



Exploring the mechanisms of metal co-catalysts in photocatalytic reduction reactions: Is Ag a good candidate?

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ABSTRACT

Metal co-catalysts are essential for enhancing photocatalytic performance, especially in reduction reactions using semiconductor photocatalyst materials as a consequence of the reduced recombination kinetics of charge carriers by spatial charge separation. Generally Au, Pd, Pt, and their alloys are more promising candidates than Ag for photocatalytic H₂ evolution experiments, although Ag can trap more electrons having more negative reduction potential than that of Au, Pd, and Pt. Here we have synthesized and examined well-defined Au, Ag, and core-shell structured Au–Ag nanoparticles as co-catalysts for TiO₂ in photocatalytic H₂ evolution. By varying the dissolved oxygen in the reaction suspension, we found that selective photocatalytic reduction can be achieved by fine tuning the co-catalyst materials. Whilst Au NPs are superior for proton reduction, Ag NPs exhibits excellent performance for oxygen reduction. All core-shell structured Au–Ag NPs show non-selectivity in photocatalytic reduction of proton and oxygen.

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1. Introduction

Photocatalysis shows huge potential in water/air purification, organic synthesis, CO₂ reduction, and water splitting applications [1–4]. Upon irradiation with photon energy larger than that of the bandgap of a semiconductor photocatalyst, electrons (e⁻) from the valance band (VB) of the photocatalyst can be excited to the conduction band (CB), leaving holes (h⁺) in the VB. The separated e⁻ and h⁺ are capable of performing redox reactions with surface adsorbed electron acceptors (A) and donors (D) when the CB position is more negative than that of the redox potential of A and the VB position is more positive than that of the redox potential of

D, respectively. However, most pristine semiconductor photocatalysts are characterized by poor efficiencies due to rapid charge carrier recombination kinetics and very slow redox reaction rates, which limits the application of photocatalysis.

An effective approach to improve the photocatalytic performance of a pristine semiconductor photocatalyst is by surface modification of co-catalysts (*i.e.*, promoters), which may improve the spatial charge separation of charge carriers and also accelerate the redox reaction rates of the surface adsorbed A and D [5,6]. To facilitate the interfacial charge transfer, a physical contact of the semiconductor with the co-catalysts and a driving force (potential difference of the band positions) are essential in transporting the charge carriers from the semiconductor to the co-catalysts. Besides, it is also important that the spatially separated charge carriers at the co-catalyst can be utilized to perform reactions.

Metal (*i.e.*, Au, Pd, and Pt) nanoparticles (NPs), oxides (*i.e.*, RuO₂, NiO, and IrO₂), and even metal complexes (*i.e.*, [CoIII(dmgH)₂pyCl] and [(μ-SPh-4-NH₂)₂Fe₂(CO)₆]) have been employed as co-catalysts for various photocatalytic reactions [7–9]. Au, Pd, Pt, and the corresponding alloy NPs are the most extensively studied co-

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catalysts due to their superior performance and excellent stability. It was recently found that the core–shell structured Au–Pd and Au–Pt NPs exhibited significant enhanced performance for H₂ evolution and selective oxidation of benzene [10–13]. Kinetic analysis and theoretical calculations reveal that such enhanced photocatalytic performance observed for the core–shell NPs result from the improved charge trapping and releasing rates, which originated from the optimized density and position of unoccupied d orbital states of the metal NPs [10]. However, the scarcity of these metals limits large scale applications.

Partially replacing Pt, Pd, or Au by less expensive metals (*i.e.*, Ag and Cu) in the co-catalyst may solve this issue. Among these metal species, Ag has attracted great attention as a replacement of Au and Pt due to its relatively low price and suitable electronic properties for reduction reactions [14–16]. The work function of Ag is in the range of 4.3–4.7 eV depending on different crystal facets [17], which is slightly smaller than those of Au (5.1–5.4 eV) and Pt (5.1–5.9 eV), indicating a higher Fermi level (or more negative electrochemical potential) of the trapped e⁻ in Ag than that of Au and Pt. A lower work function also means that the Schottky barrier height at Ag/TiO₂ junction is smaller than that of Au/TiO₂ and Pt/TiO₂, indicating more electrons can go through the barrier and trapped by Ag [14]. Furthermore, the capacity of Ag NPs for trapping e⁻ is also better than that of Au and Pt. Takai and Kamat measured the e⁻ storage on Au, Pt, and Ag NPs injected from photoexcited TiO₂ by a titration method in deaerated conditions, and discovered that 440 e⁻ can be stored in 1 μM of Ag NPs, which is significantly better than using Au (280 e⁻/μM) or Pt (190 e⁻/μM) NPs [18]. It is speculated that two parameters may facilitate Ag NPs to trap more electrons than that of Au and Pt. First, the electronic conductivity of Ag (6.3 × 10⁷ S m⁻¹) is higher than that of Au (4.1 × 10⁷ S m⁻¹) and Pt (9.4 × 10⁶ S m⁻¹). Although these are measured using bulk materials, it indicates the electron transfer between Ag atoms is easier than that of Au and Pt, therefore avoiding collision and recombination of the photogenerated electrons. Second, AgO may also serve as an excellent electron trapping centre, and the existence of AgO on the surface of Ag should be possible in water–ethanol environment. Both parameters suggest that Ag NPs are promising candidates for photocatalytic reduction co-catalysts for H₂ evolution and CO₂ reduction. However, employing Ag NPs as co-catalyst typically shows relatively low photocatalytic reduction performances compared to those of Au and Pt [19–21], which was largely unexpected according to the prediction from the Fermi level and capacity for e⁻ storage. Tsukamoto et al., suggested that the poor performance of Ag NPs as a co-catalyst for H₂O₂ formation by O₂ reduction may originate from the relatively large Schottky barrier (~1.3 eV) at the photocatalyst (TiO₂ here)/Ag interface that hinders the charge transfer from TiO₂ to Ag, and alloying Ag with Au improves the performance due to reduction of the Schottky barrier [14]. Although this assumption did not agree with the titration results mentioned above [18], possibly due to the simplified assignment of the Schottky barrier energy, however, it indicates that the identity of e⁻ acceptor may alter the kinetics of trapped e⁻ thus influencing the performance. Nevertheless, different deposition methods result in variations of size, composition, and microstructure of the metal NPs, which complicates the interpretation of their intrinsic reactivities. Therefore the mechanisms of metal co-catalysts in photocatalytic reduction reactions are still unclear and require careful investigation.

Here we have investigated Au, Ag, and Au–Ag core–shell NPs with well-defined particle size, chemical compositions, and shell thickness as co-catalysts for photocatalytic reduction reactions using TiO₂ as the semiconductor photocatalyst. Photocatalytic hydrogen evolution at various dissolved oxygen concentrations have been performed to study how the co-catalysts interact with different electron acceptors (H⁺ and O₂). Three synthesis methods based on sol immobilization named photoreduction (PD), sequen-

tial reduction (SR), and double reduction (DR) have been utilized to deposit these metal NPs on TiO₂ surface to check if the preparation conditions have any influence on our observations.

2. Experimental

2.1. Materials synthesis

For the synthesis of core-shell structured metal NPs supported on TiO₂, we first prepared 1 wt% of Au supported on TiO₂ (Au/TiO₂) by standard sol immobilization [22]. An example for synthesis of 1 wt% Au–TiO₂ follows an aqueous solution of the HAuCl₄·3H₂O of the desired concentration (typically 1.27 × 10⁻⁴ M) was prepared. To this solution, polyvinyl alcohol (PVA) (1 wt% solution, Aldrich, weight averaged molecular weight MW = 9000–10,000 g mol⁻¹, 80% hydrolysed) was added (PVA/Au (wt/wt) = 0.65). Subsequently, a 0.1 M freshly prepared solution of NaBH₄ (>96%, Aldrich, NaBH₄/Au (mol/mol) = 5) was then added to form a dark red/brown solution. After 30 min of sol generation, the colloid was immobilized by adding TiO₂ (Aeroxide TiO₂ P25, Evonik Degussa) acidified to pH 1 by sulphuric acid, under vigorous stirring conditions. The amount of TiO₂ required was calculated so as to have a final metal loading of 1 wt%. After 2 h immobilization, the slurry was filtered and washed thoroughly with deionized water (2 L MilliQ water) to remove all dissolvable species (*i.e.*, Na⁺ and Cl⁻) and dried at 120 °C for 8 h. The monometallic Ag on TiO₂ (Ag/TiO₂) was prepared in a same fashion as reference for mechanism study. The Au_{core}–Ag_{shell} bimetallic NPs was prepared by the deposition of Ag on as-prepared Au/TiO₂. Three synthesis methods have been utilized to deposit Au_{core}–Ag_{shell} NPs with one monolayer (ML) of Ag on TiO₂.

2.1.1. Photodeposition method (PD)

One gram of Au/TiO₂ photocatalyst was dispersed in deionised (DI) water and sonicated for 1 h to form a homogeneous suspension. Then the AgNO₃ solution that contains n(Ag⁺) corresponding to one ML of n(Ag) was mixed with the Au/TiO₂ suspensions. The photodeposition was performed by irradiation for 2 h with a Lot–Oriol solar simulator (LSO104, 150W) under continuous stirring. Finally the Au_{core}–Ag_{shell} NPs with one ML of Ag on TiO₂ was obtained by filtration and drying at 120 °C for 8 h.

2.1.2. Double reduction method (DR)

The aforementioned Au/TiO₂ photocatalyst–DI water suspension was mixed with appropriate AgNO₃ solution and excessive NaBH₄ to achieve the reduction process. After 0.5 h of reduction, the suspension was filtered and dried at 120 °C for 8 h to obtain Au_{core}–Ag_{shell} NPs on TiO₂.

2.1.3. Sequential reduction method (SR)

The AgNO₃ solution was added into the freshly prepared Au colloid [23], and was subsequently reduced by addition of NaBH₄. After 0.5 h, TiO₂ was added into the colloid with H₂SO₄ (pH ~2) to immobilize the freshly formed Au_{core}–Ag_{shell} NPs. The fresh Au_{core}–Ag_{shell}/TiO₂ was filtered and dried at 120 °C for 8 h.

2.2. Catalyst characterisation

2.2.1. Transmission electron microscopy (TEM)

The morphologies of the catalysts and the particle size distribution of metal NPs were studied by TEM using a JEOL-2100 microscope with a LaB₆ filament (accelerating voltage 200 kV). The samples for TEM characterizations were dispersed in high purity ethanol by sonication for 10 min, and then dropped on a copper TEM grid coated by carbon film.

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