

Plasmonic Au nanoparticles supported on both sides of TiO₂ 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 TiO₂ hollow spheres (HSs) was developed, in which both sides of TiO₂ 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-TiO₂ shell-Au NPs, denoted as Au@Au(TiO₂), was rendered and confirmed by the transmission electron microscopy analysis. Au@Au(TiO₂) 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(TiO₂) by 77% and Au@P25 by 52%, respectively, in phenol degradation.

Keywords TiO₂ 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], TiO₂ has trivial response to the visible light (wavelength: 390–700 nm) [7,8] hindering the develop-

ment of visible-light-driven photocatalysts based on TiO₂ 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 TiO₂ with an aim to enhance the response of the TiO₂-based photoelectrochemical materials in the visible region. Recently, the integration of plasmonic gold or silver nanoparticles (NPs) with TiO₂ [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 TiO₂ 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 TiO₂ 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 TiO₂ absorber against their high tendencies to aggregate presents a challenge to design stable hybrid nanostructures for practical settings. TiO₂ hollow spheres

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(HSs) [20,23,24] have attracted increasing interests due to their tunable structural properties (e.g., size, shell thickness and crystallinity) and hence their photoelectrochemical properties [23,24]. The unique void of TiO₂ HSs was also employed to encapsulate and stabilise plasmonic metal NPs [17,20,25–27] yielding yolk (metal NP)-shell (TiO₂) arrangements, e.g., Au(TiO₂ HSs (' represents the encapsulation of Au NP in HSs), with improved thermal stability of the metal cores. Though few excellent samples of the yolk-shell Au(TiO₂ HSs nanoreactors have shown good performance in photocatalytic oxidation of CO [20] and water splitting [26], their applications in liquid phase environmental remediation with bigger organic molecules are still limited due to (i) the restricted accessibility of the metal core and (ii) the inadequate availability of metal species (usually the single core configuration was designed to avoid aggregation).

Molecular dynamics simulations have shown that the surface layer of a metal NP possessed liquidlike properties [28] favouring the aggregation of adjacent metal NPs. In fact, the outer surface of TiO₂ HSs is convex in all directions perfect to provide spatial confinement for separating metal drops. To date, the confinement effect of metal NPs created by the curvature of the TiO₂ HSs has been mostly neglected, and only a few examples showed the effectiveness of using the outer surface of TiO₂ HSs to stabilise plasmonic metal NPs [8]. Herein, we demonstrate the design and synthesis of plasmonic Au-TiO₂ HSs nanostructure with Au NPs deposited on both sides of the anatase TiO₂ HS, i.e., a single encapsulated Au core and multiple Au NPs confined by the convex curved outer surface of the TiO₂ HS, denoted as Au@Au(TiO₂ (@ represents the deposition of Au NP on HSs), to improve the photocatalytic efficiency of the system.

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 (J&K Scientific) 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, $\geq 99\%$) 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), tetraethyl orthosilicate (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.

The precipitated silica nanoparticles were extracted by centrifugal separation and washed with ethanol then re-dispersed in 5 mL of ethanol.

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 CuK α 1 radiation, $\lambda = 1.5406$ 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 ($420 \leq \lambda \leq 780$ 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 $\lambda_{\max} = 664, 270$ 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

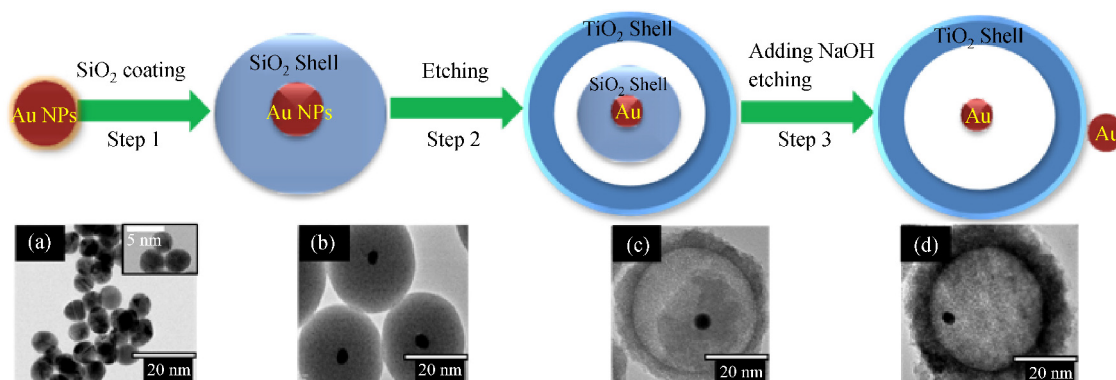


Fig. 1 Scheme of synthesis and formation of the single Au core-anatase TiO₂ shell nanostructure. (a-d) TEM images showing the morphological evolution of the yolk-shell Au(TiO₂)

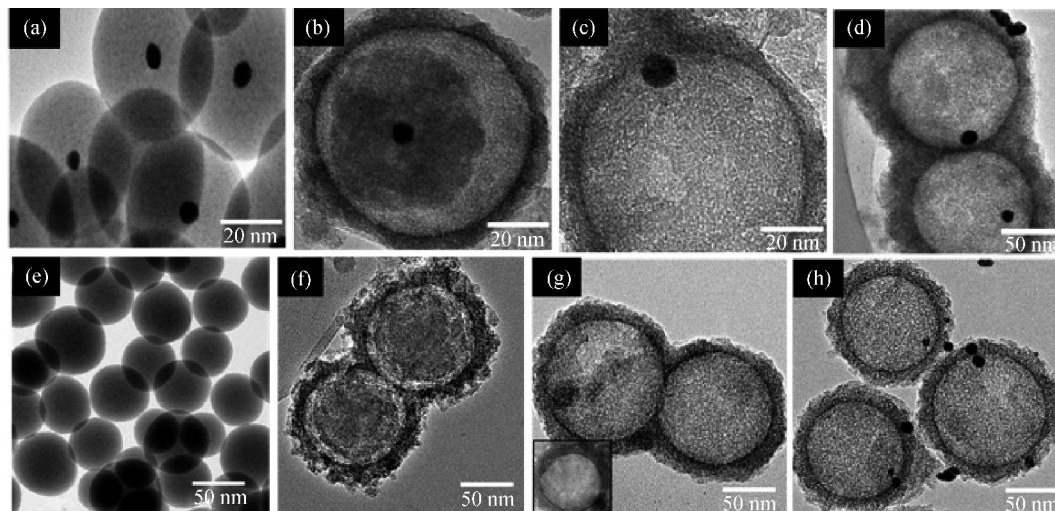


Fig. 2 TEM images of the as-prepared materials: (a) Au(SiO₂), (b) core-core-shell Au(SiO₂/TiO₂), (c) yolk-shell Au(TiO₂), (d) Au@Au(TiO₂), (e) SiO₂ core, (f) SiO₂/TiO₂ core-shell, (g) TiO₂ HSs, (h) Au@TiO₂ HSs

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 ($420 \leq \lambda \leq 780$ 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

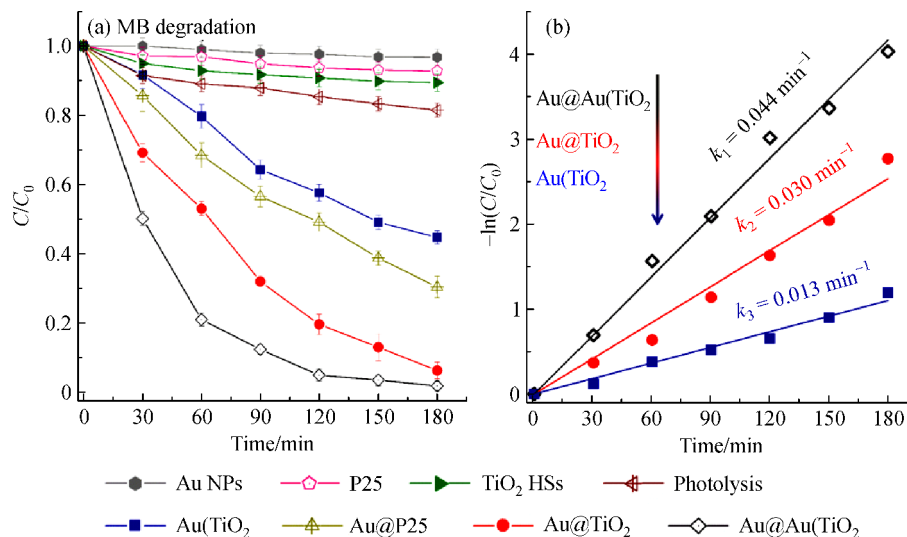


Fig. 3 (a) The rate of MB degradation under visible light promoted by various TiO₂ photocatalysts; (b) The corresponding pseudo-first-order kinetic rate plot

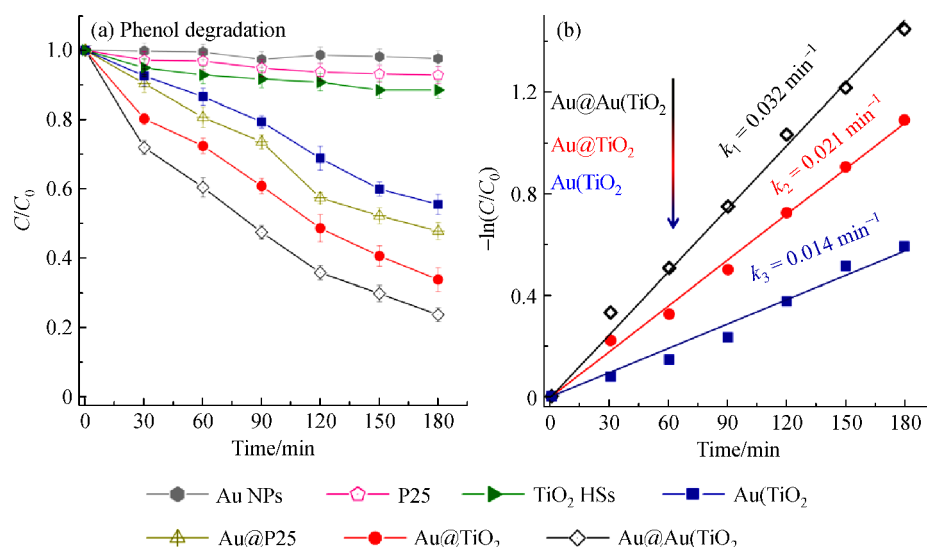


Fig. 4 (a) The rate of phenol degradation under visible light promoted by various TiO₂ photocatalysts; (b) The corresponding pseudo-first-order kinetic rate plot

also improved by the HSs structure as explained in the previous work [17]. For the Au-based TiO₂ hybrid nanomaterial, the decolorisation of MB and degradation of phenol were improved for the same period of the 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 decolorisation 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 decolorisation, 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 decolorisation 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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