Supplementary Information (SI) for Nanoscale.

Supporting Information

Loading Pt clusters is more conducive to improving photocatalytic hydrogen evolution performance compared to single atoms and particles

Experimental section.

Chemicals. Tetrabutyl titanate (TBOT), chloroplatinic acid (H_2PtCl_6), disodium ethylenediaminetetraacetate (EDTA-2Na), and polyvinylpyrrolidone (PVP-K20) were purchased from Aladdin Chemical Reagent Co., Ltd. All commercially available reagents and solvents are used as is and do not require further purification.

Preparation of TiO_2 nanosheets. The specific steps are as follows: add 3ml of HF dropwise to 25ml ($Ti(OBu)_4$) under vigorous stirring and keep for 10 minutes. Then transfer the mixture to a 50ml high-pressure vessel and place it at a constant temperature of 150 ℃ for 2 hours. Wash the obtained precipitate several times with water and ethanol, then dry the precipitate overnight under vacuum at 60 ℃ and calcine it at 350 ℃ for 2 hours to obtain TiO_2 nanosheets.

Material characterizations. To characterize the crystal structures of catalysts, powder X-ray diffraction (XRD) was conducted using a PANalytical X'Pert Power apparatus (Netherlands) operated at Cu Kα radiation. Transmission electron microscopy (TEM, Thermo Fisher Scientific Talos F200S) was utilized to investigate the morphology of the samples. HAADF-STEM images and STEM-EDS mapping images of samples were collected on a FEI Titan Themis. The X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi) was performed to explore the surface composition, where the C 1s peak at 284.8 eV (i.e. the surface adventitious carbon) was used as the calibration peak. UV-vis were collected on Shimadzu UV-3600 spectrometer (BaSO4 as a reference background, absorbance was calculated using the Kubelka-Munk method). Time-resolved fluorescence emission spectra (TRPL) were collected on a fluorescence spectrophotometer (FLS1000) at room temperature. A steady state fluorescence spectrometer (Shimadzu RF-6000) was utilized to get the photoluminescence spectra (PL).

Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution experiment was performed in a Pyrex vessel connected to a closed glass circulation and evacuation system (Beijing Perfectlight, Labsolar-6A). A 300 W Xe lamp was used as a light source. A 20 mg of photocatalysts dispersed in 100 ml of solution containing 10 % (v/v) methanol was prepared with distilled water. Firstly, the slurry in the reactor was vacuumed for 30 minutes in order to remove the dissolved gas molecular and to assure that the reactor can be operated in an anaerobic condition. During the photocatalytic hydrogen production test, the catalyst was kept in suspension by continuous magnetic stirring at room temperature during the whole experiment. The reaction was conducted at 25 °C and controlled by cooling circulating water. During hydrogen evolution, the evolved H2 was measured by chromatograph (GC7900, Techcomp) with a TCD detector using Ar as the carrier gas. In addition, the wavelength-dependent apparent quantum yield

(AQY) was measured under a 300 W Xe lamp with monochromatic light (λ = 350/380 nm). The AQY was calculated by the following equation:

$$AQY = \frac{2 \times number\ of\ evolved\ H_2\ molecules}{number\ of\ incident\ photons} \times 100\%$$

Photoelectrochemical measurements

The three-electrode system was used to achieve the electrochemical impedance spectroscopy (EIS), Mott-Schottky (MS) test and photocurrent measurements by electrochemical workstation (Zahner CIMPS-2). All the measurements were performed on a standard three-electrode system using Pt plate as the counter electrode, saturated calomel electrode as the reference electrode, and 0.4 M Na2SO4 as the electrolyte. The glassy carbon working electrode was made as follows: a combination of 20 mg of the photocatalytic material and 2.5 mg of acetylene black was homogenized by grinding for a duration of 10 min. It was then added to a solution containing 1.2 μL of polytetrafluoroethylene (PTFE) and 600 μL of anhydrous ethanol and sonicated to obtain a uniformly dispersed suspension. The suspension was then coated on a 1 × 1 cm^2 FTO glass. It was dried in an oven at 60 °C and kept for later use.

DFT Calculations Details and Models

Computational Details. All calculations in this work were performed using the Vienna Ab-initio Simulation Package (VASP5.4.4) package. We utilized the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional (GGA+PBE) to capture the exchange-correlation interactions. The electron-ion interaction was described using the Projector-Augmented Wave (PAW) method, focusing on the electronic structure of TiO_2 to mitigate the underestimation of the electronic band gap and counteract the excessive delocalization of electron density. A Hubbard U parameter of 4.0 eV for titanium was set for Ti, enhancing the qualitative representation of TiO_2's structural and electronic characteristics. The PAW method explicitly treated the electrons of oxygen (2s, 2p), titanium (3p, 4s, 3d), and platinum (6s, 5d), with a plane-wave basis set cut-off energy of 400 eV. For structural optimizations, we sampled the Brillouin zone using a 1x1x1 k-point grid, automatically generated via the Monkhorst-Pack method, and employed a denser 3x3x1 k-point mesh for electronic properties calculations. The convergence criteria were set at 10^{-4} eV for energy and 0.02 eV/Å for force.

Model for Pt/TiO_2 Composites. To model Pt clusters, a large supercell approach was adopted for the anatase (101) surface, consisting of a (2x3) periodic slab with three TiO_2 layers (72 Ti and 36 O atoms) and a 15 Å vacuum space to prevent periodic image interactions. For the reduced TiO_2(110) surface simulation, we removed two rows of bridge oxygen atoms. Three Pt configurations on TiO_2(101) were investigated: Pt_P/TiO_2, featuring a 27-atom trilayer Pt(111) nanoparticle on the pristine three-layered TiO_2(110) surface; and Pt_{SA}/TiO_2 and Pt_C/TiO_2, with the Pt cluster initially modeled based on the gas-phase stable, high-symmetry icosahedral Pt_{13} cluster.

Thermodynamic Analysis of HER. Based on the widely-used computational hydrogen electrode (CHE) model, the Gibbs free energy changes for HER are calculated. The HER is described by the following reaction:

$$H^+ \, (aq) + \; e^- \rightarrow 1/2H_2 \, (g) \, (\Delta G_{*H})$$

At electrode potential U = 0 V (versus RHE), the Gibbs free energy change (ΔG) is given by:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta E_{sol}$$

, where ΔE signifies the energy differential between various intermediates as derived from DFT calculations. ΔE_{ZPE} accounts for the corrections due to zero-point energies, and $T\Delta S$ represents the entropy changes at room temperature (298.15 K), both of which are essential for achieving a comprehensive thermodynamic assessment. Additionally.

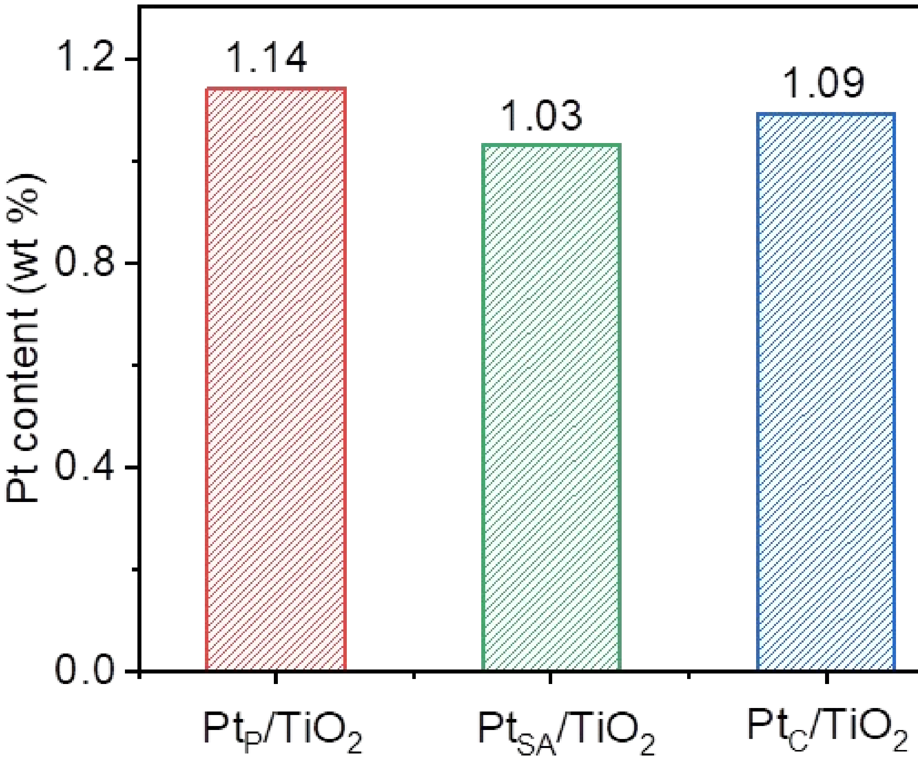

Fig. S1. Mass content of Pt. Comparing the Pt content on the Pt_P/TiO_2, Pt_{SA}/TiO_2 and Pt_C/TiO_2.

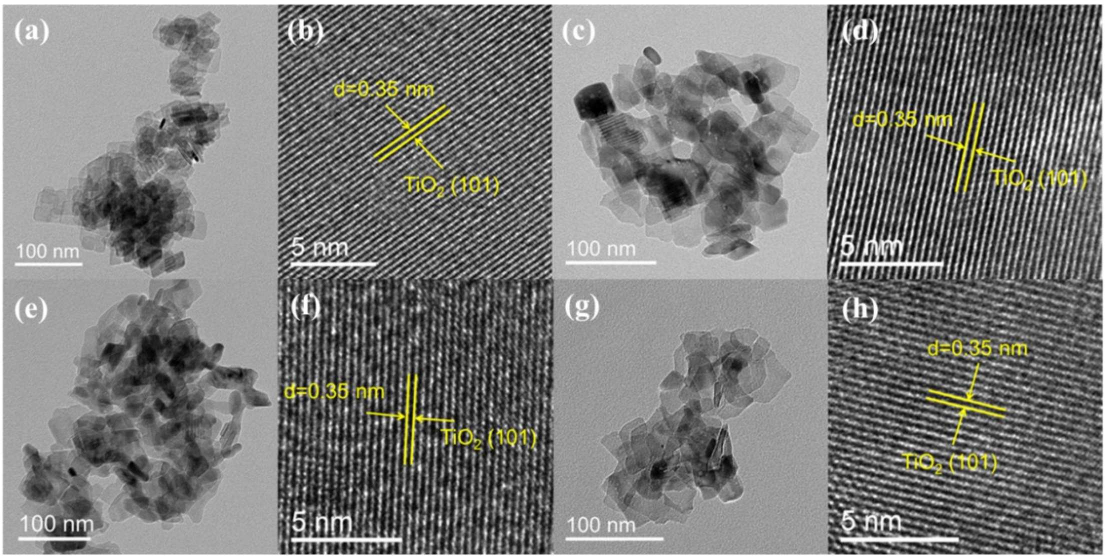

Fig. S2. TEM images of (a-b) TiO_2, (c-d) Pt_P/TiO_2, (e-f) Pt_{SA}/TiO_2 and (g-h) Pt_C/TiO_2 materials

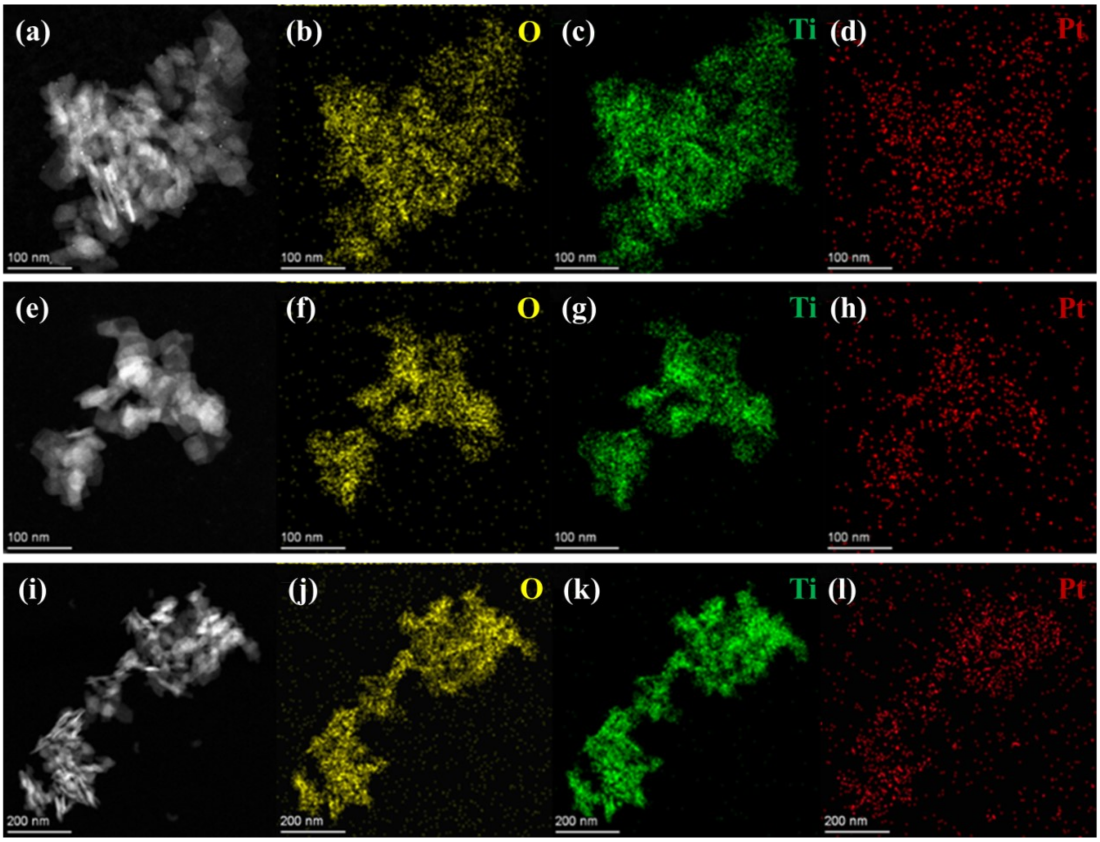

Fig. S3. Elemental mappings of O, Ti and Pt. (a-d) Pt_P/TiO_2, (e-h) Pt_{SA}/TiO_2, (i-l) Pt_C/TiO_2.

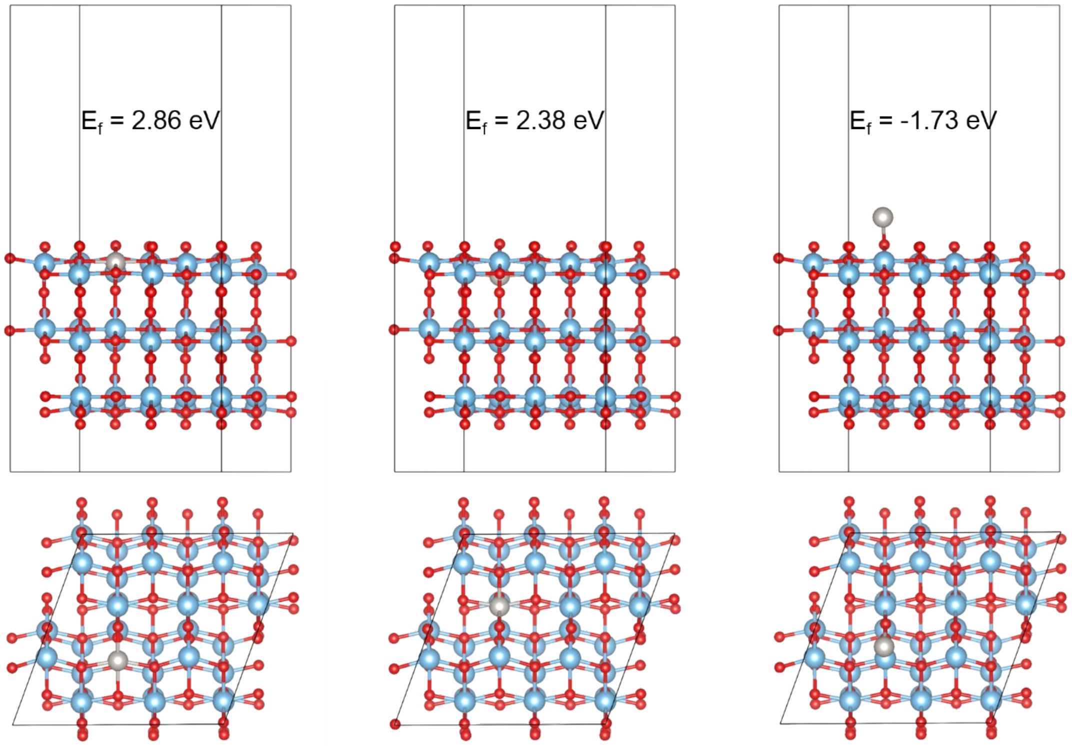

Fig. S4. Schematic illustration of possible Pt candidate binding sites on anatase TiO_2 (101) surface and their corresponding formation energy based on the DFT results. (a) Pt substituted Ti 5c site, (b) Pt substituted Ti 6c site, (c) Pt adsorption on TiO_2 (101) surface. The blue, red, silvery and white ball color represent Ti, O, Pd and H atoms, respectively.

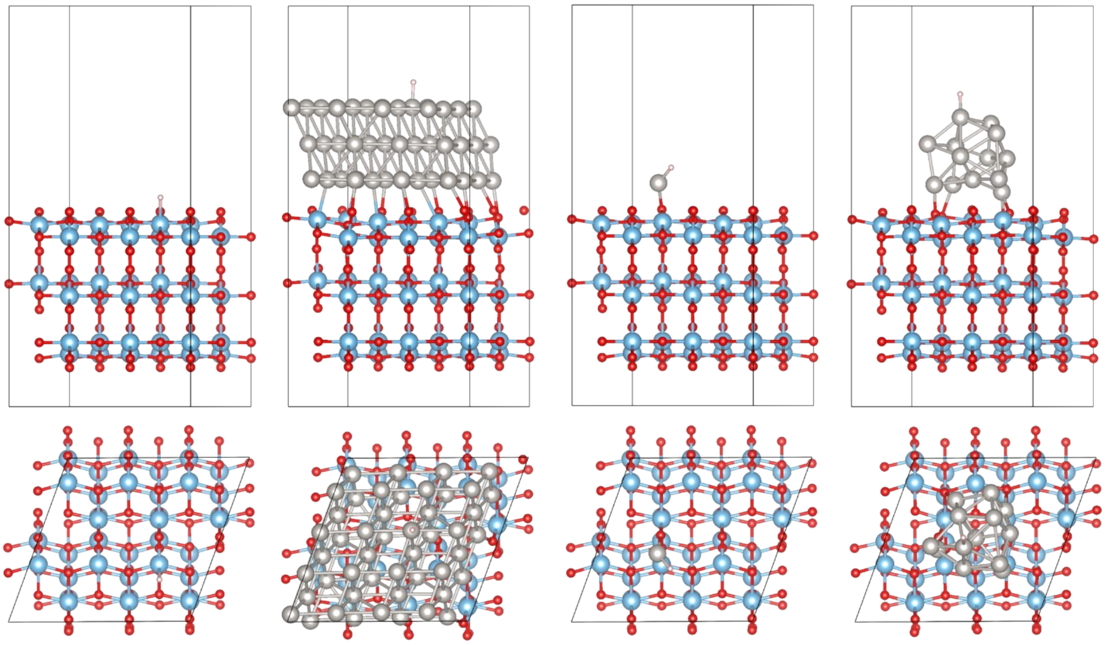

Fig. S5. Optimized structural models and configuration of hydrogen adsorption of TiO_2, Pt_P/TiO_2, Pt_{SA}/TiO_2 and Pt_C/TiO_2.

Sample	Parameters	Lifetime(ns)	Relative percentage	χ^2	Average lifetime(ns)
TiO_2	τ_1	1.1907	68.67	1.0407	4.8151
	τ_2	12.7590	31.33		
$Pt_P/TiO2$	τ_1	1.3976	54.12	1.0670	8.7374
	τ_2	17.3954	45.88		
$Pt_{SA}/TiO2$	τ_1	1.2544	53.70	1.1209	6.9036
	τ_2	13.4548	46.30		
$Pt_C/TiO2$	τ_1	1.4674	52.33	1.0912	9.5580
	τ_2	18.4395	47.67		

Tab. S1. Fitting data for TRPL.