Enhanced full-spectrum water splitting by confining plasmonic Au nanoparticles in N-doped TiO₂ bowl nanoarrays

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Integration of surface plasmon into photocatalysis has been of great interest, as it may extend the spectral range of light absorption towards full solar spectrum. In this communication, we have developed a facile surfactant-free nanofabrication approach to confine dense Au nanoparticles in N-doped TiO₂ bowl nanoarrays. By tuning the light absorption of TiO₂ to sufficiently overlap the plasmonic band of Au nanoparticles, the utilization of plasmonics in charge generation and separation by resonant energy transfer is well synergized with the Schottky junction for enhanced photocatalytic water splitting, achieving H₂ production rates of 637 μmol g⁻¹ h⁻¹ in full spectrum and 132 μmol g⁻¹ h⁻¹ in visible region, respectively. This work represents a step towards large-scale photocatalyst fabrication and full-spectrum photocatalysis, and opens a new window to rationally designing hybrid structures for photocatalysis.

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1. Introduction

Solar energy conversion and environmental remediation have become critical issues with the increasing energy and environmental demands. Sunlight-driven water splitting for hydrogen production provides a promising approach to transform solar energy into hydrogen fuel [1–3]. In principle, the photocatalytic water splitting process mainly includes three steps: i) absorption of light to excite semiconductor electrons for the transition from valence band (VB) to conduction band (CB); ii) separation of electrons from holes, and their diffusion to the surface of catalysts; and iii) use of electrons for H⁺ reduction and holes for water oxidation, respectively. Since the discovery of photocatalytic activity under ultraviolet (UV) irradiation [4], TiO₂ has been considered as a pioneering material for photocatalyst owing to its photochemical stability and low toxicity. Given the wide bandgap (e.g., anatase TiO₂, Eg = 3.2 eV), however, TiO₂ can only absorb the light in the UV region, which accounts for about 5% of the solar spectrum.

In quest to improve the photocatalyst efficiency, both the light absorption and electron–hole (e–h) separation should be optimized. A number of studies such as doping have been directed to narrow the bandgap of TiO₂, thereby extending the photoresponse to visible (vis) spectral region [5–8]. However, the incorporation of doping ions into the TiO₂ lattice generally leads to the emergence of sub-bandgaps, aggravating the detrimental recombination of e–h pairs. In efforts to suppress the e–h recombination, the establishment of Schottky junction between semiconductor and metal represents a typical approach to trap electrons or holes on the metal (depending on their work functions) [9], which naturally integrates noble metal nanoparticles into the semiconductor system. In addition to the Schottky junction, certain noble metal (e.g., Au and Ag) nanoparticles possess fascinating surface plasmonic properties in vis-light region, which can help expand the spectral range of energy utilization [10–13]. The surface plasmon may improve the e–h generation/separation via two different mechanisms: i) local electromagnetic field enhancement (LEMF) to increase interband transition rate in the semiconductor by the strong local field, and ii) resonant energy transfer (RET) from the plasmonic dipoles to the e–h pairs in the semiconductor through a near-field electromagnetic interaction [14–16]. Thus the LEMF-induced charge separation mechanism can only work for the energies above the bandgap, limiting the light-absorption spectral range. Unlike the LEMF, the RET is not limited by the electronic band structure of semiconductor, and enhances carrier creation and separation at the energies both above and below the bandgap [14]. As the plasmonic bands of Au and Ag nanoparticles are mainly located in vis-spectral range [17–18], the RET mechanism would be anticipated to play the major role in the performance improvement for wide-bandgap semiconductor TiO₂.

To facilitate the RET process, one can engineer the TiO₂–Au hybrid structures from two different angles [14]: i) tailoring the
The capillarity force, the TiO$_2$ sol penetrated and cooled down by adding ice, and the PS nanospheres started to

1 and 2)

3. Preparation of monolayer PS templates with TiO$_2$ sol (steps 1 and 2)

Microscope glass slides were cut into pieces with 2.5 $\times$ 2.5 cm$^2$. The glass pieces were ultrasonicated in ethanol, acetone and DI water in turn, boiled in a solution containing hydrogen peroxide and DI water (3:7) for 1 h, and washed with DI water before use. The monodispersity polystyrene (PS) nanosphere suspension was diluted by adding ice. Subsequently, 0.5-mL isopropyl alcohol was mixed with 9.5-mL tetraisopropyl titanate, which was then dropwised slowly into the mixture of 62.5-mL deionized (DI) water and 20-mL acetic acid. Finally, the PS templates with TiO$_2$ sol were successfully self-assembled. As soon as all the solvent was evaporated, the PS nanospheres initially evaporate the solvent, during which the PS nanospheres initially self-assembled. As soon as all the solvent was evaporated, the glass slide was slowly immersed into the TiO$_2$ sol that was pre-cooled down by adding ice, and the PS nanospheres started to form a monolayer on the sol surface and further self-assembled. With the capillarity force, the TiO$_2$ sol penetrated and filled the bottom of PS nanoarrays. During this process, cooling down the sol by adding ice could help the PS nanospheres assemble in a packed way. Finally, the PS templates with TiO$_2$ sol were successfully transferred to ITO glass.

4. Fabrication of TiO$_2$ bowl nanoarrays and N-doped TiO$_2$ (NH$_3$ or N$_2$) bowl nanoarrays (Step 3)

The TiO$_2$ bowl nanoarrays were prepared by simply annealing the sample on ITO glass (obtained from the last step) in a tube-type furnace in air at 450 °C for 2 h, with a heating rate of 5 °C min$^{-1}$. As for N-doped TiO$_2$ bowl nanoarrays, 50-μL trimethyamine was dropped onto the sample, which was then annealed in NH$_3$ or N$_2$ at 450 °C for 2 h, with a heating rate of 1 °C min$^{-1}$. The PS nanospheres were evaporated while the TiO$_2$ was transformed into anatase-phase crystals at 450 °C, yielding TiO$_2$ bowl nanoarrays.

5. Integration of Au nanoparticles with TiO$_2$ bowl nanoarrays and N-doped TiO$_2$ (NH$_3$ or N$_2$) bowl nanoarrays (Step 4)

An ultrahigh vacuum (UHV) electron-beam evaporation system (Shenyang Scientific Instruments, China, DZS-500) was used to deposit a layer of 4-nm Au film on TiO$_2$ bowl nanoarrays and N-doped TiO$_2$ bowl nanoarrays. The evaporation rate was maintained at 0.01 nm s$^{-1}$ under the pressure of about 10$^{-4}$ mbar. Finally, the Au-evaporated TiO$_2$ samples were annealed in Ar at 480 °C for 90 min, with a heating rate of 5 °C min$^{-1}$.

6. Photoelectrochemical characterizations

The measurements were carried out on a CHI 660D electrochemical station (Shanghai Chenhua, China) in ambient conditions under irradiation of a 300-W Xe lamp (Solaredge 700, China). UV, visible or full-spectrum light was used as illumination source, which was realized in the presence or absence of 400-nm cutoff filter (short-wave-pass or long-wave-pass), respectively. The power densities of UV and visible light were measured to be 2.7 and 100 mW cm$^{-2}$, respectively. Standard three-electrode setup was used with the fabricated samples as photoelectrode, a Pt foil as counter electrode, and an Ag/AgCl electrode as reference electrode. The three electrodes were inserted in a quartz cell filled with 0.5-M Na$_2$SO$_4$ electrolyte. The Na$_2$SO$_4$ electrolyte was purged with Ar for 30 min prior to the measurements. The photocurrent responses of the prepared photoelectrodes (i.e., I–t) were operated by measuring the photocurrent densities under chopped light irradiation (light on/off cycles: 10 s) at a bias potential of 0.6 V vs. Ag/AgCl electrode for 200 s. The transient open-circuit voltage decay (OCVD) measurements were taken for 500 s in all, and the light on and off were controlled at 50 s and 200 s from the start, respectively. The average lifetime of the photogenerated carriers ($\tau_n$) were obtained from the OCVD according to Eq. (1):

$$\tau_n = -\frac{k_BT}{q} \left(\frac{dV_{OCVD}}{dt}\right)^{-1}$$

(1)

where $k_B$ is the Boltzmann constant, $T$ is the temperature (in Kelvin), and $q$ is the unsigned charge of an electron.

7. Photocatalytic water splitting measurements

To investigate the photocatalytic activities of samples for H$_2$ production, 2-cm$^2$ photocatalysts (106 μg) were immersed into 20-mL deionized water in a home-made quartz bottle, followed by saturation with Ar to eliminate oxygen. The light-irradiation experiment was performed by using a 300-W Xe lamp (Solaredge 700, China). The light source and power intensity were the same as those for photocurrent measurements. As for the 550-nm cutoff measurements, a 550-nm cutoff filter (short-wave-pass or long-wave-pass) was used. The photocatalytic reaction was typically performed for 4 h. The amount of H$_2$ evolved was measured by gas chromatography (GC, 7890 A, thermal conductivity detector, TCD,
The amount of O$_2$ evolved was measured by both NeoFox Sport Oxygen Sensor (Ocean Optics) and GC TCD, which yielded comparable readings. Three replicates were collected for each sample with relative error $<10\%$. The single-wavelength photocatalytic water splitting was measured using the same experimental setup for the photocatalytic hydrogen production above. The catalyst (1 mg) was immersed into 20-mL deionized water and irradiated by a 300-W Xe lamp applying the band-pass filter for 4 hours. The average intensity of irradiation was determined to be 2.7 mW cm$^{-2}$, and the irradiation area was 2 cm$^2$.

8. Results and discussion

The core concept of this fabrication process is to utilize the self-assembled PS nanospheres as templates, combined with e-beam Au evaporation and annealing processes. As illustrated in Fig. 1a, we first self-assemble PS nanospheres on the interface between TiO$_2$ sol and the air (Step 1). With a capillarity force, the TiO$_2$ sol can penetrate the gaps of nanosphere arrays and fill the bottom of PS nanospheres. As a follow-up step, the templates of PS nanospheres are transferred to indium tin oxide (ITO) glass, with TiO$_2$ sol filled at the bottom (Step 2). As shown in the scanning electron microscopy (SEM) image (Fig. 1b), the PS nanospheres are well packed in a hexagonal pattern.

The sample on the ITO glass is further annealed in NH$_3$ with the addition of trimethylamine, which allows removing the PS templates and transforming the TiO$_2$ sol into N-doped anatase TiO$_2$ (Step 3). The SEM image in Fig. 1c indicates that the resulted sample possesses a bowl-like structure and inherits the hexagonal array pattern from its precursor. The sample is further characterized by X-ray diffraction (XRD, Fig. S1), whose peaks all can be indexed to anatase TiO$_2$ (JCPDS no. 21-1272) – an ideal crystal phase with high photocatalytic activity. The N-doping in TiO$_2$ has been verified by X-ray photoelectron spectroscopy (XPS, Fig. S2) and energy-dispersive X-ray spectroscopy (EDS, Fig. S3). Such a bowl-like structure dramatically boosts the surface area of sample as indicated by N$_2$ sorption measurements (Fig. S4), which can provide more active sites for catalytic reactions.

The bowl-like structure also provides an excellent platform for the integration of Au nanoparticles. With a facile electron-beam (e-beam) evaporation, a 4-nm Au layer can be deposited on the TiO$_2$ bowls, which is transformed into Au nanoparticles with an average size of 20 nm after annealed in Ar at 480°C (Step 4). As indicated by Fig. 1d, the Au nanoparticles are well confined in the TiO$_2$ bowls. Intuitively, this unique hybrid structure may offer multiple merits for photocatalysis: i) the monolayer configuration...
provides sufficient surface area for photocatalytic reactions; ii) Au nanoparticles have an intimate contact with the TiO2 bowl, establishing a Schottky junction; and iii) dense Au nanoparticles are confined in a single TiO2 bowl to bring about intense plasmonic light absorption.

This fabrication approach allows facilely tuning the bandgaps of TiO2 from 3.2 to 2.7 eV by altering the N-doping conditions (see Fig. 2a). Figures S5 and S6 show two samples fabricated via a similar procedure except for use of air or N2/trimethylamine instead of NH3/trimethylamine in the Step 3, respectively. The SEM images indicate that the resulted samples possess the same morphologies as the one treated with NH3/trimethylamine. This set of samples thus provide the model systems for examining the roles of spectral overlap between semiconductor and plasmonic metal in photocatalysis. As indicated by UV–vis spectroscopy (Fig. S7), the light absorption of TiO2 is tuned by N-doping towards longer wavelengths to sufficiently overlap with the plasmonic band of Au nanoparticles (400–520 nm), extending the light-harvesting range of photocatalysts. In addition, the densely confined Au nanoparticles exhibit an emerging absorption band above 520 nm due to the plasmonic coupling between the nanoparticles, suggesting the strong local electromagnetic field [17–18].

As the RET process requires that the semiconductor light absorption and metal plasmonic band have sufficient spectral overlap, it is anticipated that the controllable overlap integrals would allow maneuvering photocatalytic performance in vis-spectral range. In principle, such a RET process would prolong the lifetime of carriers for improved charge generation and separation. To assess the effect on carrier lifetime, we have collected transient open-circuit voltage decay (OCVD) on the samples in full spectrum (Fig. S8). The OCVD has been demonstrated as a tool to resolve charge kinetics [19–21]. As illustrated in Fig. 2b–d, the average carrier lifetimes for all the TiO2 bowl nanoarrays in the absence of Au are nearly maintained the same, no matter whether the samples are doped with N. It indicates that the intrinsic charge separation is very comparable in the TiO2 samples.

As Au nanoparticles are integrated into the TiO2 bowl nanoarrays, two effects can be induced to prolong carrier lifetimes: Schottky junction, and RET process. First, the Schottky junction between TiO2 and Au can increase the average carrier lifetime of photogenerated carriers about 2 times, according to the comparison of bare TiO2 with Au nanoparticles-confined TiO2 bowl nanoarrays (undoped, Fig. 2d). This increased lifetime can be mainly ascribed to the Schottky junction effect, just because RET process can barely work when the undoped TiO2 has very limited spectral overlap with Au. To better examine the behavior of charge separation by the Schottky junction, we have employed photocurrent measurements to characterize the samples under UV light irradiation (λ < 400 nm). As shown in Figure S9, the photocurrents can be enhanced roughly 2 times with the addition of Au nanoparticles, as the TiO2-Au Schottky junction traps the photoexcited electrons from TiO2 to Au and thus spatially separates the e-h pairs [9]. The enhancement by Au nanoparticles under UV illumination is comparable for all the TiO2 samples.

Second, the average carrier lifetimes for the TiO2 bowl nanoarrays integrated with Au nanoparticles are gradually prolonged by increasing the spectral overlap between TiO2 and Au (i.e., the N-doping, see the comparison of Fig. 2b–d). Remarkably, the
NH₃-doped TiO₂ nanoarrays with Au nanoparticles exhibit roughly 2.5 times longer lifetime as compared with the non-doped ones with Au. The RET process facilitated by the spectral overlap should have made a key contribution to this improvement, as the Schottky junction is anticipated to have the same efficacy on the charge separation regardless of whether the TiO₂ interfaced with Au is doped with N. The RET effect is directly reflected by photocurrent measurements under vis-light irradiation (Fig. S10). By improving N-doping, more spectral overlap integrals are enabled between TiO₂ and Au to facilitate the RET process, yielding larger photocurrents. It suggests that the RET process can be promoted by extending the light absorption of TiO₂ towards vis-spectral region.

Upon elucidating the processes involved in the system, we are in a position to implement our design in photocatalytic water splitting. Fig. 3a–c shows the average rates of photocatalytic H₂ production for all the samples, which agrees with the trend of photocurrent measurements under UV and visible illumination, respectively. It clearly demonstrates the importance of charge generation and separation to photocatalytic water splitting. To better appreciate the functions of Schottky junction and RET process in the reactions, we measure the photocatalytic performance at single wavelengths of incident light. As shown in Fig. 3d, the H₂ production rates of all the TiO₂ samples can be comparably improved by their integration with Au at \( \lambda < 400 \) nm, which should be caused by the Schottky junction. In sharp contrast, the improvement on H₂ production rates by Au has a strong correlation with N-doping (i.e., the light absorption range of TiO₂) at \( \lambda = 400–520 \) nm, determined by the RET mechanism.

An important characteristic of RET mechanism is to enhance carrier creation and separation at the energies both above and below the bandgap [14], so photocatalyst performance can be further boosted under full-spectrum irradiation. As expected, the H₂ production rates in full spectrum are higher than the sum of those under UV and visible illumination for all the Au-integrated samples (Fig. 3a–c). The full-spectrum enhancement factor is increased by N-doping, owing to the RET mechanism. With the maximal enhancement of RET process by NH₃-treated doping, the full-spectrum rate can reach 1.6 times higher than the sum of UV- and vis-light rates (Fig. 3a).

Based on the observations above, we can briefly summarize the major processes involved in the designed system in full solar spectrum (Fig. 4a). UV light (and partial visible light for N-doped TiO₂) can photoexcite TiO₂ semiconductor to generate the e⁻–h pairs whose separation is improved by the electron trapping of TiO₂-Au Schottky junction. Meanwhile, vis-light irradiation activates the surface plasmon of Au nanoparticles, whose RET process can substantially promote the e⁻–h generation and separation. The separated electrons will in turn be trapped by the Schottky junction. Nevertheless, the RET mechanism relies on the simultaneous photoexcitation of TiO₂ and Au, so it can better work under full-spectrum irradiation.

As a result, the Au nanoparticles-confined NH₃-doped TiO₂ bowl nanoarrays achieve the H₂ production rates of 0.637 mmol h⁻¹ g⁻¹ in full spectrum and 0.132 mmol h⁻¹ g⁻¹ under visible light, respectively, which well exceed the corresponding rates of other samples (Fig. 4b). The 2:1 ratio of H₂ to O₂ clearly demonstrates that the synergetic utilization of RET with Schottky junction can perfectly drive the water splitting process. The sample shows excellent performance stability in a 24-h durability test (Fig. 4c). This performance well exceeds many other oxide-based photocatalysts. For instance, some oxide
semiconductors such as WO$_3$ and CeO$_2$ are incapable of producing H$_2$ given their conduction band structures, despite their resistance to photocorrosion [22]. To enable the H$_2$ production, they have to be integrated with another semiconductor for Z scheme and Pt co-catalyst for H$_2$ evolution [23,24]. For many other oxide-based structures (e.g., Au–ZnO and Au–Fe$_2$O$_3$), the photocatalytic H$_2$ production requires sacrificial agents [25–27] or an external bias through a photoelectrochemical (PEC) device [28,29]. Apparently, our catalyst has achieved direct photocatalytic water splitting to produce both H$_2$ and O$_2$ without the need of any sacrificial agents, with excellent reproducibility and durability. As a matter of fact, TiO$_2$ is a well-known wide-bandgap semiconductor material with remarkable photostability and satisfactory photocatalytic activity compared with other oxide photocatalysts such as Cu$_2$O and ZnO [30]. Thus the plasmonic RET working in visible region, implemented in this excellent semiconductor, offers superior performance in direct photocatalytic water splitting to the Au/TiO$_2$ examples in literature [31].

It should be mentioned that the surface plasmon of Au nanoparticles and CeO$_2$ are incapable of producing H$_2$ given their conduction band structures, despite their resistance to photocorrosion [22]. To enable the H$_2$ production, they have to be integrated with another semiconductor for Z scheme and Pt co-catalyst for H$_2$ evolution [23,24]. For many other oxide-based structures (e.g., Au–ZnO and Au–Fe$_2$O$_3$), the photocatalytic H$_2$ production requires sacrificial agents [25–27] or an external bias through a photoelectrochemical (PEC) device [28,29]. Apparently, our catalyst has achieved direct photocatalytic water splitting to produce both H$_2$ and O$_2$ without the need of any sacrificial agents, with excellent reproducibility and durability. As a matter of fact, TiO$_2$ is a well-known wide-bandgap semiconductor material with remarkable photostability and satisfactory photocatalytic activity compared with other oxide photocatalysts such as Cu$_2$O and ZnO [30]. Thus the plasmonic RET working in visible region, implemented in this excellent semiconductor, offers superior performance in direct photocatalytic water splitting to the Au/TiO$_2$ examples in literature [31].

It should be mentioned that the surface plasmon of Au nanoparticles may also generate the hot electrons that overcome the Schottky barrier and flow into the conduction band of TiO$_2$ [20,21,32–35]. As indicated by Fig. 3d, H$_2$ production has been observed for $\lambda > 520$ nm where the N-doped TiO$_2$ does not absorb light. Here the light absorption originates from the plasmonic coupling between Au nanoparticles. Thus this H$_2$ production should be attributed to the injection of plasmonic hot electrons into TiO$_2$ conduction band and the reaction occurring on TiO$_2$ surface. The flow of hot electrons follows the opposite direction to the electron trapping by the Schottky junction, and as such, it would appear as a detrimental side effect under full-spectrum irradiation. To depict the role of plasmonic hot electrons, we have measured the photocatalytic performance at $\lambda < 550$ nm and $\lambda > 550$ nm in comparison with full spectrum. It indicates that the photocatalysis can be enhanced by filtering out the spectral region (i.e., $\lambda > 550$ nm) where only plasmonic hot electrons work (see Fig. 4d). Although the hot electrons are detrimental to full-spectrum photocatalysis, their effect on the overall efficiency is quite limited as indicated by our measurements (Fig. 4d) and previous studies [20].

9. Conclusion

In conclusion, we have developed a facile surfactant-free nanofabrication approach to confine Au nanoparticles in N-doped TiO$_2$ bowl nanoarrays, which improves the contact of metal with semiconductor surface. The N-doping extends the light absorption of TiO$_2$ to visible region that better overlaps the plasmonic band of Au nanoparticles. This design well synergizes the Schottky junction with the plasmonic RET process, enabling improved photocatalytic water splitting performance in full spectrum. The nanofabrication technique demonstrated here should be easily extended to the fabrication of other semiconductor-metal hybrid photocatalysts with the same structure by simply altering the sol compositions and e-beam evaporation metals. Thus this work represents a step towards large-scale photocatalyst fabrication and full-spectrum photocatalysis, and opens a new window to rationally designing hybrid structures for photocatalysis.

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Appendix A. Supplementary material

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References


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