

Supporting information

**Structural design of Au nanoparticles' whereabouts and clustering
with TiO₂ porous nanospheres for enhance solar hydrogen
production**

Minmin Gao[†], Connor Kang Nuo Peh[†], Ghim Wei Ho^{*†§}

[†]Department of Electrical and Computer Engineering, National University of Singapore,
4 Engineering Drive 3, Singapore 117576.

[§]Engineering Science Programme, National University of Singapore, 9 Engineering Drive 1,
117576, Singapore

E-mail: elehw@nus.edu.sg

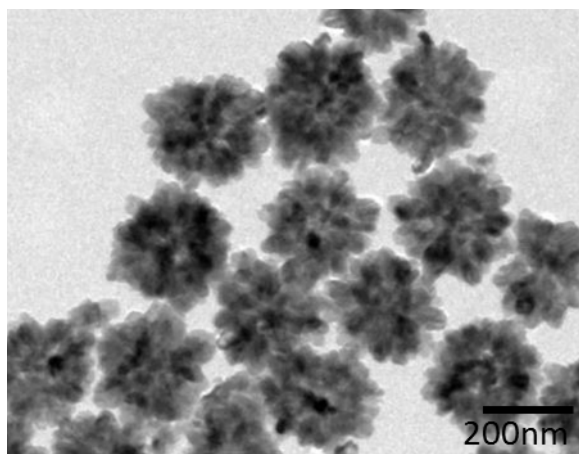


Fig. S1: TEM image of TiO₂ nanospheres.

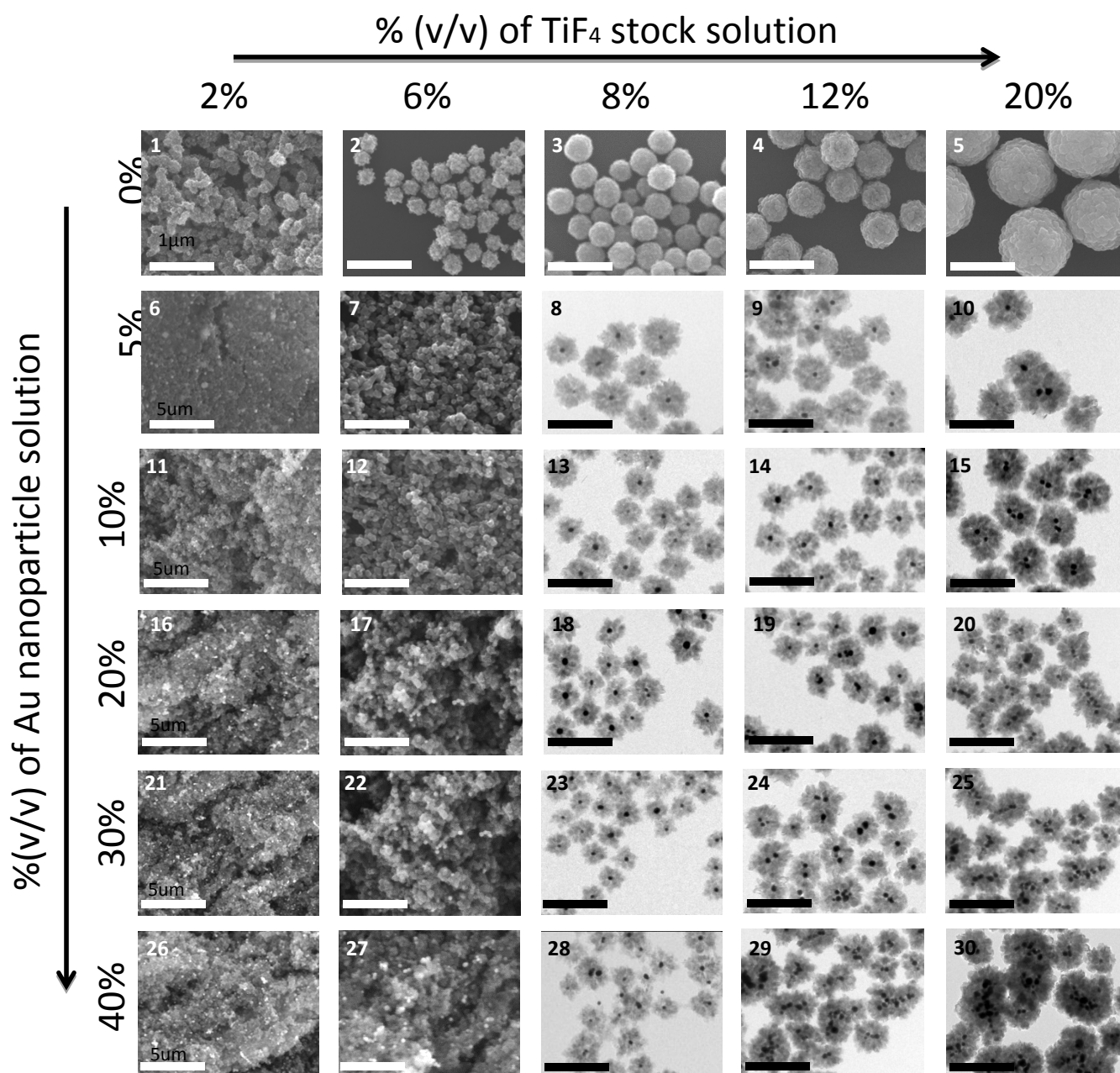


Fig. S2: SEM and TEM images of the synthesized samples with various concentrations of Au nanoparticles and TiF₄.

$$\%(\text{v/v}) \text{ of TiF}_4 \text{ stock solution} = \frac{\text{volume of } 0.04\text{M TiF}_4 \text{ stock solution}}{\text{total volume of reaction solution}}$$

$$\%(\text{v/v}) \text{ of Au nanoparticle solution} = \frac{\text{as - prepared Au nanoparticle solution}}{\text{total volume of reaction solution}}$$

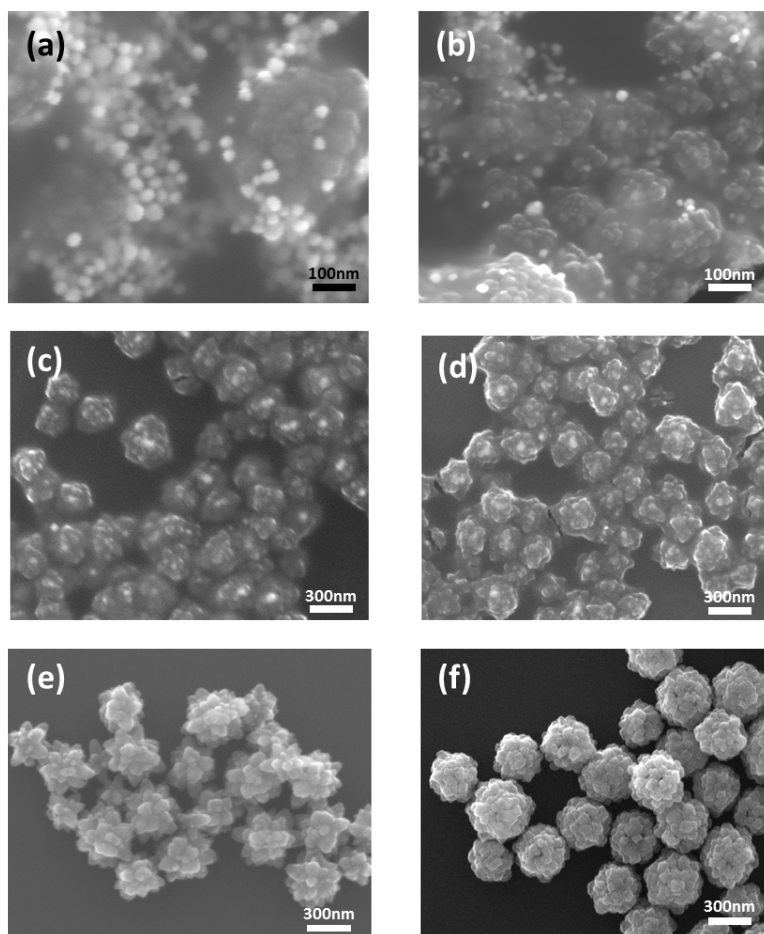


Figure S3: SEM images of time evolution of Au@TiO₂ core-shell nanospheres.

In this work, the photocatalytic H₂ production study was carried out under UV-visible illumination, where we observed that the LSPR effect is not the dominant mechanism for the enhancement of H₂ production. We have noted that when UV as well as both UV-visible light are irradiated onto the Au_{multi}@TiO₂ and TiO₂ samples, there is no increase in the rate of hydrogen production (figure S4), which suggest that the LSPR effect of Au nanoparticles is not the predominant mechanism responsible for the improved photocatalytic activity. Though, the LSPR peak is present as shown by UV-vis measurements (Fig.4b and c), there are many other factors that could affect the photocatalytic activity, such as the resonant coupling, energy transfer and interface trap states between the metal and semiconductor as well as the size and morphology of the metal nanoparticles.¹ Also most of the LSPR studies show the transfer of electrons from Au nanoparticles to the semiconductor.² However, in our work, the transient absorption decay spectra (Fig. 5a) show the transfer of electrons from TiO₂ to Au nanoparticles. Hence, the charge separation mechanism is proposed (Fig.6) based on the transient absorption decay and PEC measurements. Another project in progress is focused on the study of photocatalytic activity under pure visible illumination (unlike this work which uses UV-Vis illumination), which includes the study of LSPR, hot electrons and interface trap states effects.

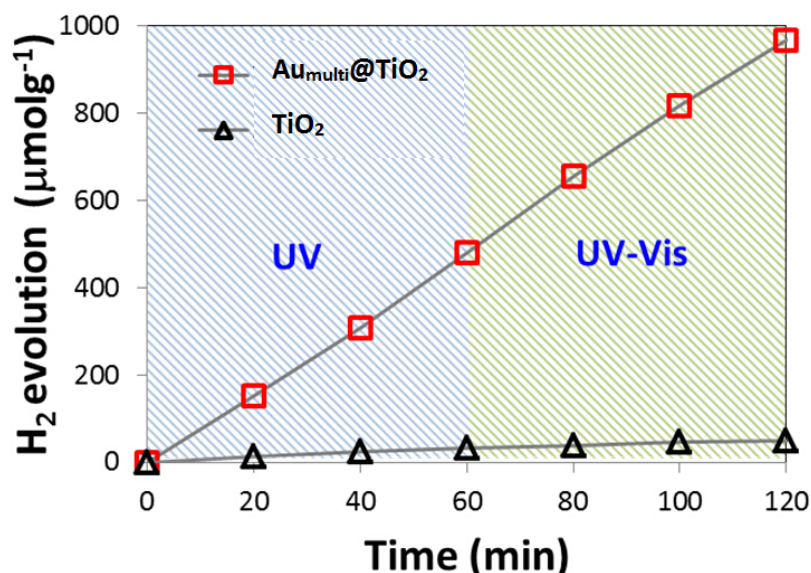


Figure S4: Photocatalytic H₂ evolution of TiO₂ and Au_{multi}@TiO₂ under UV and UV-Vis light irradiation. A UV LED with and without tungsten lamp were used to generate UV and UV-visible light spectrum respectively.

References:

¹ Qu, Y.; Duan, X. Progress, challenge and perspective of heterogeneous photocatalyst *Chem. Soc. Rev.*, **2013**, 42, 2568-2580.

²Bian, Z.; Tachikawa, T.; Zhang, P.; Fujitsuka, M.; Majima, T. Au/TiO₂ Superstructure-Based Plasmonic Photocatalysts Exhibiting Efficient Charge Separation and unprecedented Activity *J. Am. Chem. Soc.* **2014**, 136, 458–465; Zhang, Z.; Li, A.; Cao, S-W, Bosman, M.; Li S.; Xue, C. Direct evidence of plasmon enhancement on photocatalytic hydrogen generation over Au/Pt decorated TiO₂ nanofibers *Nanoscale*, 2014, 6, 5217.