

## Electronic Supplementary Information (ESI)

# Enhanced photocatalytic CO<sub>2</sub> valorization over TiO<sub>2</sub> hollow microspheres by synergetic surface tailoring and Au decorating

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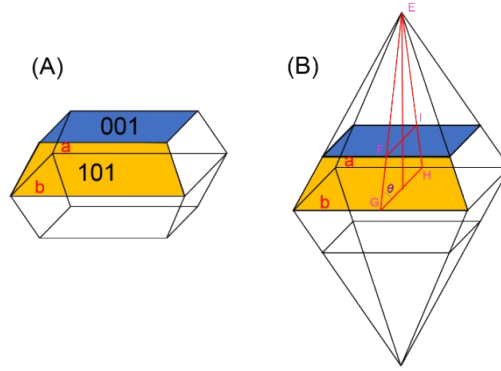
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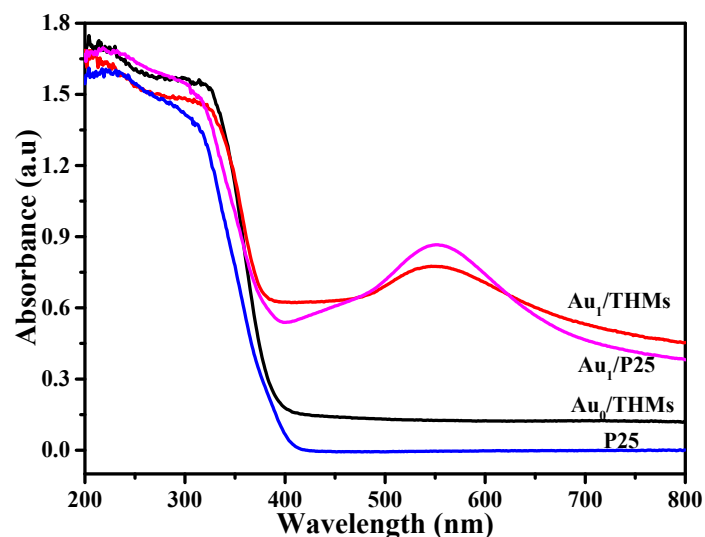
**Fig. S1.** A) Slab model of anatase TiO<sub>2</sub> single crystal. B) Equilibrium model of anatase TiO<sub>2</sub> single crystal.

Percentage of {001} facets can be calculated as follows<sup>1</sup>:

$$\begin{aligned}
 S_{001} &= 2a^2 \\
 S_{101} &= 8\left(\frac{1}{2}EG \times b - \frac{1}{2}EF \times a\right) \\
 S_{001}\% &= \frac{S_{001}}{S_{001} + S_{101}} \\
 &= \frac{2a^2}{2a^2 + 8\left(\frac{1}{2}EG \times b - \frac{1}{2}EF \times a\right)} \\
 &= \frac{a^2}{a^2 + 4\left(\frac{1}{2} \times \frac{b}{\cos\theta} \times b - \frac{1}{2} \times \frac{a}{\cos\theta} \times a\right)} \\
 &= \frac{a^2}{a^2 + \frac{b^2 - a^2}{\cos\theta}} = \frac{1}{\frac{b^2}{a^2} - 1} \\
 &= \frac{\cos\theta}{\cos\theta + \frac{b^2}{a^2} - 1} \\
 &= \frac{\cos\theta}{\cos\theta + \left(\frac{a}{b}\right)^{-2} - 1} \\
 &= \frac{\cos 68.3^\circ}{\cos 68.3^\circ + \left(\frac{13}{19}\right)^{-2} - 1} = 25.23\%
 \end{aligned}$$

Here  $\theta$  is the theoretical value (68.3°) for the angle between the {001} and {101} facets of anatase. As indicated in the slab model, two independent parameters  $b$  and  $a$  denote lengths of the side of the bipyramid and the side of the square {001} ‘truncation’ facets

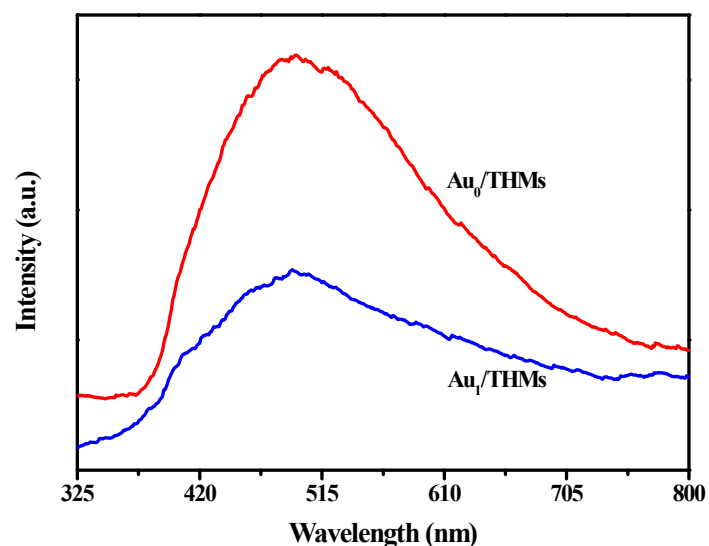
measured in Fig. 2e, respectively. Their dimensions were estimated to be  $a \approx 13$  nm and  $b \approx 19$  nm.



**Fig. S2** UV-vis diffuse reflectance spectra for sample Au<sub>0</sub>/THMs, Au<sub>1</sub>/THMs, P25 and Au<sub>1</sub>/P25.

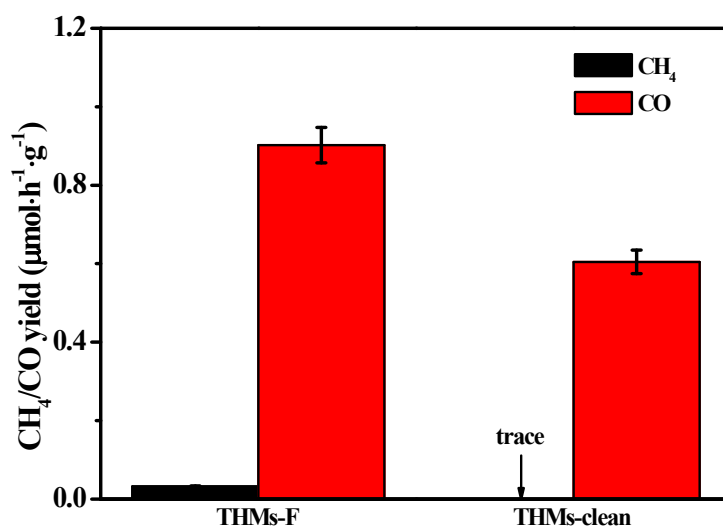
In the present study, we have shown that, relative to P25, the sample Au<sub>0</sub>/THMs exhibited higher UV-absorption ability (at least, in the range of 200~ 350 nm), (Fig 5a and Fig. S2). However, because the light shielding effect of surface decorated Au nanoparticles with size of about 15 nm, the UV-absorption ability of sample Au<sub>1</sub>/THMs was impaired to some extent (Fig 5a), which was still somewhat higher than that of P25.

The light absorption spectrum of Au<sub>1</sub>/P25 was shown in Fig S2 for comparison. Interestingly, the UV-absorption ability of sample Au<sub>1</sub>/P25 was enhanced, relative to P25. This result may be associated the fact those Au nanoparticles deposited on P25 were much smaller,<sup>2</sup> leading to stronger SPR effect and weaker light shielding effect (Fig S2). Moreover, the UV-absorption ability of sample Au<sub>1</sub>/P25 was higher than that of sample Au<sub>1</sub>/THMs. It is worth mentioning that such stronger UV-absorption of Au<sub>1</sub>/P25 versus Au<sub>1</sub>/THMs shall be mainly originated from the difference in size of surface decorated Au nanoparticles.



**Fig. S3** Steady-state PL spectra of the Au<sub>0</sub>/THMs and Au<sub>1</sub>/THMs.

PL spectra (Fig S3) of the two typical samples were also recorded with a Fluorescence spectrophotometer (F-4500, Hitachi, Japan) using 325 nm excitation light. The PL results (Fig S3) can clearly showed that, the characteristic PL peak of TiO<sub>2</sub> ( $\approx 495$  nm) was obviously quenched after introducing the Au nanoparticles, which indicating that the recombination of the photogenerated charge carrier was greatly inhibited in Au<sub>1</sub>/THMs.<sup>3</sup> The resulting efficient charge separation would increase the lifetime of the charge carriers, enhance the interfacial charge transfer efficiency, consistent with higher transient photocurrent (Fig 7a).



**Fig. S4** Comparison of the CH<sub>4</sub> and CO generation rate for surface fluorinated THMs (THMs-F, the same sample as Au<sub>0</sub>/THMs in the main text) and surface clean THMs (THMs-clean) conducted under full spectrum light irradiation for 1h.

In order to clarify whether the surface adsorbed F ion (based on XPS result) on the surface of THMs (TiO<sub>2</sub>) has significant influence on photocatalytic CO<sub>2</sub> reduction performance, the following control experiment was designed. Based on the previous studies, by a simple alkaline washing method, the surface adsorbed F ions can be easily removed.<sup>4</sup> In this study, after the as-prepared surface fluorinated THMs (labeled as THMs-F, the same sample as Au<sub>0</sub>/THMs in the main text) were soaked in 0.1 M NaOH solution for 30 min, surface fluorine-free THMs are obtained. Then, the sample was washed with deionized water for 6 times to maintain a neutral surface, and dried at 50°C for 12 h, the surface clean sample is labeled as THMs-clean. The photocatalytic CO<sub>2</sub> reduction result (Fig. S4) showed that, both CH<sub>4</sub> and CO yields of THMs-clean were slightly lower than that of THMs-F counterpart under full spectrum light irradiation. So it was confirmed that the F ion on the surface of THMs had positive effects during the photocatalytic CO<sub>2</sub> reduction. In fact, it was well demonstrated in previous studies that, the surface fluorination had positive effects in improving charge dynamics.<sup>5</sup>

## References

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