

## COMMUNICATION

# Synergetic promotion of the photocatalytic activity of TiO<sub>2</sub> by gold deposition under UV-visible light irradiation†

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**Under UV-visible light irradiation, multiple synergetic promotion effects on the photocatalytic activity of TiO<sub>2</sub> by gold deposition can be observed, and plasmonic Au/TiO<sub>2</sub> shows great potential for photocatalytic solar conversion.**

Semiconductor photocatalysis has attracted significant attention due to its promising application in environment remediation and solar energy conversion. TiO<sub>2</sub> is the initial semiconductor photocatalyst investigated,<sup>1</sup> and still regarded as a benchmark photocatalyst under UV irradiation.<sup>2</sup> Great efforts have been attempted both to narrow the bandgap of TiO<sub>2</sub> to realize visible light response and to reduce the recombination of photo-generated electron-hole pairs under irradiation.<sup>3</sup> Loading of an appropriate co-catalyst on TiO<sub>2</sub> can effectively reduce the surface recombination of photo-generated electron-hole pairs and significantly enhance the photocatalytic activity.<sup>4</sup> Recently, surface plasmon resonance (SPR) on certain conducting metals, *e.g.* Au and Ag, has been successfully applied to photocatalysis under visible light irradiation and it is proved to be a promising means to achieve visible light response.<sup>5</sup> The electrons in conducting metals might be excited by the localized SPR with visible light absorption and subsequently transferred to the conduction band of the attached semiconductors. The electrons transferred to the surface of semiconductors and the holes remaining on the surface of conducting metals can act as redox centres to initiate photocatalytic reactions.<sup>5a</sup> Alternatively, the SPR on conducting metals may enhance the local electric field of neighbouring semiconductors, and, therefore, enhance the photocatalytic efficiency of semiconductors.<sup>5d</sup>

Despite emerging reports on SPR photocatalysis, the detailed mechanism remains a matter of debate and direct experimental evidence on SPR is to be disclosed. Moreover, research studies on plasmonic photocatalysis are focused on the visible light response of photocatalysts, and SPR photocatalysis under UV-visible light

irradiation is not studied. Herein, we demonstrate that the deposition of Au nanoparticles with finite sizes on TiO<sub>2</sub> results in multiple synergetic promotion effects on the photocatalytic activity under UV-visible light irradiation. The results present visualized evidence on SPR photocatalysis and will shed light on the design of efficient composite photocatalysts under sunlight irradiation.

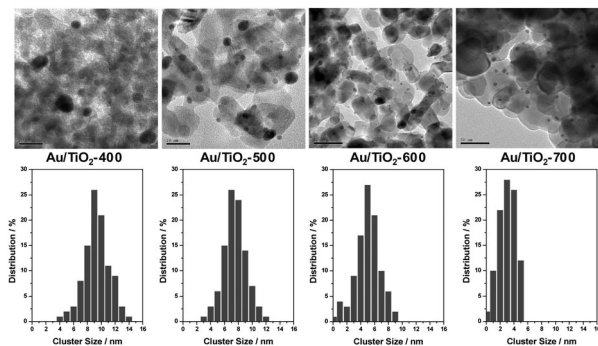
Anatase TiO<sub>2</sub> was prepared *via* a hydrothermal method and the anatase structure could be well-preserved after calcination. With increasing calcination temperature from 400 to 700 °C, both the crystallinity and the crystallite size of TiO<sub>2</sub> increase, while the surface area decreases distinctly (see ESI,† Fig. S1 and Table S1). Meanwhile, the density of surface defects, *i.e.* the number of surface defects per surface area, of anatase TiO<sub>2</sub> increases unexpectedly, as revealed by ESR and O 1s XPS results (Fig. S2 and S3 and corresponding discussion, ESI†).<sup>6</sup> Calcined anatase TiO<sub>2</sub> samples were employed as supports and Au nanoparticles were loaded through photo-deposition processes. Interestingly, the size of Au nanoparticles on TiO<sub>2</sub> gradually decreases with increasing density of surface defects of TiO<sub>2</sub>. The average sizes of Au nanoparticles are determined to be 9.4, 7.5, 5.3 and 3.1 nm for Au/TiO<sub>2</sub>-400, Au/TiO<sub>2</sub>-500, Au/TiO<sub>2</sub>-600 and Au/TiO<sub>2</sub>-700, respectively (Fig. 1). After photo-deposition, the density of surface defects on TiO<sub>2</sub> dramatically decreases according to ESR and XPS results (Fig. S2 and S3, ESI†). So, it is possible to adjust the size of Au nanoparticles deposited on TiO<sub>2</sub> *via* photo-deposition processes by controlling the density of surface defects of TiO<sub>2</sub> supports.

The light absorption behaviour of as-prepared Au/TiO<sub>2</sub> photocatalysts is investigated by UV-Vis spectroscopy. Besides the intrinsic absorption at around  $\lambda = 370$  nm corresponding to the band-band transition of anatase TiO<sub>2</sub>, strong photo-absorption can be observed at around  $\lambda = 540$  nm on Au/TiO<sub>2</sub> (Fig. S4, ESI†), which is attributed to the SPR of Au nanoparticles. The plasmon band overlaps with an interband transition in Au, where electrons in the filled 5d states are excited to the 6s states above the Fermi level.<sup>7</sup> The intensity of the SPR band in Au/TiO<sub>2</sub> increases distinctly with increasing size of Au nanoparticles (Fig. S4, ESI†), which is consistent with literature reports.<sup>8</sup>

The photocatalytic hydrogen evolution activity of as-prepared Au/TiO<sub>2</sub> was investigated under irradiation of lights with

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**Fig. 1** TEM of Au/TiO<sub>2</sub> samples and the corresponding size distribution of Au nanoparticles.

different wavelengths, *i.e.* UV light at 320–400 nm, visible light at 400–780 nm and UV-visible light at 320–780 nm. TiO<sub>2</sub> supports do not show any photocatalytic activity under visible light irradiation. After the deposition of Au nanoparticles, significant visible light photocatalytic activity can be obtained (Fig. S5, ESI<sup>†</sup>). Anatase TiO<sub>2</sub> exhibits considerable photocatalytic activity under UV or UV-visible light irradiation, while the photocatalytic activity under UV-visible light irradiation is slightly lower (Fig. S6, ESI<sup>†</sup>). A possible explanation is that the incident protons with an energy of <3.2 eV can be absorbed by TiO<sub>2</sub> without excitation, and therefore, influence the absorption and excitation of protons with an energy of >3.2 eV. Au/TiO<sub>2</sub> samples show very high photocatalytic activity under UV light irradiation, exceeding corresponding TiO<sub>2</sub> supports 80–125 times. Different to the case of TiO<sub>2</sub>, the photocatalytic activity of Au/TiO<sub>2</sub>-400, Au/TiO<sub>2</sub>-500 and Au/TiO<sub>2</sub>-600 under UV-visible light irradiation is obviously higher than that under UV light irradiation (Fig. S6, ESI<sup>†</sup>). The SPR of Au seems to have a positive effect on the photocatalytic activity under UV light irradiation.

The photocatalytic activities of TiO<sub>2</sub> and Au/TiO<sub>2</sub> under irradiation with different wavelengths are summarized in Table 1. First, the deposition of Au on TiO<sub>2</sub> can transform TiO<sub>2</sub> into a visible light photocatalyst *via* the SPR effect. The observed photocatalytic activity of Au/TiO<sub>2</sub> under visible light irradiation correlates well with the SPR intensity (Fig. S5, ESI<sup>†</sup>). Then, Au can act as an efficient co-catalyst and greatly promote the photocatalytic activity of TiO<sub>2</sub> under UV light irradiation. Au/TiO<sub>2</sub> exhibits a hydrogen evaluation rate two orders of magnitude higher than the corresponding TiO<sub>2</sub> support. The Au particle size does not have a decisive role in the promotion effects, similar to the report of Idriss *et al.*<sup>9</sup> Lastly, the SPR of Au can promote the photocatalytic activity of Au/TiO<sub>2</sub> under UV light irradiation. The promotion effect of Au on the activity of TiO<sub>2</sub> under UV-visible light irradiation is significantly higher than that under UV light irradiation, indicating that Au is not just being used as a co-catalyst. Since the visible light photocatalytic activity caused by the SPR effect of Au is negligible compared to the UV light activity, we conclude that the SPR effect of Au shows significant positive effects on the UV light photocatalytic activity of Au/TiO<sub>2</sub>. The difference in the hydrogen evolution rates under irradiation with different wavelengths, *i.e.*  $\Delta$  defined as  $\text{Rate}_{(\text{UV-Vis})} - \text{Rate}_{(\text{UV})} - \text{Rate}_{(\text{Vis})}$ , correlates well with the SPR intensity of Au (Fig. S7, ESI<sup>†</sup>). A rational explanation is that the SPR on Au can enhance the local electric

**Table 1** Hydrogen evolution rates in photocatalytic reforming of methanol

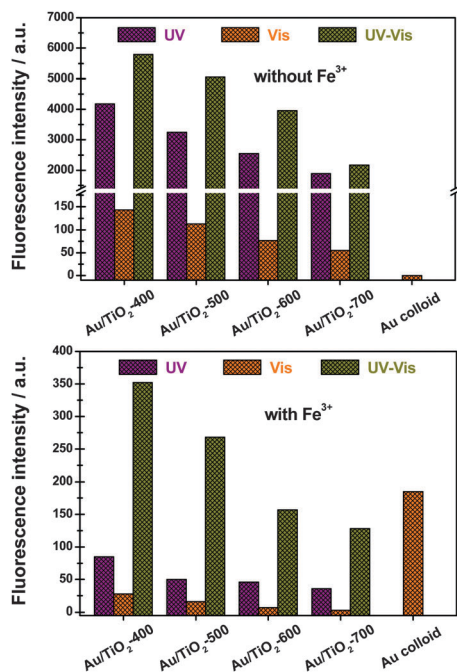
Sample	Hydrogen evolution rate/ $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$			$\Delta^b$
	UV	Vis	UV-Vis	
TiO <sub>2</sub> -400	103.1	≈ 0	81.5	−21.6
Au/TiO <sub>2</sub> -400	12 846.5	12.6	18 952.2	6093.1
Ratio-400 <sup>a</sup>	124.6	—	232.6	—
TiO <sub>2</sub> -500	87.0	≈ 0	69.7	−17.3
Au/TiO <sub>2</sub> -500	10 726.6	9.1	14 658.2	3922.5
Ratio-500 <sup>a</sup>	123.3	—	210.3	—
TiO <sub>2</sub> -600	70.2	≈ 0	59.1	−11.1
Au/TiO <sub>2</sub> -600	8417.2	6.7	9987.3	1563.4
Ratio-600 <sup>a</sup>	119.9	—	169.1	—
TiO <sub>2</sub> -700	71.9	≈ 0	64.5	−7.4
Au/TiO <sub>2</sub> -700	5732.4	3.8	5589.9	−146.3
Ratio-700 <sup>a</sup>	79.7	—	86.7	—

<sup>a</sup> Au/TiO<sub>2</sub> relative to TiO<sub>2</sub>. <sup>b</sup>  $\Delta = \text{Rate}_{(\text{UV-Vis})} - \text{Rate}_{(\text{UV})} - \text{Rate}_{(\text{Vis})}$ .

field of neighbouring TiO<sub>2</sub>,<sup>10</sup> and therefore, promote separation of photo-generated electron-hole pairs under irradiation. The promotion effects are very much dependent on the SPR intensity of Au on TiO<sub>2</sub>. On the whole, we present here the study on the synergetic effect between Au nanoparticles and TiO<sub>2</sub> supports under UV-visible light irradiation, different to literature studies on Au/TiO<sub>2</sub> under UV or visible light irradiation.<sup>3,9</sup>

Recently, a fluorescence technique has been developed to detect the OH radicals generated under irradiation using, for example, terephthalic acid as the chemical trap. There are two pathways for the generation of OH radicals during photocatalysis, *i.e.* the reductive pathway ( $\text{O}_2 + e_{\text{cb}}^- + \text{H}^+ \rightarrow \text{HOO} \rightarrow \text{OH}$ ) and the oxidative pathway ( $h_{\text{vb}}^+ + \text{OH}^- \rightarrow \text{OH}$ ).<sup>11</sup> The reductive pathway is proved to be the major one in semiconductor photocatalysis and the formation of OH radicals is mainly a photo-reduction process.<sup>12</sup> Here, the fluorescence technique is employed to detect the OH radicals formed under irradiation with different wavelengths, so as to give some hints on the mechanism of SPR photocatalysis. As shown in Fig. S8 (ESI<sup>†</sup>), significant fluorescence signals, caused by trapped OH radicals, can be clearly observed for all Au/TiO<sub>2</sub> samples under UV light irradiation. The fluorescence intensities of different Au/TiO<sub>2</sub> samples correlate well with their photocatalytic activities under UV light irradiation. If excess ferric ions are added in the reaction system as acceptors of photo-generated electrons, the fluorescence intensities decline dramatically, indicating that the reductive pathway dominates in the formation OH radicals. The ratio between the reductive and the oxidative pathway is calculated to be 45–55 for different samples (Fig. S11, ESI<sup>†</sup>).

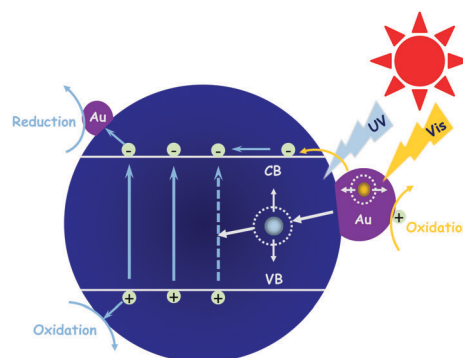
Under visible light irradiation, significant fluorescence signals due to trapped OH radicals can be observed for Au/TiO<sub>2</sub> and the ratio between the reductive and the oxidative pathway is calculated to be 4–18 (Fig. S11, ESI<sup>†</sup>), much lower than that obtained under UV light irradiation. Since TiO<sub>2</sub> cannot be excited under visible light irradiation, the OH radicals detected should originate from the photo-generated electrons and/or holes induced by the SPR of Au. On the other hand, under visible light irradiation no significant fluorescence signals corresponding to trapped OH radicals can be observed on Au colloid in the absence of ferric ions because the photo-generated electron-hole pairs undergo rapid recombination on conducting metal Au before the production of OH radicals either through the oxidative pathway or through the



**Fig. 2** Fluorescence intensity caused by trapped OH radicals at time-on-stream of 30 min with/without  $\text{Fe}^{3+}$  under irradiation with different wavelengths.

reductive pathway. While significant fluorescence signals corresponding to trapped OH radicals are observed on Au colloid in the presence of ferric ions (Fig. S12, ESI<sup>†</sup>). The ferric ions present can react with photo-generated electrons on Au colloid and the remaining photo-generated holes can subsequently oxidize the hydroxyls into radicals. Here the ferric ions act as sacrificial agents to promote the separation of photo-generated electron-hole pairs on Au colloid. Comparing the formation of OH radicals on Au and Au/TiO<sub>2</sub> under visible light irradiation in the absence of ferric ions (Fig. 2), we come to the conclusion that the TiO<sub>2</sub> support greatly promotes the separation of photo-generated electron-hole pairs from SPR of Au. That is, the photo-generated electrons excited by SPR of large Au particles can transfer to the conduction band of the neighbouring TiO<sub>2</sub>,<sup>3</sup> which might further transfer to small Au particles driven by the Fermi level equilibration.<sup>13</sup> TiO<sub>2</sub> is a favourable support for Au particles due to its high electron injection ability. Under UV-visible light irradiation, more OH radicals are formed through the oxidative pathway than those under UV or visible light irradiation (Fig. 2). According to the fluorescence intensity corresponding to the formation of OH radicals from the reductive and oxidative pathways, the synergetic promotion effect on the separation of photo-generated electron-hole pairs over the Au/TiO<sub>2</sub> photocatalyst under UV-visible light irradiation is clearly confirmed, which is responsible for its enhanced photocatalytic activity.

The synergetic promotion effects of Au particles on the photocatalytic activity of TiO<sub>2</sub> are illustrated in Fig. 3. Electrons in large Au nanoparticles are excited by the localized SPR with visible light absorption and subsequently transfer to the conduction band of adjacent TiO<sub>2</sub>. Meanwhile, large Au nanoparticles can enhance the local electric field of adjacent TiO<sub>2</sub> and promote the separation of electron-hole pairs under UV light irradiation. Small Au nanoparticles on TiO<sub>2</sub> can act as efficient co-catalysts and trap the



**Fig. 3** Promotion effects of Au particles on the photocatalytic activity of TiO<sub>2</sub> under UV-visible light irradiation.

photo-excited electrons from the conduction band of TiO<sub>2</sub>. Under UV-visible light irradiation, triple synergetic promotion effect on the separation of photo-generated electron-hole pairs over TiO<sub>2</sub> by gold deposition with both large and small particles can be achieved.

In summary, we report the synergetic promotion of the photocatalytic activity of TiO<sub>2</sub> by gold deposition under UV-visible light irradiation. Theoretically, the synergetic promotion of photocatalysts with different intrinsic light absorbance by localized SPR is possible, which should lead towards the design of highly efficient photocatalysts under sunlight irradiation.

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