



## Research Paper

## Towards enhancing photocatalytic hydrogen generation: Which is more important, alloy synergistic effect or plasmonic effect?



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## ABSTRACT

Synergistic effect in alloys and plasmonic effect have both been explored for increasing the efficiency of water splitting. In depth understanding and comparison of their respective contributions in certain promising systems is highly desired for catalyst development, yet rarely investigated so far. We report herein our thorough investigations on a series of highly interesting nanocomposites composed of Pt, Au and C<sub>3</sub>N<sub>4</sub> nanocomponents, which are designed to benefit from both synergistic and plasmonic effects. Detailed analyses led to an important conclusion that the contribution from the synergistic effect was at least 3.5 times that from the plasmonic effect in the best performing sample, Pt<sub>50</sub>Au<sub>50</sub> alloy decorated C<sub>3</sub>N<sub>4</sub>. It showed remarkable turnover frequency of > 1.6 mmol h<sup>-1</sup> g<sup>-1</sup> at room temperature. Our work provides physical insights for catalyst development by rationally designing samples to compare long-known synergistic effect with recently emerging, attractive plasmonic effect and represents the first case study in the field.

## 1. Introduction

Energy and environmental issues represent two of the greatest challenges facing humanity in this century [1–3]. Despite tremendous efforts to develop renewable energy sources, the majority of energy used so far is still derived from non-renewable fossil fuels [4–7]. One attractive solution to this problem is solar water splitting with semiconductor photocatalysts that leads to the generation of clean fuel of hydrogen [8–12]. During the past few decades, a great deal of research has been focused on the development of more efficient photocatalytic systems and deeper understanding of relevant photocatalytic mechanisms. This technology, however, still suffers from low efficiency, poor stability, and/or high production cost. For example, a state-of-the-art photocatalyst was recently reported to show an overall solar-to-hydrogen conversion efficiency of 2.0% and robust stability for at least 200 days during recycled utilization [13]. Much needs to be done, in

particular, to improve the water splitting efficiency of photocatalysts. To achieve more satisfactory photocatalytic performance, alloy catalysts have attracted great attention recently. The synergetic effect between different active sites in an alloy catalyst can possibly endow the catalyst with much improved catalytic properties [14]. For example, Ye et al. reported the enhancement in visible-light photocatalytic H<sub>2</sub> production through Au–Cu alloy strategy, and revealed that the synergetic effect has an important influence on water splitting [15].

A recently emerging approach for enhancing photocatalysis is to use the plasmonic effect in metal nanoparticles (NPs). Surface plasmon resonance (SPR) arises from the collective oscillation of free electrons in plasmonic structures and is characterized by strong light absorption and/or scattering, as well as the generation of intense electric fields near the metal surface [16,17]. All these characteristics may be exploited for enhancing water splitting [18,19]. Basically, there are three major underlying mechanisms for plasmon-enhanced

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photocatalysis: (i) SPR induced hot electron transfer from the metal to semiconductor, (ii) enhancement in the local electromagnetic field and thus increased electron-hole pair generation rates in the semiconductor, and (iii) enhancement in scattering and thus the increase of the average photon path length in the system [18–23]. For example, Moskovits et al. reported an efficient, autonomous plasmon-enhanced whole water splitting system based on Au nanorod arrays [24]. The H<sub>2</sub> production rate was  $5 \times 10^{13}$  H<sub>2</sub> molecules cm<sup>-2</sup> s<sup>-1</sup> under 1 sun irradiation (AM 1.5G), thanks to SPR induced energetic charge carriers in Au nanorods. Although a lot of studies have clearly demonstrated that SPR can enhance photocatalytic reactions, the overall efficiencies are not satisfactory. Better understanding of mechanisms and accordingly rational system design are needed for further improvements. A general understanding is that, both electron and energy transfer between plasmonic NPs and semiconductor catalysts, important for gaining benefits from plasmonic effects in photocatalysis, can be more efficient at a shorter distance [25,26]. Specifically for hot electron transfer, the intimate contact between plasmonic nanostructures and semiconductor catalysts is highly desired. So ideally, ligand-free plasmonic metal surface is preferred for maximizing plasmon-enhanced photocatalysis with all other conditions being the same [21,27,28]. Furthermore, excited plasmonic NPs themselves can participate catalytic reactions directly. For instance, holes remained in plasmonic NPs following hot electron transfer can be directly used in and contribute to catalytic photodegradation of organic molecules [29]. In this regard, ligand-free plasmonic NPs are also preferred. Nonetheless, organic ligands are usually required to control NPs growth and prevent their coalescence in common wet chemical methods, which can obstruct the accessibility of reactants to the surface active sites of NPs, resulting in a decrease of their catalytic activity [30]. From this point of view, pulsed laser ablation in liquid (PLAL) appears as an interesting approach to yield “bare” NPs [31,32]. As demonstrated in our recent work, in addition to yielding much higher catalytic activities than chemically prepared ones, monodisperse Au NPs synthesized through a PLAL approach further feature the easy formation of intimately contacted NPs/semiconductor composites without using any linker molecules and thus ensures efficient hot electron transfer [20,33,34]. On the other hand, Pt<sub>x</sub>Au<sub>100-x</sub> (in this particular case, x = 50; at%) alloy NPs prepared via the similar method demonstrated significantly enhanced catalytic activity by a factor of 3–4 compared to pure Pt and Au NPs in nitrophenol reduction, suggesting a very strong synergistic effect in this alloy structure [35]. This exciting result motivated us to further explore if light is involved to excite SPR in catalytic reactions, whether the plasmonic effect will override the already quite impressive synergistic effect. It is worthwhile to point out that although both the plasmonic effect and the synergistic effect in alloys have been separately studied, their in depth comparison has rarely been reported. Moreover, in many cases, both effects can co-exist and entangle in a single system. It is indeed not trivial to disentangle enhancement mechanisms and identify the dominant one in a complex system. Such knowledge, however, can be extremely helpful for future catalysts development.

Herein, we intended to answer a fundamentally and technologically important question: for enhancing photocatalytic hydrogen generation, which approach is more effective, by exploring the synergistic effect in alloys or by using the plasmonic effect? We based our investigation on a very promising catalytic system containing carbon nitride (C<sub>3</sub>N<sub>4</sub>), Pt, Au, and Pt<sub>x</sub>Au<sub>100-x</sub> (x = 0, 30, 50, 70, 100 at%) NPs with a “bare and clean” surface were fabricated by the PLAL in pure water and studied in detail using X-ray absorption spectroscopy with synchrotron irradiation in order to understand the alloy structure and build up a structural model at the atomic level. Then, we used these NPs to decorate C<sub>3</sub>N<sub>4</sub> and the formation process is shown in Scheme 1. The hydrogen generation activity of the C<sub>3</sub>N<sub>4</sub> supported Pt<sub>x</sub>Au<sub>100-x</sub> alloy NP catalysts (denoted as Pt<sub>x</sub>Au<sub>100-x</sub>/C<sub>3</sub>N<sub>4</sub>) was assessed and compared with C<sub>3</sub>N<sub>4</sub> supported monometallic Pt and Au NPs, and their mixtures (denoted as Pt/C<sub>3</sub>N<sub>4</sub>, Au/C<sub>3</sub>N<sub>4</sub>, and Pt + Au/C<sub>3</sub>N<sub>4</sub>, respectively). We observed that

Pt<sub>50</sub>Au<sub>50</sub>/C<sub>3</sub>N<sub>4</sub> sample exhibited the best hydrogen generation ability under visible light, even though mixed Pt + Au/C<sub>3</sub>N<sub>4</sub> samples exhibited much stronger plasmon absorption in the visible region. The turnover frequency (TOF) of this sample reached as high as 1.6025 mmol h<sup>-1</sup> g<sup>-1</sup> at room temperature. Further by doing electrochemical and wavelength-resolved measurements and theoretical calculations, relevant mechanisms are discussed and a key role of the synergistic effect in the alloy NPs was identified and highlighted. In addition to achieving impressive TOF for H<sub>2</sub> generation, this work represents the first systematic investigation and comparison of the synergistic and plasmonic effects in samples expected to benefit from both.

## 2. Experimental

### 2.1. Preparation of targets for laser ablation

Different ratios of Pt and Au micropowders (Pt<sub>x</sub>Au<sub>100-x</sub>, x = 100, 70, 50, 30, 0) were mechanically mixed for 0.5 h and then compression molded [35]. Typically, 0.5 g of Pt-Au powder mixtures at different ratios were placed into a steel die with a diameter of 8 mm and pressed with a total pressure of 12 tons to form a compact pellet using a C-ARVER Press for 20 min. All the operations were performed at room temperature. The pellet has a thickness of 1.5 mm and a diameter of 8 mm. They were used for laser ablation.

### 2.2. Synthesis of NP colloids by laser ablation

Laser ablation was carried out with a KrF excimer laser (GSI Lumonics PM-846, wavelength: 248 nm; exciting voltage: 37 kV; pulse duration: 17 ns; repetition rate: 20 Hz). The laser beam was focused using an objective lens, with a focal length of 7.5 cm, onto the pellet target. The target was placed at the bottom of a 5 mL baker filled with pure water. The depth of the solution layer above the target was ~10 mm. The lens-to-target distance was fixed in order to guarantee the consistency of the ablation spot size (~0.4 mm × 0.5 mm) on the target. The laser fluence on the target was set at ~40.0 J cm<sup>-2</sup>. The actual amounts of Pt and Au in all the samples were determined by Neutron activation analysis method.

### 2.3. Synthesis of C<sub>3</sub>N<sub>4</sub>

Typically, 30 g of urea was placed into an alumina crucible with a cover, and then the crucible was heated in a muffle furnace at 250 °C for 1 h, 350 °C for 2 h and 550 °C for 2 h with a heating rate of 2 °C min<sup>-1</sup>. The yielded yellow powder was washed with nitric acid (0.1 mol L<sup>-1</sup>) and distilled water to remove any residual alkaline species (e.g. ammonia) adsorbed on the surface of the product, and then the product was dried at 80 °C for 12 h.

### 2.4. Synthesis of NP/C<sub>3</sub>N<sub>4</sub> catalysts

To 40 mg of C<sub>3</sub>N<sub>4</sub>, different volumes of freshly prepared Pt<sub>x</sub>Au<sub>100-x</sub> (x = 100, 70, 50, 30, 0) NP solution were added and mixed by shaking. Then, a few drops of HCl aqueous solution (0.1 mol L<sup>-1</sup>) was added to the above solution and the pH value was about 5. The mixture solution was incubated at room temperature for ~30 min to assemble metal NPs onto the surface of C<sub>3</sub>N<sub>4</sub>. After centrifugation, a solid product precipitated and supernatant became clear and completely colorless, indicating that all the metal NPs were efficiently loaded onto C<sub>3</sub>N<sub>4</sub>. We were able to modulate the loading of Pt, Au and alloy NPs on the surface of C<sub>3</sub>N<sub>4</sub> using various volumes of freshly prepared NP solutions and further confirm their content using neutron activation analysis (NAA).

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