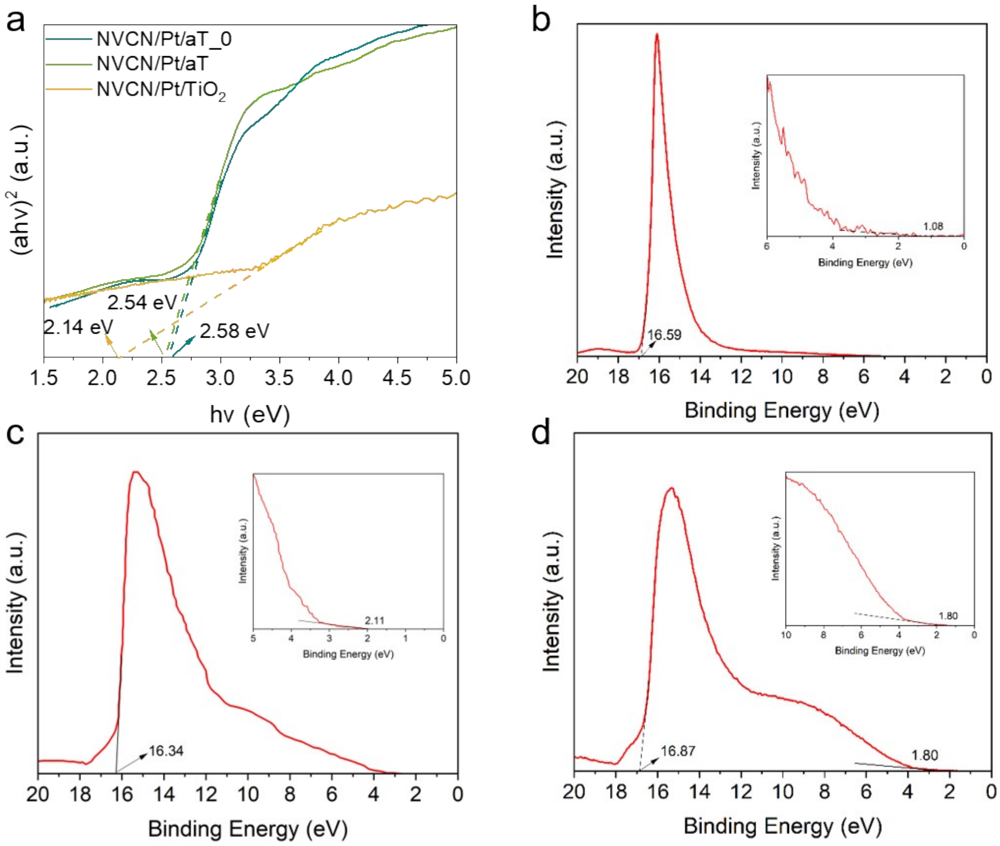

Figure S9. The (a) Tauc plots for bandgap estimation. UPS spectra of (b) NVCN/Pt/aT_0, (c) NVCN/Pt/aT and (d) NVCN/Pt/TiO_2.

The E_{VB} algorithm is as follows:

$$E_{VB} = h\nu - (E_{\mathrm{cutoff}} - E_{\mathrm{onset}})$$

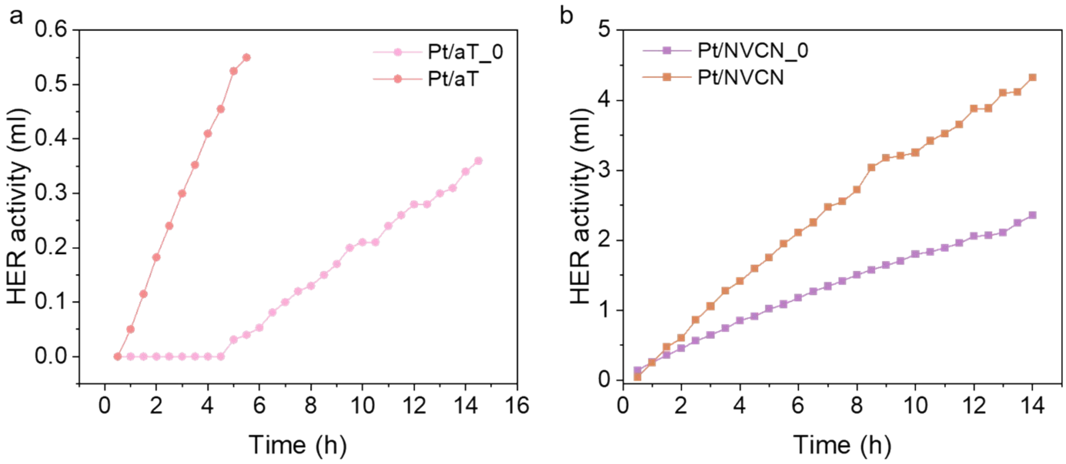

Figure S10. Catalytic performances of (a) Pt/aT and (b) Pt/NVCN before and after annealing.