Plasmonic Au nanoparticles supported on both sides of TiO$_2$ hollow spheres for maximising photocatalytic activity under visible light

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Abstract A strategy of intensifying the visible light harvesting ability of anatase TiO$_2$ hollow spheres (HSs) was developed, in which both sides of TiO$_2$ HSs were utilised for stabilising Au nanoparticles (NPs) through the sacrificial templating method and convex surface-induced confinement. The composite structure of single Au NP yolk-TiO$_2$ shell-Au NPs, denoted as Au@Au(TiO$_2$, was rendered and confirmed by the transmission electron microscopy analysis. Au@Au(TiO$_2$ showed enhanced photocatalytic activity in the degradation of methylene blue and phenol in aqueous phase under visible light surpassing that of other reference materials such as Au(TiO$_2$ by 77% and Au@P25 by 52%, respectively, in phenol degradation.

Keywords TiO$_2$ hollow spheres, plasmonic Au nanoparticles, confinement, visible light, photocatalytic degradation

1 Introduction

Titanium dioxide is a semiconductor that has attracted increasing interests in photocatalytic and photovoltaic applications [1–4] because of the great oxidative potential of its positive holes ($E = +3.0$ V versus standard hydrogen electrode) [5], especially in the anatase form. However, due to the wide band-gap of 3.2 eV (for the anatase form) [6], TiO$_2$ has trivial response to the visible light (wavelength: 390–700 nm) [7,8] hindering the development of visible-light-driven photocatalysts based on TiO$_2$ for energy and environmental applications [6,9]. Various strategies [8,10–14] such as (i) metal (e.g., transition metals Cu, Co) [11] with and non-metal doping (e.g., p-block elements N, B, F) [12,15,16] and (ii) crystal structure and morphology engineering [13,14] are being developed to adjust the band structure and trap states of TiO$_2$ with an aim to enhance the response of the TiO$_2$-based photoelectrochemical materials in the visible region. Recently, the integration of plasmonic gold or silver nanoparticles (NPs) with TiO$_2$ [8,17–22] have been proposed to enhance the photocatalytic and photovoltaic activity in the visible region due to the strong surface plasmon resonance (SPR) excitation of such metal NPs, by which can enhance the concentration of charge carriers. One specific example presented by Zhang et al. [22] is the hybrid plasmonic Au nanoparticle (NP)-loaded hierarchical hollow porous TiO$_2$ spheres, which showed the enhanced the overall catalytic activity in 4-nitrophenol reduction [22]. In general, the energy-transfer mechanisms SPR were concluded as: (i) direct charge injection from metal to semiconductor, (ii) near-field electromagnetic and (iii) resonant photon-scattering mechanisms [21], depending largely on the geometric configuration of the composites. The synergic effect of plasmonic metal NPs and TiO$_2$ semiconductor can be manipulated by controlling the relative arrangement of the two building blocks. For instance, the electric field intensity enhancement was found dropped significantly by more than one order of magnitude when the distance between adjacent plasmonic Ag NPs were increased from 1 to 10 nm [21]. However, to stabilise nanosized metal particles on TiO$_2$ absorber against their high tendencies to aggregate presents a challenge to design stable hybrid nanostructures for practical settings. TiO$_2$ hollow spheres
2 Materials and methods

2.1 Synthesis of core-shell Au(SiO2)

All glassware was thoroughly cleaned with aqua regia (three parts HCl, one part HNO3) for 12 h and rinsed with deionised water (DI). 5 mL sodium citrate (1%, Tianjin Chemical Reagent No 1 Plant) was dispersed into 50 mL HAuCl₄·3H₂O aqueous solution (4 × 10⁻⁴ mol/L) under sonication and then heated to 95°C. After 5 min, 37.5 mL of 400 mmol/L myristyltrimethylammonium bromide (TTAB, Sigma-Aldrich, ≥99%) was added to the solution and the mixture was maintained at 95°C for 15 min under vigorous stirring. The obtained TTAP-capped Au aqueous solution (20 mL), tetraethylorthosilicate (28%, Tianjin Chemical Reagent No 1 Plant, 0.96 mL), dehydrated ethanol (99.8%, Tianjin Guangfu Fine Chemical Institute, 23 mL) and ammonia solution (26%, Tianjin Guangfu Fine Chemical Institute, 0.62 mL) were then mixed and stirred for 4 h at room temperature.

2.2 Synthesis of yolk-shell Au(TiO2)

Au(SiO2) was dispersed in a mixture of hydroxypropyl cellulose (HPC, Tokyo Chemical Industry Co., Ltd., 0.1 g), ethanol (20 mL) and DI (0.1 mL) and stirred for 40 min. Titanium tert-butoxide (98%, Tianjin Chemical Reagent No 1 Plant, 1 mL) in ethanol (5 mL) solution was added in the mixture at a rate of 0.5 mL/min. The mixture was stirred at 900 r/min and 85°C under refluxing condition for 100 min. The final product was separated by centrifugation, washed with ethanol, and kept in 5 mL of ethanol to form Au(SiO2(TiO2 nanocomposites. The Au(SiO2(TiO2 was calcined in air at 500°C (2°C/min) for 2 h to remove all organic compounds and crystallise the amorphous TiO2. The calcined samples were dispersed in 20 mL water under sonication and heated to 50°C. 1.5 mL aqueous NaOH solution (2.5 mol/L, Tianjin Guangfu Fine Chemical Institute) was added in the aqueous Au(SiO2(TiO2 solution and the solution was heated to 70°C. Finally, aqueous NaOH solution (2.5 mol/L, 1 mL) was added and the resulting solution was stirred for 6 h to remove the SiO2 core and obtain yolk-shell Au(TiO2.

2.3 Synthesis of Au@Au(TiO2)

Yolk-shell Au(TiO2 (0.1 g) and sodium citrate (1%, Tianjin Chemical Reagent No 1 Plant, 5 mL) were dispersed into 50 mL HAuCl₄·3H₂O aqueous solution (4 × 10⁻⁴ mol/L) under sonication. The mixture was heated to 95°C and maintained at 95°C for 20 min under vigorous stirring. The product was separated by centrifugal separation, washed with DI and dried at 100°C for 10 h. The same procedure was used for depositing Au NPs on other supports.

2.4 Characterisation of materials

N₂ adsorption-desorption at −196°C was performed using a Micromeritics Tristar 3000 analyser to determine the specific surface area (the Brunauer–Emmett–Teller method) and the pore size distribution (the Barrett-Joyner-Halenda method). X-ray diffraction (XRD) patterns of materials were recorded on a Bruker D8 Focus diffractometer (nickel-filtered CuKα1 radiation, λ = 1.5406 Å, 40 kV, 40 mA) at a scanning rate of 0.02° per step and 0.15 s per step in a 2θ range of 10°–85° (and 5°–65°). Transmission electron microscopy (TEM) imaging was completed using an FEI Tecnai G2 F20 operating at 100 kV. Samples were dispersed in ethanol and pipetted onto the copper grid-supported transparent carbon foil and dried prior to imaging. Scanning electron microscopy imaging of materials was undertaken using a JEM-2100F. Diffuse reflectance spectra (DRS) of materials were
obtained using a SHIMADZU UV-2550 spectrophotometer equipped with a 60 nm diameter integrating sphere using BaSO₄ as the reflectance sample.

2.5 Evaluation of photocatalytic activity

The photocatalytic activity of materials was evaluated by photodegradation of methylene blue (MB, 98%, Tianjin Damao Chemical Co., Ltd.) and phenol (Tianjin Damao Chemical Co., Ltd.). 50 mg photocatalyst was firstly added into a 100 mL quartz photoreactor containing the solution with the substrate (12 mmol/L) and ultrasonicated for 2 min. The mixture was magnetically stirred for 30 min in the dark to ensure good dispersion of the photocatalyst in the solution the adsorption-desorption equilibrium between substrate molecules and the photocatalyst. The same 50 mg photocatalyst was also used for phenol solution (100 µmol/L). A visible light source (420 £ 780 nm) was introduced by a 300 W xenon lamp (Beijing Perfectlight Technology Co. Ltd., LS-SXE300-CUV, equipped with an AM 1.5-filter power intensity = 100 mW/cm²) 10 cm above the liquid surface. The ambient temperature of the reaction was maintained by water cooling during the reaction. Every 30 min, a 2 mL sample was taken and analysed for the concentration of the substrate. For MB and phenol, the absorbance intensity at their maximum absorbance wavelength of λmax = 664, 270 nm was monitored using a SHIMADZU UV-2550 spectrophotometer.

3 Results and discussion

The synthesis and morphological evolution of the yolk-shell Au(TiO₂) nanostructure and the corresponding TEM images were illustrated in Figs. 1 and 2. A three-step method was used (Fig. 1) to synthesise the yolk-shell Au(TiO₂) nanostructure, i.e., (i) Synthesising Au(SiO₂) nanoparticles using the Stöber method (Fig. 2(a)) [29]; (ii) Coating Au(SiO₂) with anatase TiO₂ via hydrolysis-condensation and calcination (Fig. 2(b)) [17,23]; and (iii) Removing SiO₂ core to render the yolk-shell Au(TiO₂ with NaOH-based chemical etching (Fig. 2(c)). The method enabled the solitary inclusion of one myristyltrimethylammonium bromide-capped Au NP of 7±2 nm. The average shell thickness and diameter of the anatase TiO₂ shell are about 25±2 and 140±10 nm, respectively. The developed TiO₂ shell was highly porous with a specific surface area of 187 m²/g (Figs. S1, S2 and Table S1, cf. Electronic Supplementary Material (ESM)). To further utilise the outer surface of the porous TiO₂ shell, Au NPs (ca. 1 wt-%) were deposited on the yolk-shell Au(TiO₂) yielding the Au NP core-TiO₂ shell-Au NPs hybrid structure as shown in Fig. 2(d). Au NPs with similar diameters were found well-dispersed on the outer surface of anatase TiO₂ shell in the as-prepared Au(TiO₂) (Fig. 2(d)). The convex outer surface of TiO₂ HSs was believed to avoid the aggregation of Au NPs. High-resolution transmission electron microscopy (HR-TEM) analysis also showed the well-resolved crystalline Au NPs with a fine crystal lattice spacing of 0.2355 nm (inset of Fig. 2(d)), corresponding to (111) plane of the face-centred cubic gold. For the purpose of comparison, TEM images of pure SiO₂ core, core-shell SiO₂(TiO₂, TiO₂ HSs and Au@TiO₂ HSs were prepared and shown in Figs. 2(e-h). It was found that the hollow spherical structure of porous TiO₂ remained largely intact during the synthesis (Fig. S1). XRD patterns of TiO₂ HSs, Au@TiO₂, Au(TiO₂ and Au@Au(TiO₂ (Fig. S3, cf. ESM) showed characteristic diffraction peaks of the anatase TiO₂ phase (JCPDS file no. 21-1272) and the Au metal phase (JCPDS file no. 01-1174). As compared to Au(TiO₂, the intensity of Au peaks in Au@Au(TiO₂ are much stronger, which can be attributed to the extra Au NPs loaded on TiO₂ shell. UV-Vis DRS analyses (Fig. S4, cf. ESM) showed that there was no absorption observed in the visible region for TiO₂ HSs. With the decoration of plasmonic Au NPs, the surface plasmon resonance (SPR) peaks at around 550 nm emerged [30,31]. In comparison with pure Au nanocrystal (ca. 520 nm), the redshift in SPR peaks of Au-based TiO₂

![Fig. 1 Scheme of synthesis and formation of the single Au core-anatase TiO₂ shell nanostructure. (a-d) TEM images showing the morphological evolution of the yolk-shell Au(TiO₂)](image)
materials can be ascribed to the effect of the high-refractive-index anatase TiO2 shell [32,33]. In addition, the variation in SPR intensities found in Au-based TiO2 composites (Au@Au(TiO2, Au(TiO2 and Au@TiO2) suggests that the optical properties of TiO2 HSs can be tuned by controlling the deposition location of Au NPs. Yolk-shell Au@Au(TiO2 showed the strongest SPR intensity among these samples, which is related to a substantial increase in its scattering coefficient promoted by the Au NPs located on both sides of TiO2 shell. The photocatalytic activity of materials was evaluated under visible light irradiation (420 ≤ λ ≤ 780 nm) using MB and phenol as probe molecules shown in Figs. 3 and 4.

Comparative photocatalytic studies were carried out using materials developed alongside naked Au NPs and Au NPs supported on P25 catalyst (Au@P25) and results were shown in Figs. 3(a) and 4(a). The chemical catalysis effect of Au NPs was trivial because naked Au NPs were found inactive in both cases. Commercial P25 and TiO2 HSs showed the poor catalytic activity with both MB and phenol (i.e., < 7% conversions after 180 min illumination) suggesting that the plasmon-enhanced light absorption and plasmonic sensitisation of Au NPs indeed improved the photocatalytic activity of TiO2 materials. Au@TiO2 HSs showed better activities than Au@P25 in both photocatalytic model reactions. This is attributed to the high specific surface area of TiO2 HSs (187 m2/g) providing abundant active sites for converting the probing molecules, while only 36 m2/g for commercial P25 (Table S1). In addition, the light harvesting and scattering ability were

![Fig. 2](image_url) TEM images of the as-prepared materials: (a) Au(SiO2, (b) core-core-shell Au(SiO2(TiO2, (c) yolk-shell Au(TiO2, (d) Au@Au(TiO2, (e) SiO2 core, (f) SiO2(TiO2 core-shell, (g) TiO2 HSs, (h) Au@TiO2 HSs

![Fig. 3](image_url) (a) The rate of MB degradation under visible light promoted by various TiO2 photocatalysts; (b) The corresponding pseudo-first-order kinetic rate plot
also improved by the HSs structure as explained in the previous work [17]. For the Au-based TiO₂ hybrid nanomaterial, the decolourisation of MB and degradation of phenol were improved for the same period of time, following the order of activity as: Au@Au(TiO₂ > Au@TiO₂ HSs > yolk-shell Au(TiO₂).

The degradation rate of both probing molecules followed first-order kinetics concerning their concentrations. The rate can, therefore, be interpreted using the pseudo-first-order reaction model (Figs. 3(b) and 4(b)). The previous study by the action spectrum has shown that the degradation of MB was induced mainly by the SPR excitation of Au NPs in Au-TiO₂ materials rather than the sensitisation of the dye molecules [30]. By comparing the rate constants in the decolourisation of MB, Au@TiO₂ HSs showed a better activity (0.030 min⁻¹) than that of yolk-shell Au(TiO₂ (0.013 min⁻¹). In the yolk-shell Au (TiO₂, e−h pairs are produced inside the TiO₂ shell, whereas the catalytic reactions take place mostly at the outer surface of TiO₂ HSs. Therefore, the transportation of e−h pairs through the TiO₂ shell increases the probability of e−h recombination leading to the relatively low activity in photocatalysis in comparison with that of Au@TiO₂ HSs. To decorate the inner and outer surface of TiO₂ HSs simultaneously, the photocatalytic activity of Au@Au (TiO₂ increased significantly with a constant of 0.044 min⁻¹ for MB decolourisation, more than three times higher than that of yolk-shell Au(TiO₂. Based on the results above, the utilisation of both sides of TiO₂ shell was proven to be efficient to boost the photocatalytic activity of Au NP-TiO₂ HS nanostructures. This can be attributed mainly to the improved light-harvesting capacity of TiO₂ HSs caused by the multiple intensified local electromagnetic fields across the TiO₂ shell. Accordingly, the interfacial hot electron transfer from Au NPs to TiO₂ shell upon the excitation of the LSPR (plasmonic sensitisation) was also intensified effectively as the synergistic effect. Additionally, due to the confinement of Au NPs both within the TiO₂ HSs and on their convex external surfaces, the developed Au@Au(TiO₂ photocatalyst also demonstrated good stability in the model reaction. The photocatalyst remained sufficiently active even after three successive recycles in the decolourisation of MB in the aqueous phase (Fig. S5, cf. ESM).

4 Conclusions

In conclusion, a hybrid structure of Au nanoparticles (NPs) and anatase TiO₂ HSs was synthesised, in which Au NPs were confined on both sides of the TiO₂ HSs enabled by the silica templating-NaOH etching and convex surface-induced confinement. The sandwich yolk-shell structures of Au NPs and TiO₂ HSs, termed Au@Au(TiO₂), were determined by TEM characterisation, in which multiple Au NPs decorated on a single Au yolk-TiO₂ shell nanostructure were found. According to the UV-Vis DRS analysis, Au@Au(TiO₂ showed the strongest SPR intensity at about 550 nm compared to Au(TiO₂ and Au@TiO₂. Comparative studies of Au@Au(TiO₂, Au(TiO₂, Au@TiO₂ and Au@P25 in the photocatalytic degradation of two model molecules (i.e., MB and phenol) under visible light irradiation were carried out. Au@Au(TiO₂ exhibited the enhanced activity for both reactions with the degradation rate of MB and phenol as 99% and 78%, respectively, after 180 min due to the multiple intensified local electromagnetic fields across the TiO₂ shell. The strategy of sequential decorating both sides of TiO₂ shells...
is generic and applicable to another semiconductor hollow spherical materials (e.g., BiVO₄ and SnO₂), which is beneficial to develop highly efficient photocatalysts for photoelectrochemical applications such as solar cells and water splitting.

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**References**

1. Schrauben J N, Hayroun R, Valdez C N, Braten M, Fridley L, Mayer J M. Titanium and zinc oxide nanoparticles are proton-coupled electron transfer agents. Science, 2012, 336(6086): 1298–1301
2. Gratzel M. Photoelectrochemical cells. Nature, 2001, 414(6861): 338–344
3. Caravaca A, Daly H, Smith M, Mills A, Chanssi S, Hardacre C. Continuous flow gas phase photoreforming of methanol at elevated reaction temperatures sensitised by Pt/TiO₂. Reaction Chemistry & Engineering, 2016, 1(6): 649–657
4. Caravaca A, Jones W, Hardacre C, Bowker M H. Hydrogen production by the photocatalytic reforming of cellulose and raw biomass using Ni, Pd, Pt and Au on titania. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science, 2016, 472
5. Palmisano L, Scafani A. Thermodynamics and kinetics for heterogeneous photocatalytic processes. In: Schiavello M, ed. Heterogeneous Photocatalysis. New York: John Wiley & Sons, 1997, 109–132
6. Cong Y, Zhang J, Chen F, Anpo M. Synthesis and characterization of nitrogen-doped TiO₂ nanophotocatalyst with high visible light activity. Journal of Physical Chemistry C, 2007, 111(19): 6976–6982
7. Meng Q, Wang T, Liu E, Ma X, Ge Q, Gong J. Understanding electronic and optical properties of anatase TiO₂ photocatalysts co-doped with nitrogen and transition metals. Physical Chemistry Chemical Physics, 2013, 15(24): 9549–9561
8. Lu J, Su F, Huang Z, Zhang C, Liu Y, Ma X, Gong J. N-Doped Ag/TiO₂ hollow spheres for highly efficient photocatalysis under visible-light irradiation. RSC Advances, 2013, 3(3): 720–724
9. Wang H, Zhang L, Chen Z, Hu J, Li S, Wang Z, Liu J, Wang X. Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances. Chemical Society Reviews, 2014, 43(15): 5234–5244
10. Pan H, Zhang Y W, Shenoy V B, Gao H. Effects of H-, N-, and (H, N)-doping on the photocatalytic activity of TiO₂. Journal of Physical Chemistry C, 2011, 115(24): 12224–12231
11. Pelaez M, Nolan N, Pillai S, Seery M, Falaras P, Patrick A G, Jeremy S M, Hamilton W J, Byrne J A, O’Shea K, et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental, 2012, 125: 331–349
12. Dozzi M V, Selli E. Doping TiO₂ with p-block elements: Effects on photocatalytic activity. Journal of Photochemistry and Photobiology C, Photochemistry Reviews, 2012, 14: 13–28
13. Kamat P V. TiO₂ nanostructures: Recent physical chemistry advances. Journal of Physical Chemistry C, 2012, 116(22): 11849–11851
14. Li L, Yan J, Wang T, Zhao Z J, Zhang J, Gong J, Guan N. 10 nm rutile titanium dioxide nanoparticles for efficient visible-light-driven photocatalytic hydrogen production. Nature Communications, 2015, 6(1): 5881
15. Ansari S A, Khan M M, Ansari M O, Cho M H. Nitrogen-doped titanium dioxide (N-doped TiO₂) for visible light photocatalysis. New Journal of Chemistry, 2016, 40(4): 3000–3009
16. Li L, Meng F, Hu X, Qiao L, Sun C Q, Tian H, Zheng W. TiO₂ band restructuring by B and P dopants. PLoS One, 2016, 11(4): e0152726
17. Lu J, Zhang P, Li A, Su F, Wang T, Liu Y, Gong J. Mesoporous anatase TiO₂ nanocups with plasmonic metal decoration for highly active visible-light photocatalysis. Chemical Communications (Cambridge), 2013, 49(52): 5817–5819
18. Tian Y, Tatsuma T. Mechanisms and applications of plasmon-induced charge separation at TiO₂ films loaded with gold nanoparticles. Journal of the American Chemical Society, 2005, 127(20): 7632–7637
19. Awazu K, Fujimaki M, Rockstuhl C, Tominaga J, Murakami H, Ohki Y, Yoshida N, Watanabe T. A plasmonic photocatalyst consisting of silver nanoparticles embedded in titanium dioxide. Journal of the American Chemical Society, 2008, 130(5): 1676–1680
20. Lee I, Joo J B, Yin Y D, Zaera F. A yolk@shell nanoarchitecture for Au/TiO₂ catalysts. Angewandte Chemie International Edition, 2011, 50(43): 10208–10211
21. Linic S, Christopher P, Ingram D B. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. Nature Materials, 2011, 10(12): 911–921
22. Zhang Q, Jin X, Xu Z, Zhang J, Rendón U F, Razzari L, Chaker M, Ma D. Plasmonic Au-loaded hierarchical hollow porous TiO₂ spheres: Synergistic catalysts for nitroaromatic reduction. Journal of Physical Chemistry Letters, 2018, 9(18): 5317–5326
23. Joo J B, Dahl M, Li N, Zaera F, Yin Y. Tailored synthesis of mesoporous TiO₂ hollow nanostructures for catalytic applications. Energy & Environmental Science, 2013, 6(7): 2082–2092
24. Joo J B, Zhang Q, Dahl M, Lee I, Goebl J, Zaera F, Yin Y. Control
of the nanoscale crystallinity in mesoporous TiO$_2$ shells for enhanced photocatalytic activity. Energy & Environmental Science, 2012, 5(4): 6321–6327

25. Dillon R J, Joo J B, Zaera F, Yin Y, Bardeen C J. Correlating the excited state relaxation dynamics as measured by photoluminescence and transient absorption with the photocatalytic activity of Au@TiO$_2$ core-shell nanostructures. Physical Chemistry Chemical Physics, 2013, 15(5): 1488–1496

26. Lee Y J, Joo J B, Yin Y, Zaera F. Evaluation of the effective photoexcitation distances in the photocatalytic production of H$_2$ from water using Au@void@TiO$_2$ yolk-shell nanostructures. ACS Energy Letters, 2016, 1(1): 52–56

27. Lee I, Joo J B, Yin Y, Zaera F. Au@Void@TiO$_2$ yolk-shell nanostructures as catalysts for the promotion of oxidation reactions at cryogenic temperatures. Surface Science, 2016, 648: 150–155

28. José-Yacamán M, Gutierrez-Wing C, Miki M, Yang D Q, Piyakis K N, Sacher E. Surface diffusion and coalescence of mobile metal nanoparticles. Journal of Physical Chemistry B, 2005, 109(19): 9703–9711

29. Liz-Marzan L M, Giersig M, Mulvaney P. Synthesis of nanosized gold-silica core-shell particles. Langmuir, 1996, 12(18): 4329–4335

30. Bian Z, Tachikawa T, Zhang P, Fujitsuka M, Majima T. Au/TiO$_2$ Superstructure-based plasmonic photocatalysts exhibiting efficient charge separation and unprecedented activity. Journal of the American Chemical Society, 2014, 136(1): 458–465

31. Prikulis J, Hanarp P, Olofsson L, Sutherland D, Käll M. Optical spectroscopy of nanometric holes in thin gold films. Nano Letters, 2004, 4(6): 1003–1007

32. Seh Z W, Liu S H, Low M, Zhang S Y, Liu Z L, Mlayah A, Han M Y. Janus Au-TiO$_2$ photocatalysts with strong localization of plasmonic near-fields for efficient visible-light hydrogen generation. Advanced Materials, 2012, 24(17): 2310–2314

33. Wu X F, Song H Y, Yoon J M, Yu Y T, Chen Y F. Synthesis of core-shell Au@TiO$_2$ nanoparticles with truncated wedge-shaped morphology and their photocatalytic properties. Langmuir, 2009, 25(11): 6438–6447