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# Preparation of Noble Metal Nanoparticles and Their Application in Photocatalytic Water Splitting

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**Abstract.** Photocatalytic water splitting represents a sustainable method to the production of hydrogen, leveraging sunlight to drive the dissociation of water molecules into hydrogen and oxygen through the semiconductor photocatalysts enhanced by noble metal nanoparticles. This paper will explore the fundamental principles of photocatalysis, including energy band theory and the critical role of noble metals such as platinum, gold, palladium, and silver in facilitating electron transfer, reducing recombination, and improving catalytic efficiency. Key synthesis methods for noble metal nanoparticles, including chemical reduction, hydrothermal, and environmentally friendly approaches are discussed, emphasizing factors like particle size, shape, and surface modifications that influence its performance and stability. Applications in systems like CdS-based catalysts and phosphorus-modified palladium nanoparticles demonstrate significant enhancements in the rate of hydrogen evolution, with comparisons that highlight the trade-offs between activity, cost, and endurance. Challenges such as photocorrosion and electron-hole recombination are analyzed, alongside synergistic effects from plasmonic properties and multi-metal configurations. The discussion underscores the potential of optimized noble metal systems for efficient, large-scale hydrogen generation, while identifying future directions for improved stability and visible light utilization to advance clean energy technologies.

**Keywords:** Photocatalytic water splitting; noble metal; nanoparticles.

## 1. Introduction

Photocatalytic water splitting is a very exciting area of research because it offers a very “easy” way to produce hydrogen fuel using only very basic sources—sunlight and water. This approach relies on photocatalysts, which are materials that absorb light energy to break water molecules into hydrogen and oxygen. Unlike fossil fuels, which release harmful greenhouse gases like carbon dioxide during the production process, this one is clean and sustainable, making it an up-and-coming solution for storing solar energy. With global energy demands increasing and environmental problems from fossil fuels worsening, many countries, like those in the European Union, are setting ambitious renewable energy goals, such as reaching 32% renewable energy by 2030 [1]. Hydrogen is seen as a key green fuel because it can be made from solar or wind power and stored for later use, addressing the issue of inconsistent renewable energy sources. While water electrolysis powered by photovoltaic cells is efficient, it is too costly for widespread use, so researchers are now exploring cheaper alternatives like photocatalytic water splitting, which combines energy conversion and storage in only one step.

At the core of this process is photocatalysis, where light activates a photocatalyst to foster redox reactions without the material being consumed. When illuminated, the photocatalyst’s electrons are excited from the valence band to the conduction band, generating electron–hole pairs that drive chemical reactions [2]. Semiconductors like $TiO_2$ and CdS are commonly used here, as their band structures allow effective electron transfer and light absorption. However, a key limitation is the rapid recombination of these charge carriers, which lowers efficiency. To overcome this issue, noble metal nanoparticles such as Pt, Au, and Pd are introduced as cocatalysts. They can form Schottky barriers at the semiconductor interface, trapping electrons and promoting hydrogen evolution reactions. Their small size and high surface area enhance charge separation and provide more active sites for catalysis.

Additionally, plasmonic metals like Au and Ag extend light absorption into the visible range through localized surface plasmon resonance, further improving photocatalytic activity [3].

Air pollution is becoming a major global issue, especially in industrial and developing countries where vehicle exhaust can cause environmental and health problems. To find clean, sustainable fuels is essential, and hydrogen obviously stands out as a great option. Unlike fossil fuels, hydrogen almost cannot be found naturally, instead it is an energy carrier, like electricity, that must be produced artificially. When burned, it mainly produces water, with only tiny amounts of nitrogen oxides, making it nearly pollution-free [4]. It burns quickly, has a high octane rating, and avoids creating toxic or ozone-forming substances, which makes it ideal for vehicles and power generation. Hydrogen can be made from renewable sources, such as through photocatalytic water splitting, allowing solar and wind energy to be converted into fuel without harmful carbon emissions. This not only reduces reliance on fossil fuels but also supports cleaner air, especially in large concrete jungles with poor air quality. However, efficient and affordable hydrogen production methods are in need, and photocatalytic water splitting with noble metal nanoparticles shows great potential for large-scale clean fuel production under mild conditions [5].

## 2. Synthesis of Noble Metal Nanoparticles

### 2.1. Common Preparation Methods

Broadly speaking, there are two approaches that can make noble metal nanoparticles: top-down or bottom-up. Top-down methods start with the original bulk metal and reduce it through physical processes like milling, but these often result in rough surfaces and varied sizes, limiting precision. Bottom-up methods build nanoparticles from atoms or clusters, offering a more controllable and less costly way [6].

### 2.1.1. Chemical Reduction

Chemical reduction, a popular bottom-up method, can reduce metal ions in solution with a reducing agent and stabilizers to prevent clumping. By adjusting agents, solvents, and stabilizers, researchers control nucleation and growth, affecting size and distribution. For example, citrate reduction produces gold and silver nanoparticles with diameters from a few to tens of nanometers.

### 2.1.2. Sol-gel Method

The sol-gel method involves hydrolysis and condensation of metal precursors to form a gel, yielding uniform nanoparticles in a matrix. Hydrothermal synthesis, using high temperature and pressure in water, creates specific shapes and narrow size distributions.

### 2.1.3. Photochemical Method

Photochemical methods, driven by light, are energy-efficient and control facets via wavelength and intensity. Green synthesis, using natural reducing agents, can minimize toxic waste and produce high-quality particles at the same time. Purification, through washing or centrifugation, removes impurities for applications in catalysis [7].

### 2.2. Factors Affecting Particle Size, Shape, and Distribution

Particle size and shape determine a lot of factors, such as surface area, optical properties, and interactions, making nucleation and growth control critical. High nucleation rates produce plenty of small particles, while slower growth leads to larger ones. Stabilizers, solvents, temperature, and reagent concentrations influence all these processes. Capping agents bind to specific crystal planes, shaping particles into geometries like spheres, cubes, or rods [8]. Achieving narrow size distributions requires balancing rapid nucleation and controlled growth. Poor dispersion will cause aggregation, reducing active surface area. Shapes like rods or platelets expose different facets, affecting catalytic activity. Size and distribution are measured using techniques like TEM, SEM, and UV-Vis spectroscopy [9].

### 2.3. Stability and Surface Modification Techniques

Stability is very important to prevent aggregation, preserve activity, and resist environmental stress. Colloidal stability comes from electrostatic repulsion and steric stabilization via polymers or ligands. Surface modifications, like ligand exchange or thin coatings, can protect against oxidation and aggregation while enabling functionalization at the same time. However, thick coatings can block catalytic sites, so thin, porous layers are preferred the other way. In biomedical application areas, biocompatibility is key, and green synthesis can help by reducing toxic byproducts. Purification removes unreacted precursors, ensuring nanoparticles suit catalysis or sensing while maintaining accessible surfaces.

## 3. Application in Photocatalytic Water Splitting

### 3.1. CdS-Based Catalysts and Hydrogen Evolution

Cadmium sulfide (CdS) is widely-used in photocatalytic water splitting due to its ability to absorb visible light. However, rapid electron-hole recombination and photochemical corrosion reduce efficiency a lot, especially in conditions without sacrificial agents. Hydrothermal synthesis is common, with parameters like stirring speed, temperature, and time affecting particle size and surface area. For example, at 220°C and 600 rpm, CdS nanoparticles are uniform and achieve hydrogen production rates over 9000 $\mu mol \cdot h^{-1} \cdot g^{-1}$ [10]. Adding polyethylene glycol (PEG400) as a surfactant improves dispersion levels, increasing yields by 1.4 times and slightly shifting absorption to capture more visible light. Combining CdS with 10% silver sulfide (Ag2S) further boosts rates to over 17,000 $\mu mol \cdot h^{-1} \cdot g^{-1}$ by narrowing the bandgap and enhancing charge separation, as electrons transfer to Ag2S, reducing recombination. Techniques like XRD and SEM confirm uniform structures, but corrosion remains a challenge, pushing research toward better stability.

### 3.2. Pd-Based Nanoparticles and Phosphorus Modification

Palladium (Pd) is highly active for hydrogen evolution, but during reactions, it forms PdH, which blocks active sites and lowers performance [11]. Adding phosphorus (P) modifies the surface, reducing PdH formation and improving electron attraction. On P25 TiO2 supports, an optimal Pd-P ratio achieves rates over 4800 $\mu mol \cdot gPd^{-1} \cdot h^{-1}$ [12]. Excessive loading reduces active surface area due to shading or Coulomb blockade, where electrons struggle to move. Adding base metals like nickel (Ni) or copper (Cu) creates Pd-M-P alloys, enhancing light absorption via midgap states, but excessive additions cause larger, clumped particles. Binary Pd-P often outperforms alloys by keeping more Pd surfaces accessible. Careful element control makes Pd-P promising, but stability and optimal ratios need further study.

### 3.3. Comparison of Different Noble Metal Systems

Platinum (Pt), gold (Au), palladium (Pd), and silver (Ag) each offer unique benefits as co-catalysts. Pt excels in hydrogen evolution and charge separation but is costly and scarce. Au's plasmonic effects enhance light absorption, though its hydrogen activity is lower, and benefits depend on size and support. Ag, while affordable and plasmonic, is less stable under light. Pd balances cost and activity but faces poisoning issues. When paired with semiconductors like TiO2 or CdS, these metals improve charge separation and light harvesting. Pt often achieves the highest rates, but tuned Pd, Au, or Ag systems can approach its performance with less cost or more stability. The best choice depends on a summarization of activity, stability, cost, and semiconductor compatibility, with Pd and Au offering great potential when benchmarked against Pt [13].

### 3.4. Synergistic Effects and Mechanistic Insights

Noble metals enhance photocatalysis by improving light absorption, charge separation, and reaction kinetics. Au and Ag's plasmonic effects can extend visible light use, generating hot electrons for reduction. Pt and Pd excel in hydrogen evolution due to favorable adsorption, though performance depends on size and dispersion. Multi-metal strategies, like combining Au with Pd, create charge transfer pathways that reduce recombination. Spectroscopic and structural analyses reveal how band alignment and midgap states extend carrier lifetimes. Effective systems balance plasmonic enhancements with accessible catalytic sites, requiring precise control over particle size and interfaces [14].

## 4. Conclusion

This study highlights the transformative potential of noble metal nanoparticles in enhancing photocatalytic water splitting for hydrogen production. Semiconductors such as CdS and $TiO_2$ generate electron–hole pairs under light irradiation, but their efficiency is often limited by rapid recombination. Integrating noble metals like Pt, Au, Pd, and Ag as cocatalysts form Schottky barriers that trap electrons, extend carrier lifetimes, and accelerate hydrogen evolution reactions. Synthesis methods, particularly chemical reduction and hydrothermal processes, allow precise control over nanoparticle size and distribution, directly influencing surface area and catalytic performance. Pt remains the most effective in promoting charge separation, while Pd and Au provide cost-efficient alternatives with plasmonic enhancements that broaden light absorption. Despite challenges such as photocorrosion and nanoparticle aggregation, these tailored systems significantly improve photocatalytic activity. Future developments may involve alloying noble metals with base metals, optimizing light absorption using hybrid plasmonic structures, and improving stability through protective coatings. With advances in computational modeling and scalable green synthesis, noble metal-based photocatalysts could accelerate the shift toward a sustainable hydrogen economy, supporting global clean energy transitions and reducing dependence on fossil fuels.

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