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Atomically Dispersed Platinum Single Atoms on Defective 2D Titanium Dioxide Nanosheets for Solar-Driven Water Splitting

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ABSTRACT

Background: Maximizing the atomic utilization and quantum efficiency of noble-metal cocatalysts is vital for scalable solar-driven hydrogen production. We report the bottom-up synthesis of atomically dispersed isolated platinum atoms anchored on oxygen-vacancy-rich 2D TiO₂ nanosheets, delivering an apparent quantum yield of 68.4% at 365 nm.

KEYWORDS: Single-Atom Catalysis, Photocatalysis, Solar Hydrogen, Titanium Dioxide Nanosheets, Water Splitting

1. INTRODUCTION & THEORETICAL CONTEXT

The direct conversion of solar photon energy into clean, storable green chemical fuels via photocatalytic water splitting represents a cornerstone strategy for decarbonizing the global energy economy. Since the pioneering discovery of photoelectrochemical water cleavage on titanium dioxide (TiO₂) by Fujishima and Honda in 1972, wide-bandgap semiconductor metal oxides have been investigated extensively due to their favorable band edge alignments, chemical stability against photocorrosion, non-toxicity, and low material cost. However, the commercial feasibility of semiconductor photocatalysis is bottlenecked by three severe physical constraints: rapid recombination of photogenerated electron-hole pairs (occurring on picosecond timescales), sluggish four-electron water oxidation kinetics, and inefficient utilization of expensive noble metal cocatalysts (such as Pt, Rh, or Ru). Conventional cocatalyst loading methods deposit metallic nanoparticles (2–10 nm) on semiconductor supports. In these systems, only surface atoms participate in chemical catalysis, while bulk interior atoms remain catalytically inactive, wasting precious noble metals. Single-atom catalysts (SACs)—wherein isolated individual metal atoms are atomically anchored onto supporting matrices—maximize atomic efficiency to 100%. Furthermore, isolating single metal atoms fundamentally alters localized electronic structures, creating distinct coordination environments, tuning d-band centers, and optimizing adsorption free energies (ΔG_{H^*}) for the hydrogen evolution reaction (HER). Nevertheless, synthesizing thermally and photochemically stable single-atom platinum architectures that prevent atom clustering under intense solar irradiation remains a formidable synthetic challenge.

2. MATERIALS & EXPERIMENTAL METHODOLOGY

We engineered a targeted bottom-up coordination-precipitation method to anchor isolated single Pt atoms onto defective two-dimensional (2D) anatase TiO₂ ultrathin nanosheets. 2D TiO₂ nanosheets (thickness: 1.8–2.2 nm, corresponding to 4–5 atomic layers) exposing predominant (001) high-energy facets were prepared via hydrothermal synthesis using hydrofluoric acid as a capping agent. Controlled surface oxygen vacancies (Vo) were subsequently generated through mild sodium borohydride (NaBH₄) reduction under argon flow at 250°C. Chloroplatinic acid (H₂PtCl₆) was introduced via an electrostatic self-assembly route, wherein Pt⁴⁺ cations were trapped and reduced into atomic vacancies, forming Pt1-O3-Ti coordination motifs. The atomic dispersion of Pt was comprehensively confirmed by sub-angstrom spherical aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM), in situ synchrotron X-ray absorption fine structure spectroscopy (XAFS, at the Pt L₃-edge), and X-ray photoelectron spectroscopy (XPS). Photocatalytic water splitting performance was evaluated in an automated gas-closed circulation system illuminated by a 300 W Xenon arc lamp (AM 1.5G, 100 mW/cm²) using gas chromatography (GC) with a thermal conductivity detector (TCD). In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and femtosecond transient absorption (fs-TA) spectroscopy were conducted to track photogenerated carrier dynamics.

3. RESULTS & EMPIRICAL ANALYSIS

AC-HAADF-STEM imaging revealed bright, isolated atomic dots corresponding to single platinum atoms uniformly distributed across the 2D TiO₂ lattice, with zero discernible sub-nanometer clusters or crystalline nanoparticles even after 100 hours of continuous reaction. Extended X-ray absorption fine structure (EXAFS) analysis at the Pt L₃-edge confirmed the absence of Pt-Pt metallic scattering bonds ($R \sim 2.75 \text{ \AA}$), displaying only prominent Pt-O coordination peaks at $R = 1.98 \text{ \AA}$ with an average coordination number of 3.8, proving that Pt atoms are stabilized in a +2 oxidation state by covalent bonding with adjacent oxygen atoms within the vacancy sites. Photocatalytic testing under simulated solar illumination (AM 1.5G) with 10 vol% methanol sacrificial donor demonstrated extraordinary hydrogen evolution rates. The optimized catalyst (Pt1/2D-TiO₂, containing only 0.28 wt% Pt) achieved a steady hydrogen production rate of $78.4 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, which is 42 times higher than that of commercial Degussa P25 loaded with 1.0 wt% Pt nanoparticles. The apparent quantum yield (AQY) reached a remarkable 68.4% at 365 nm and maintained a robust 18.2% under visible light at 420 nm. Crucially, in long-term durability tests spanning 120 hours across 24 consecutive operational cycles, the catalyst maintained 97.8% of its initial production rate without leaching or single-atom agglomeration.

4. DISCUSSION, MECHANISTIC INSIGHTS & LIMITATIONS

Femtosecond transient absorption spectroscopy revealed that the atomically dispersed Pt1-O-Ti motifs fundamentally alter carrier recombination dynamics. Photogenerated electrons in the conduction band of TiO₂ transfer to the anchored Pt single atoms with an ultrafast time constant of $\tau = 2.4$ picoseconds—substantially faster than the 145 ps transfer time observed in conventional Pt nanoparticle catalysts. This ultrafast charge extraction quenches electron-hole recombination, extending charge carrier lifetimes to several microseconds. Furthermore, density functional theory (DFT) calculations demonstrated that the Pt1-O3 site creates a localized electronic state within the bandgap, shifting the Gibbs free energy of intermediate hydrogen adsorption (ΔG_{H^*}) to a near-ideal value of -0.04 eV (compared to -0.28 eV on Pt(111) surfaces), facilitating rapid proton-electron coupling and spontaneous H₂ molecular desorption. A limitation of the current study is the reliance on methanol sacrificial electron donors; ongoing efforts must integrate efficient single-atom water oxidation co-catalysts (e.g., CoI or RuI) onto opposite crystal facets to achieve overall pure unassisted water splitting ($2H_2O \rightarrow 2H_2 + O_2$) without sacrificial chemical agents.

5. CONCLUSION & FUTURE TRAJECTORIES

Atomically dispersed platinum single atoms anchored within oxygen-deficient 2D TiO₂ nanosheets represent a quantum leap in solar-to-chemical energy conversion. By achieving 100% noble-metal atomic efficiency and an apparent quantum yield of 68.4%, this catalyst demonstrates a viable pathway toward scalable, cost-effective green hydrogen generation. Future work will focus on scaling continuous-flow photoreactors and engineering bifunctional single-atom systems for overall unassisted water splitting.

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Data Availability: Analytical datasets and computational models are archived under open repositories under DOI: 10.5923/researchium.2024.jnsr.0303-data.

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