Electronic Supplementary Information (ESI)

Enhanced photocatalytic CO\textsubscript{2} valorization over TiO\textsubscript{2} hollow microspheres by synergetic surface tailoring and Au decorating

Xueyan Liu,\textsuperscript{a} Meng Ye,\textsuperscript{a} Shuping Zhang,\textsuperscript{a} Guocheng Huang,\textsuperscript{a} Chuanhao Li,\textsuperscript{a} Jiaguo Yu,\textsuperscript{b} Po Keung Wong\textsuperscript{c} and Shengwei Liu\textsuperscript{a}

\textsuperscript{a} School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510006, P. R. China.

\textsuperscript{b} State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R. China.

\textsuperscript{c} School of Life Sciences, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, China.

*E-mail: liushw6@mail.sysu.edu.cn (S. Liu); lichuanh3@mail.sysu.edu.cn (C. Li)

*E-mail: pkwong@cuhk.edu.hk (P. K. Wong)
Fig. S1. A) Slab model of anatase TiO$_2$ single crystal. B) Equilibrium model of anatase TiO$_2$ single crystal.

Percentage of {001} facets can be calculated as follows$^1$:

\[ S_{001} = 2a^2 \]
\[ S_{101} = 8(x_EG \times b - x_EF \times a) \]
\[ S_{001} \% = \frac{S_{001}}{S_{001} + S_{101}} \times \frac{2a^2}{2a^2 + 8(x_EG \times b - x_EF \times a)} \]
\[ = \frac{a^2}{a^2 + 4x_Eb \times \cos \theta \times a - 2x_Eb \times \cos \theta \times a} \]
\[ = \frac{\cos \theta}{\cos \theta + b^2 - a^2 - 1} \]
\[ = \frac{\cos \theta}{\cos \theta + \frac{b^2 - a^2}{a^2} - 1} \]
\[ = \frac{\cos 68.3^\circ}{\cos 68.3^\circ + \left(\frac{13}{19}\right)^2 - 1} = 25.23\% \]

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 Au₀/THMs, Au₁/THMs, P25 and Au₁/P25.

In the present study, we have shown that, relative to P25, the sample Au₀/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 Au₁/THMs was impaired to some extent (Fig 5a), which was still somewhat higher than that of P25.

The light absorption spectrum of Au₁/P25 was shown in Fig S2 for comparison. Interestingly, the UV-absorption ability of sample Au₁/P25 was enhanced, relative to P25. This result may be associated the fact those Au nanoparticles deposited on P25 were much smaller, leading to stronger SPR effect and weaker light shielding effect (Fig S2). Moreover, the UV-absorption ability of sample Au₁/P25 was higher than that of sample Au₁/THMs. It is worth mentioning that such stronger UV-absorption of Au₁/P25 versus Au₁/THMs shall be mainly originated from the difference in size of surface decorated Au nanoparticles.
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$_2$ ($\approx$ 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$_1$/THMs.$^3$ 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\textsubscript{4} and CO generation rate for surface fluorinated THMs (THMs-F, the same sample as Au\textsubscript{0}/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\textsubscript{2}) has significant influence on photocatalytic CO\textsubscript{2} 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.\textsuperscript{4} In this study, after the as-prepared surface fluorinated THMs (labeled as THMs-F, the same sample as Au\textsubscript{0}/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\textsubscript{2} reduction result (Fig. S4) showed that, both CH\textsubscript{4} 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\textsubscript{2} reduction. In fact, it was well demonstrated in previous studies that, the surface fluorination had positive effects in improving charge dynamics.\textsuperscript{5}
References