

Review

Synthesis of Plasmonic Photocatalysts for Water Splitting

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Abstract: Production of H₂, O₂, and some useful chemicals by solar water splitting is widely expected to be one of the ultimate technologies in solving energy and environmental problems worldwide. Plasmonic enhancement of photocatalytic water splitting is attracting much attention. However, the enhancement factors reported so far are not as high as expected. Hence, further investigation of the plasmonic photocatalysts for water splitting is now needed. In this paper, recent work demonstrating plasmonic photocatalytic water splitting is reviewed. Particular emphasis is given to the fabrication process and the morphological features of the plasmonic photocatalysts.

Keywords: surface plasmon resonance; metal nanoparticle; metal nanostructure; semiconductor; solar water splitting

1. Introduction

Creating renewable energy from solar, wind, and water power has been a hot topic for a long time, because natural resources such as oil, coal, and natural gas are limited, while global energy demand is rapidly increasing. Although the growth in renewable energy generation has also been rapid, it could only provide a third of the required increase in energy generation in 2018 [1]. Solar water splitting, using a semiconductor photocatalyst, is one of the ultimate solutions to the energy problem because in principal, it only requires inexhaustible solar energy and water. Both hydrogen and oxygen generated by water splitting can be used to generate electricity using fuel cells and produce useful chemical compounds [2,3].

Studies have also localized surface plasmon resonance (LSPR) as a means to enhance the efficiency of photocatalytic performances of semiconductors [4]. Specific metal nanostructures show LSPR acts as a photosensitizer, transferring plasmonic energy to vicinal semiconductors via hot-electron transfer and resonant energy transfer [5–7]. Light scattering by LSPR can also contribute to the enhancement of photocatalysis because it elongates the optical pathways [8]. This LSPR enhancement of photocatalytic performance has huge potential, because the morphology dependence of LSPR makes it possible to absorb sunlight over the entire spectrum, though the reported enhancement factors have not been so attractive until now, as recent review articles have noted [9–11]. Therefore, in this article, the reasons for the difficulties in utilizing LSPR enhancement for photocatalysis are also discussed after reviewing the recent developments in plasmonic photocatalysts fabricated especially for solar water splitting.

2. Photocatalytic Water Splitting

Before reviewing the recent studies on plasmonic photocatalysts for water splitting, some important fundamentals are briefly discussed first. Detailed tutorial and advanced reviews on photocatalytic water splitting are available in recent articles published by Domen's group [2,12,13].

In order to split water, electrons and holes with certain reduction and oxidation potentials – $< +0$ and $> +1.23$ vs. normal hydrogen electrode (NHE), respectively, are indispensable. TiO_2 , CdSe, and some other wide-bandgap semiconductors can generate such carriers when bandgap excitation occurs. However, water splitting is carried out by the carriers only if the carrier injections into the water are thermodynamically preferable. Since carrier recombination is generally the predominant process after bandgap excitation, co-catalysts are normally deposited on the surface of semiconductors to capture the carrier(s) for the enhancement of charge separation (Figure 1A).

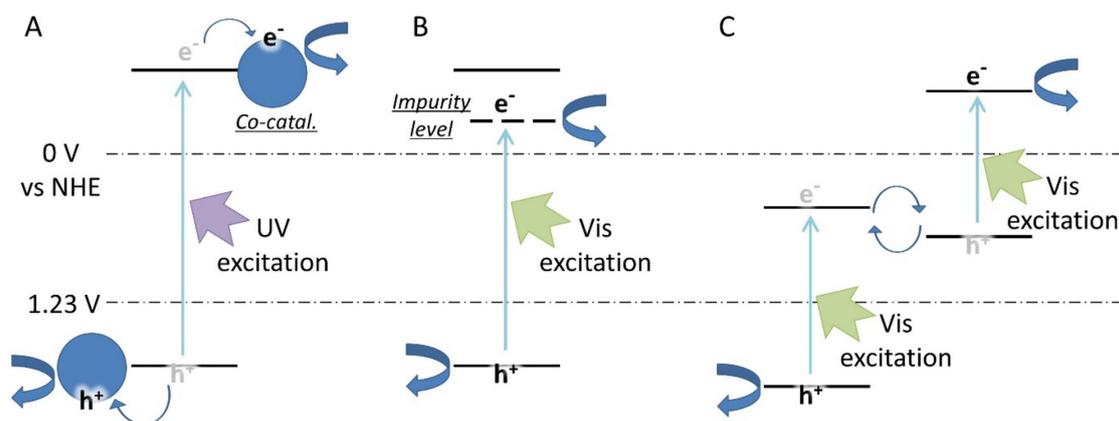


Figure 1. Schematic of energy diagrams of wide-bandgap semiconductors with (A) cocatalysts and (B) impurity energy level. (C) is a typical Z-scheme using two narrow bandgap semiconductors.

As carriers with the required potentials are generated by an excitation of wide-bandgap semiconductors, TiO_2 was initially [14] and the most widely investigated for water splitting [15,16]. TiO_2 absorbs only UV-rays, which occupy only $\sim 4\%$ of sunlight energy. Hence, the doping of metal and nonmetal species to TiO_2 has been extensively carried out to add visible light sensitivity to TiO_2 [17]. In these cases, impurity energy levels were inserted into the bandgap, so the doped TiO_2 could absorb visible light (Figure 1B). An additional advantage of doping is that some of the incorporated impurity species also work as carrier traps, which lead to carrier lifetime elongation [18,19].

Although there are many visible-light-sensitive narrow-bandgap photocatalysts with redox potential, they are unfortunately insufficient to split water. A two-step photocatalytic system, the so-called “Z-scheme”, allows these narrow-bandgap photocatalysts to be used for water splitting (Figure 1C) [20,21]. In this system, two photocatalysts are connected physically, or with reversible redox mediators such as IO_3^-/I^- , I_3^-/I^- , and $\text{Fe}^{3+}/\text{Fe}^{2+}$. The key point in achieving highly efficient photocatalysis is to select appropriate combinations of photocatalysts and redox mediators together with interface engineering to facilitate the charge transfers. Research and development on water splitting photocatalysts including oxide and non-oxide new materials for Z-scheme systems has also been thoroughly conducted [2,12,22–24].

Among the challenges in achieving higher efficiency in solar water splitting, the use of plasmonic photocatalysts has been attracting increasing attention since plasmonic photocatalysts were first announced in 2008 [25]. In the next section, general ideas on the plasmonic enhancement of photocatalysis will be briefly introduced.

3. Plasmonic Enhancement of Photocatalysis

Plasmonic photocatalysts are generally composed of noble metal nanoparticle-deposited semiconductors. When the semiconductors are n-type, a Schottky junction is formed at the interface of the metals and semiconductors, which leads to enhanced charge separation and therefore the improved efficiency of photocatalysis (Figure 2A). In addition to the Schottky junction effect, plasmonic enhancement of photocatalysis occurs in some cases. LSPR is a collective oscillation of metal nanoparticle free electrons in resonance with incident light, and the optical absorption coefficient

is large when compared to organic dyes and semiconductors [26]. The strong optical absorption leads to the generation of hot electrons and holes in metal nanoparticles, and can contribute to the enhancement of photocatalysis efficiency when the generated charges are separated via hot electron transfer from metals to semiconductors [5,6,27]. A moderate Schottky barrier energy of ~ 1 eV is preferable for hot electron transfer because the energies of hot electrons generally range between 1 and 4 eV (Figure 2B) [5]. The other advantageous features of hot electron transfer are that (1) wide bandgap semiconductors like TiO_2 can be endowed with visible light sensitivity if deposited metal nanoparticles exhibit LSPR under visible light illumination, and (2) both Schottky junction and hot electron transfer enhancements can be used simultaneously without any loss, even though the directions of electron transfer are opposite [28]. Aside from hot electron transfer, plasmon-induced resonance energy transfer is another major phenomenon contributing to photocatalysis efficiency enhancement. A few nonradiative and radiative energy transfer routes have been proposed, but the main and most important one for photocatalysis is energy transfer via near-field enhancement. Using this phenomenon, although the energy of metal nanoparticle LSPR must overlap with the bandgap energy of the semiconductor, and the valence band electrons in the semiconductor adjacent to the metal nanoparticles are excited by the strong electric field caused by LSPR (Figure 2C). The details of energy transfer in plasmonic photocatalysts have been widely studied and detailed review articles are available [4,5,29]. In short, the three phenomena summarized in Figure 2 should be appropriately used to achieve highly LSPR-enhanced photocatalysis including plasmonic solar water splitting.

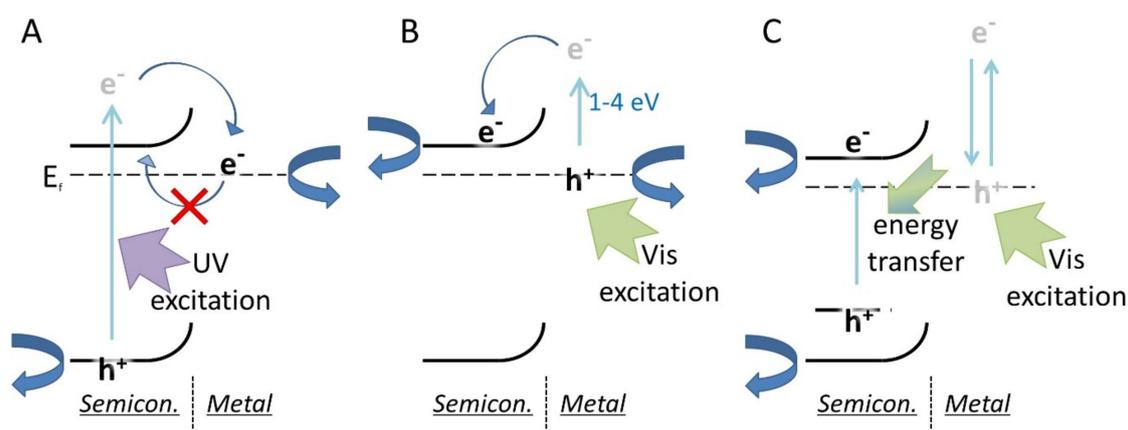


Figure 2. Schematic of energy diagrams of plasmonic photocatalyst under (A) UV and (B,C) Vis excitations.

4. Water Splitting by Plasmonic Photocatalysts

4.1. Titanium Dioxide

As above-mentioned, TiO_2 generates photo-induced electrons and holes with sufficient redox potential for water splitting, whereas it can absorb only UV-rays. Therefore, hot electron transfer, which endows visible light sensitivity to wide bandgap photocatalysts, has been employed to enhance the water splitting efficiency of TiO_2 by expanding the usable wavelength range as well as the Schottky junction effect, which improves reaction efficiency under UV radiation. The deposition of Au or Ag nanoparticles on TiO_2 has most often been carried out and shows enhanced photocurrents in water splitting, especially under visible light illumination [30–35]. An electric bias is applied in some cases to facilitate and enhance the water splitting reaction. As the morphology of metal/ TiO_2 nanocomposites strongly affects the reaction efficiency, several researchers have reported interesting studies on the effects of morphology on the efficiency. Moskovits et al. fabricated TiO_2 -deposited Au nanorod arrays using an anodic aluminum oxide template. TiO_2 was deposited on the top of the Au nanorods, and an oxygen evolution catalyst (OEC) was separately deposited on the side (Figure 3). As the LSPR wavelength of the Au nanorod can be effectively tuned by controlling the aspect ratio of the nanorod,

it was expected that the solar spectrum would be mostly covered by an LSPR peak if an appropriate morphology could be fabricated [36–38]. Results showed a surprising 20-fold higher efficiency for visible light illumination compared with UV radiation because of the unique nano-architecture of the fabricated device. The authors also found that there were fast and slow components in H_2 production via hot electron transfer. This phenomenon needs to be further investigated, as it could prove important for the future design of plasmonic photocatalyst nano-architectures [39,40].

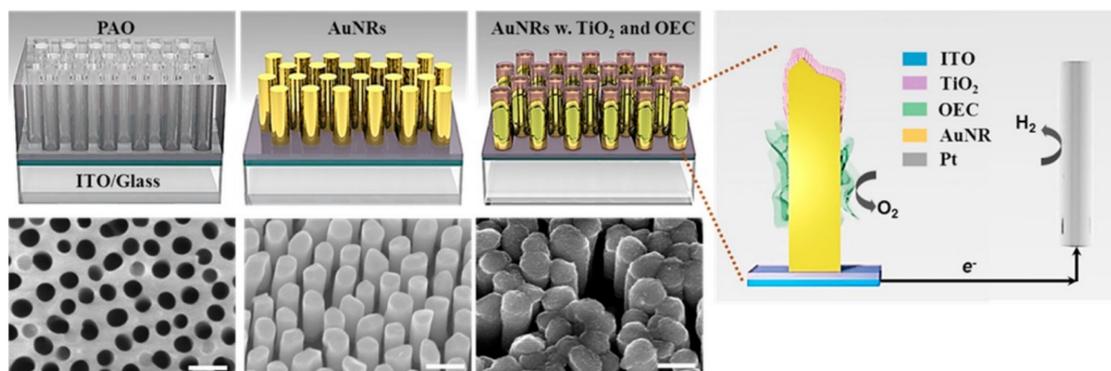


Figure 3. Schematic of the fabrication of Au nanorod arrays deposited with TiO_2 . Reprinted with permission from [39], copyright (2012) American Chemical Society.

Misawa et al. prepared Au nanoparticle-deposited TiO_2 nanotube arrays by anodization of a Ti plate followed by the chemical reduction of Au precursors (Figure 4). The nanotube array structure of TiO_2 provides a large surface area for Au deposition and water splitting reaction. The quantity and dispersion state of Au nanoparticles deposited on TiO_2 nanotube arrays were carefully controlled by changing Au precursor conditions. The results found a large quantity of highly dispersed Au nanoparticles that exhibited the largest incident photon-to-current conversion efficiency. This was presumably because of the large optical absorption and effective hot electron transfer caused by the highly dispersed large number of Au nanoparticles on the TiO_2 nanotube arrays. Even though they used no sacrificial electron donors or acceptors, the solar energy was converted to chemical reaction by 0.10%, which was about 10-fold larger than that obtained in the previous study using monolith type samples composed of $SrTiO_3$ loaded with Au nanoparticles [41,42].

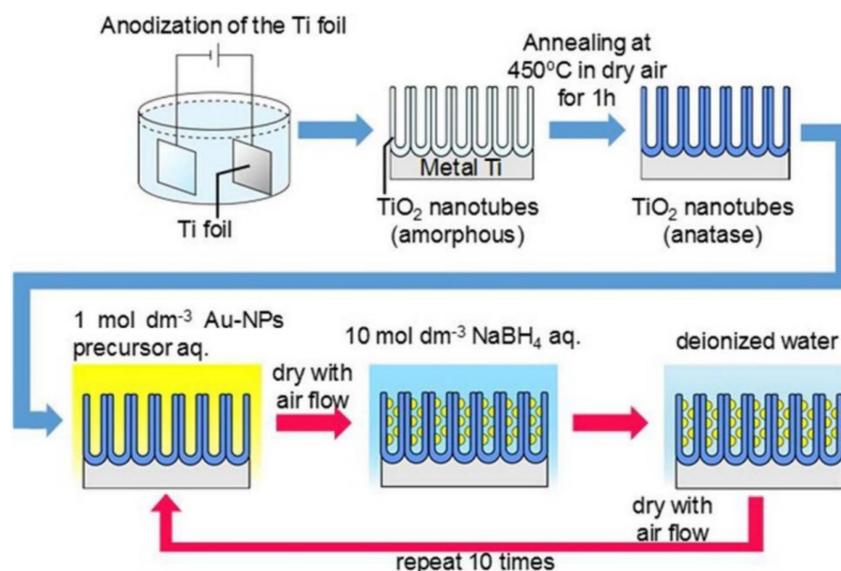


Figure 4. Schematic of the fabrication of Au nanoparticle-deposited TiO_2 nanotube arrays. Reprinted with permission from [42], copyright (2017), Royal Society of Chemistry.

Yang et al. investigated a synergistic interaction between plasmonic Au nanoparticles and oxygen vacancies in amorphous black TiO₂. TiO₂ nanoporous film was first prepared by the anodization of a Ti foil that was then reduced by NaBH₄ in order to introduce oxygen vacancies. Au nanoparticles were deposited by means of magnetron sputtering, followed by thermal dewetting in the N₂ atmosphere (Figure 5). The incorporated impurity energy levels in the TiO₂ facilitated hot electron transfer from the Au nanoparticles to the TiO₂. Thus, the generated plasmonic hot electron/hole pairs were efficiently separated. This interestingly resulted in a largely enhanced photoelectrochemical water splitting, compared to bare amorphous black TiO₂ and Au nanoparticle-deposited TiO₂. This kind of synergistic interaction between LSPR and impurity energy levels could lead to new strategies to design novel, highly efficient plasmonic photocatalysts [43].

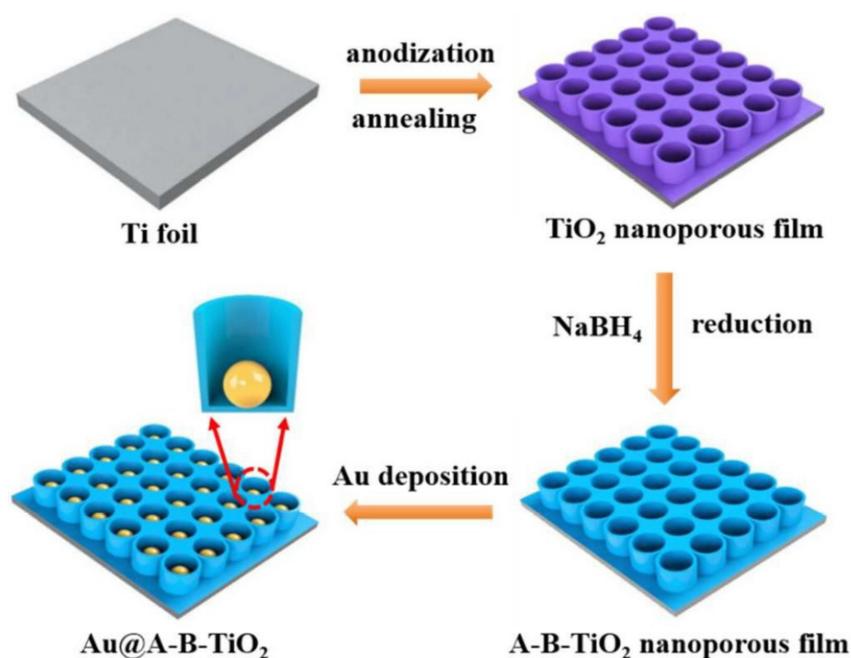


Figure 5. Schematic of the fabrication of the Au nanoparticle-deposited reduced-TiO₂ nano-porous film. Reprinted with permission from [43], copyright (2018) Royal Society of Chemistry.

TiN, ZrN, and some other transition metal nitrides have recently attracted attention because of their potential use as plasmonic materials, instead of as conventional noble metals such as Au and Ag. Naldoni et al. demonstrated that TiO₂ nanowires decorated with TiN nanoparticles showed better water splitting ability than when decorated with Au nanoparticles. The higher performance of TiN was explained mainly by the following two factors: wider absorption wavelength, and Ohmic junction formation with TiO₂. Naldoni also proposed that a further enhancement of solar water splitting could be expected because TiN nanoparticles show plasmon resonance in the red, so that the entire solar spectrum would be covered when complemented with Au nanoparticles [44].

4.2. Iron Oxide

As stated above, TiO₂ has been widely investigated as a potential photocatalytic semiconductor because of its redox potential for water splitting. Another chemical compound, iron oxide, especially in the form hematite (α -Fe₂O₃), has been recognized as a promising photocatalyst, since it is inexpensive, non-toxic, in plentiful supply, and has an appealing band gap (~2.1 eV) for sunlight absorption. The reason why α -Fe₂O₃ has not been used practically so far is that it has several critical drawbacks such as short lifetime of charge carriers (<10 ps) and short hole diffusion length (2–4 nm) compared to deep light penetration depth (~120 nm) [45–49]. It needs to be available as a nanoparticle or thin film to enable the most generated holes to reach the surface, while a large dimension is required to

effectively absorb incident light [50–52]. In order to improve the short lifetime of carriers in α -Fe₂O₃, a hole collector is often used to enhance charge separation [53]. The hole collector is called OEC when it is used for water splitting. Several kinds of OECs including Ir- and Ru-based oxides [54], and a variety of cobalt-based complexes have been investigated very recently and showed an excellent enhancement of photoelectrochemical water splitting efficiency with α -Fe₂O₃ [55–57].

Plasmonic enhancement is also soon expected to overcome these problems because of the facts stated mainly in Section 3. In short, strong optical scattering and absorption by LSPR can effectively enhance the utilization of incoming photons [8,47]. Li et al. studied the plasmonic enhancement of solar water splitting by employing incorporated α -Fe₂O₃ nanorod arrays into a gold nanohole pattern. The gold nanohole pattern was fabricated by e-beam lithography with a polystyrene nanosphere mask, followed by the growth of an α -Fe₂O₃ nanorod array using a hydrothermal method. The nanorod shape of α -Fe₂O₃ worked as an optical fiber, creating confined modes that enhanced the optical absorption of α -Fe₂O₃. At the same time, plasmonic energy transfer occurred and enabled the usage of photons with energies below the band gap. As a result, very high enhancements were observed in a wide wavelength range from 350 to 700 nm [47]. Ramadurgam et al. designed core-shell nanowire photoelectrodes composed of a Si-core, Al-mid-shell, and an α -Fe₂O₃-outer-shell (Figure 6). The theoretical comparison of the photoelectrode performances of Si–Al–Fe₂O₃, Si–Ag–Fe₂O₃, and Si–Au–Fe₂O₃ revealed that Si–Al–Fe₂O₃ had the potential to exhibit a very high efficiency rate of 14.5% solar to hydrogen, and about 93% of the theoretical maximum for bulk α -Fe₂O₃. Since Au and Ag, which are widely used as plasmon sources, are precious metals, Al has been shown to be an excellent alternative in achieving enhanced absorption of α -Fe₂O₃ and reduced the recombination of the generated charges, resulting in a high efficiency of iron-oxide-based solar water splitting [58].

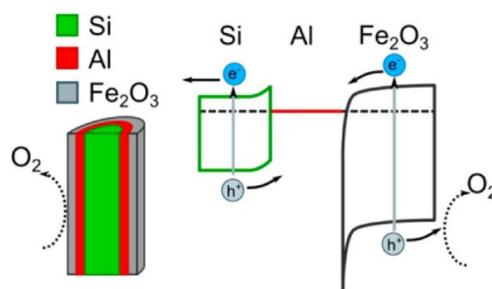


Figure 6. Schematic and energy diagram of Si–Al–Fe₂O₃ nanowire. Reprinted with permission from [58], copyright (2014) American Chemical Society.

Wang et al. prepared affordable α -Fe₂O₃ nanosheet photoanodes co-deposited with Ag nanoparticles and Co phosphate OEC (Figure 7). The α -Fe₂O₃ nanosheet was prepared by anodization of an Fe foil. Ag nanoparticles were separately synthesized via a modified Tollens' reaction [59]. The Ag nanoparticles were then deposited on the α -Fe₂O₃ nanosheet using pulse-current electrodeposition. Finally, cobalt phosphate was photo-assisted electro-deposited onto the nanosheet. A large photocurrent density of 4.68 mA cm⁻² (1.23 V vs. reversible hydrogen electrode (RHE)) was achieved presumably because of the following three points: (1) plasmonic light harvesting by Ag nanoparticles; (2) a reduced charge recombination by cobalt phosphate; and (3) electrode surface stabilization, also by cobalt phosphate [60].

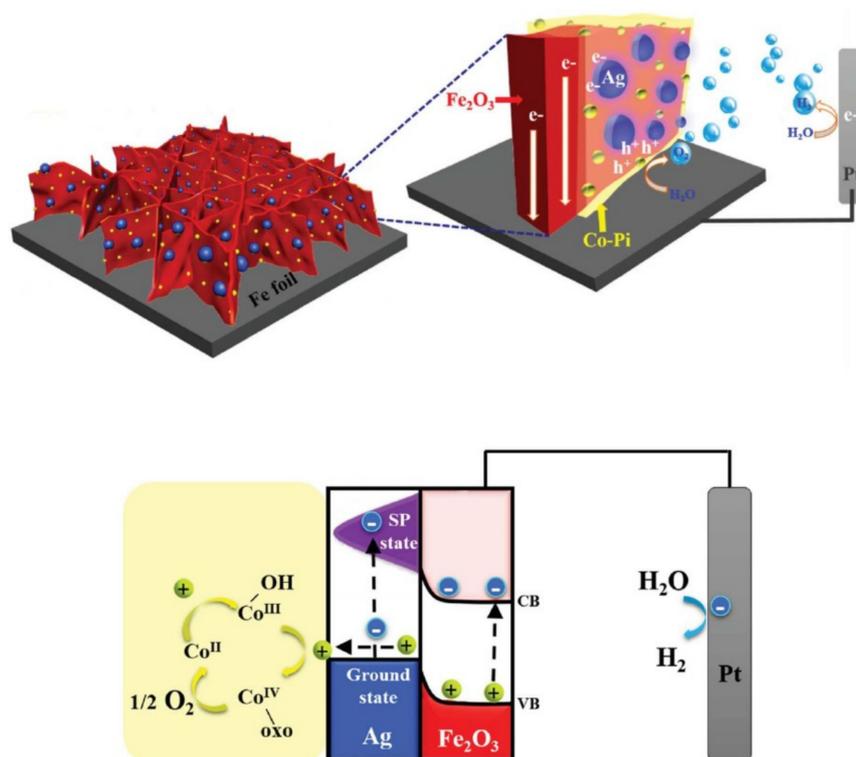


Figure 7. Schematic and energy diagram of an α - Fe_2O_3 nanosheet deposited with Ag nanoparticles. Reprinted with permission from [60], copyright (2016) Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim.

Gap-plasmon resonance is known to occur when two or more plasmonic materials/parts are close enough and exhibits an extremely enhanced local field in the nanogap area, compared with individual plasmonic materials/nanostructures [61,62]. However, it is rarely used for enhancing photocatalytic water splitting. This is mainly because the fabrication processes generally become complicated and the area where a strong local field exists is quite limited [63]. Dutta et al. recently investigated gap-plasmon enhancement for water splitting using an α - Fe_2O_3 ultra-thin film. A 200 nm thick Au layer was first deposited on an Si substrate. Then, an α - Fe_2O_3 layer with a 15 nm thickness was deposited by pulsed laser deposition. Au nano-disks were fabricated on top of the α - Fe_2O_3 layer using e-beam lithography and lifted off with a polymer mask (Figure 8). Compared to bare α - Fe_2O_3 layer on a Si substrate, the α - Fe_2O_3 layer with Au nanogaps showed a two-fold increase in photocurrent density. The enhancement observed above the α - Fe_2O_3 bandgap was attributed to the enhanced light scattering by the Au nano-disks and back reflection from the Au mirror. On the other hand, a wavelength-dependent increase was observed below the bandgap of α - Fe_2O_3 . This occurred presumably because of plasmon decay and subsequent hot hole generation. Further improvement of the photocurrent density can be expected by shifting the LSPR wavelength to the visible region above the α - Fe_2O_3 bandgap, which will enable an enhancement in inter-band excitation via plasmon energy transfer [64].

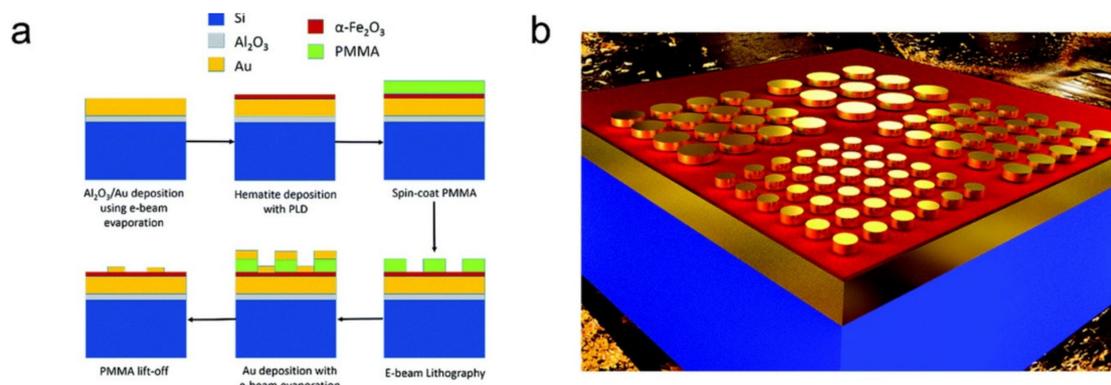


Figure 8. Schematic of the fabrication of an $\alpha\text{-Fe}_2\text{O}_3$ layer with Au nanogaps. (a) Process flow and (b) 3-dimensional image. Reprinted with permission from [64], copyright (2019) Royal Society of Chemistry.

4.3. Other Semiconductors

Compared to water reduction by plasmonic hot electrons, fundamental research on water oxidation by plasmonic holes is relatively limited. One interesting report recently revealed that plasmonic holes tend to be concentrated at the Au–TiO₂ interface, which was identified as the main reaction site for water oxidation in the plasmonic system [65]. This interfacial effect of plasmonic holes was also validated by Au–SrTiO₃, Au–BaTiO₃, etc. [65]. Nb- or Rh-doped SrTiO₃ decorated with Au nanoparticles was studied as a potential component in a water splitting device [66,67]. Zhong et al. employed Nb-doped SrTiO₃ as a semiconductor component to investigate the cocatalyst effect on H₂ evolution in plasmon-induced water splitting. Since H₂ evolution is known to be disturbed by the Schottky barrier formation and reverse water splitting reactions, the Schottky barrier was removed by inserting an In–Ga alloy interlayer between the Pt board and the Nb–SrTiO₃ substrate. Reverse reactions were also eliminated by separating the chambers for H₂ and O₂ evolutions. As a result, the cocatalyst effect became effective and a 3-fold increase of H₂ evolution was achieved when a Rh thin layer was deposited on the Pt board as a cocatalyst [66]. Wang et al. designed a plasmon-based solid Z-scheme photocatalyst, which needed no redox mediator. Au, TiO₂, Rh-doped SrTiO₃, and Ru were employed as the plasmon source, semiconductors, and cocatalyst, respectively. Upon irradiation with visible light, plasmonic hot electrons generated on the Au surface were injected into the conduction band of TiO₂, and the remaining holes were used for O₂ generation at the interface of Au and TiO₂. (Figure 9). The hot electrons injected to the TiO₂ conduction band migrated to the valence band of Rh-doped SrTiO₃ through interconnecting Au nanoparticles, due to the large work function of Au compared to TiO₂. The designed hot electron migration largely reduced the plasmon-induced hot charge recombination, which is often the predominant phenomenon accompanying LSPR. Simultaneously, the excited electrons in Rh-doped SrTiO₃ were collected by Ru cocatalyst and used for H₂ generation, accomplishing complete water splitting [67].

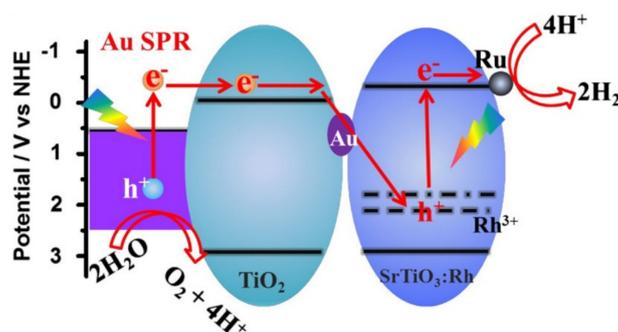


Figure 9. Energy diagram of the Au/TiO₂/Rh-doped SrTiO₃ nanocomposite. Reprinted with permission from [67], copyright (2017) Elsevier Inc.

Yang et al. made an attempt to use a non-metallic plasmonic component instead of conventional novel metals. SrTiO₃ nanotube arrays were first prepared by hydrothermal treatment of anodized TiO₂ nanotube arrays. Then, the surface of SrTiO₃ was thermochemically reduced to form a crystalline-core@amorphous-shell structure with abundant oxygen vacancies in the amorphous shell (Figure 10). Since the amorphous shell had abundant free charges, it was possible to have LSPR properties. The resonant wavelength was tunable and reversible by oxidation and reduction treatment and incident light angle adjusting, which provided flexibility for various applications in the targeted LSPR wavelength. The reduced core@shell sample showed much higher water splitting ability than the as-synthesized SrTiO₃ sample, proving that the use of non-metallic plasmonic semiconductors is a promising way to enhance catalytic reactions, especially water splitting [68].

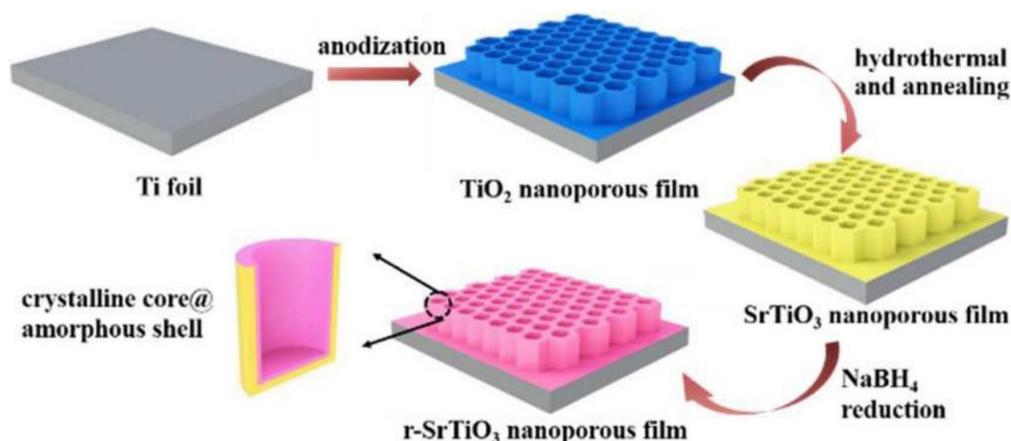


Figure 10. Schematic of the fabrication of SrTiO₃ nanotube arrays with a crystalline-core@amorphous-shell structure. Reprinted with permission from [68], copyright (2018) American Chemical Society.

WO₃ is also recognized as an applicable semiconductor for water splitting because of its moderate bandgap (2.6–2.8 eV), adequate valence band edge position (3.0 V vs. standard hydrogen electrode (SHE)), long minority carrier diffusion length (0.5–6 μm), and high chemical stability [69]. Hu et al. developed an electron-charging and reducing method for the preparation of a Au/WO₃ water splitting plasmonic photocatalyst. After WO₃ nanoplate arrays were formed on a FTO substrate by hydrothermal growth, electron-charging was carried out on the arrays by applying an electric bias in H₂SO₄ solution. The charged WO₃ was then immersed into HAuCl₄ solution to reductively deposit Au nanoparticles on WO₃. The Au/WO₃ nanocomposite photocatalyst exhibited a significant increase in oxygen evolution reaction (OER) photocurrent density. Moreover, it showed a negatively shifted OER onset potential and an improved Faraday efficiency for OER. The greatly enhanced performance observed was presumably due to the electrically good Au/WO₃ contact formed by the newly developed preparation method [70]. Several interesting attempts have also been reported using a variety of semiconductors such as CdS [71,72], ZnO [73,74], Cu₂O [75], and the Cu₂O–TiO₂ composite [76].

5. Summary and Outlook

Plasmonic enhancement for photocatalytic water splitting has been reported recently by many researchers. However, the mechanisms underlying the enhancement are still not fully understood, and so the enhancement factors reported are not as high as expected. In this paper, many combinations of plasmonic sources and semiconductors with various morphologies for plasmonic water splitting were reviewed. Noble metals such as Au and Ag have been widely used as typical plasmonic sources because of their high chemical stability, resonant wavelength in the visible range, and large field enhancement factor. On the other hand, Al and some transition metal nitrides are attracting increasing attention as they can be alternatives to the precious and expensive Au and Ag. As for semiconductors,

TiO₂ and α -Fe₂O₃ have been the most widely studied materials due to their appropriate redox potential and abundance. SrTiO₃, BaTiO₃, WO₃, CdS, ZnO, Cu₂O, etc. have also recently been employed as semiconductors because of their peculiar characteristics. It is noteworthy here that all cases reported thus far have shown a moderate improvement of water splitting efficiency by LSPR, and further studies to achieve much higher efficiency need to be carried out. Additionally, as many phenomena related to plasmonic enhancement of water splitting are well understood, the cost reduction and scale-up of plasmonic photocatalyst fabrication are vital steps to achieve practical application.

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