

SUPPLEMENTARY INFORMATION

Highly Efficient Temperature-induced Visible Light Photocatalytic Hydrogen Production from Water

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CONTENT:

1. Supplementary figures:

- EPR spectra (Fig.S1)
- Product yield vs temperature (Fig. S2)
- Effect of H₂O/methanol ratio on temperature-induced photocatalytic hydrogen production (Fig. S3)
- Results of control experiments comparing Pt, TiO₂, and SiO₂ for photocatalytic hydrogen production (Fig. S4)

2. Supplementary Movie:

- Photocatalytic hydrogen production process (Movie S1)

3. References

1. SUPPLEMENTARY FIGURES:

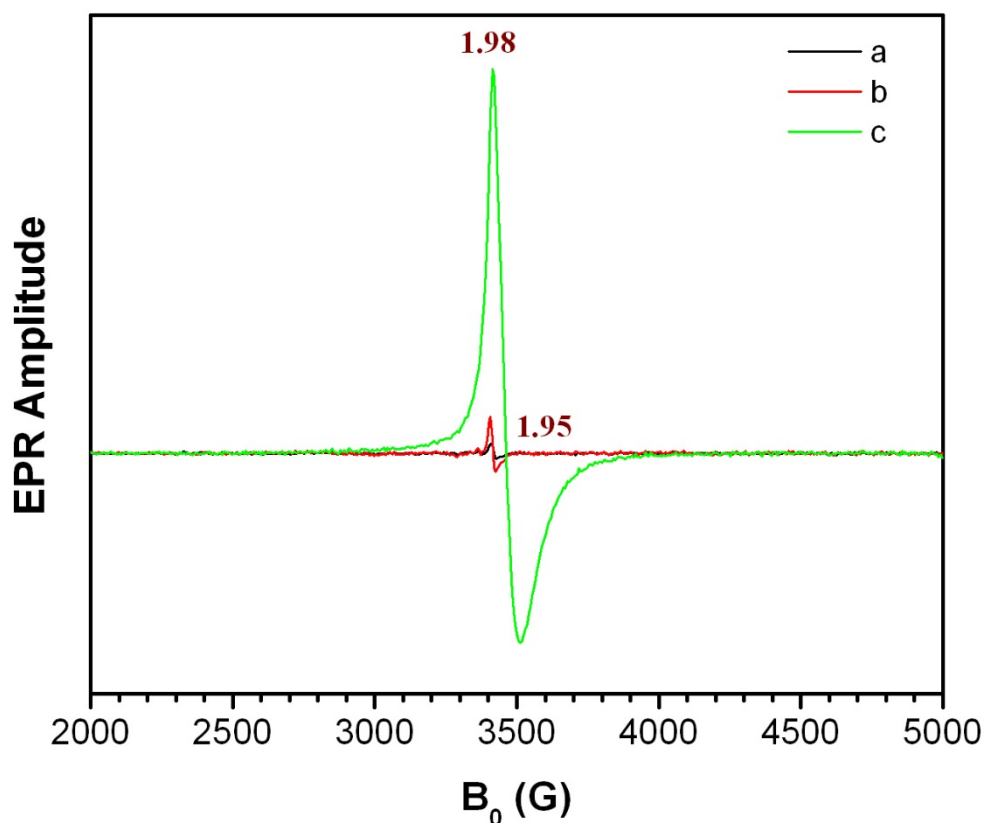


Fig. S1. EPR spectra of (a) pristine (white) TiO_2 , (b) Pt/TiO_2 without hydrogenation, and (c) black Pt/TiO_2 prepared by hydrogenation. The spectra were recorded at 77 K with g value of 1.98 for white TiO_2 and unreduced Pt/TiO_2 and 1.95 for black Pt/TiO_2 . It is well-known that a peak at $g = 1.95\sim 1.98$ is characteristic of a paramagnetic Ti^{3+} center.^{S1} The peak intensity of Ti^{3+} is very small for white TiO_2 and unreduced Pt/TiO_2 , indicating their negligible amount of Ti^{3+} . In contrast, the black Pt/TiO_2 exhibits a large amount of Ti^{3+} associated with a large peak of Ti^{3+} in EPR spectrum.

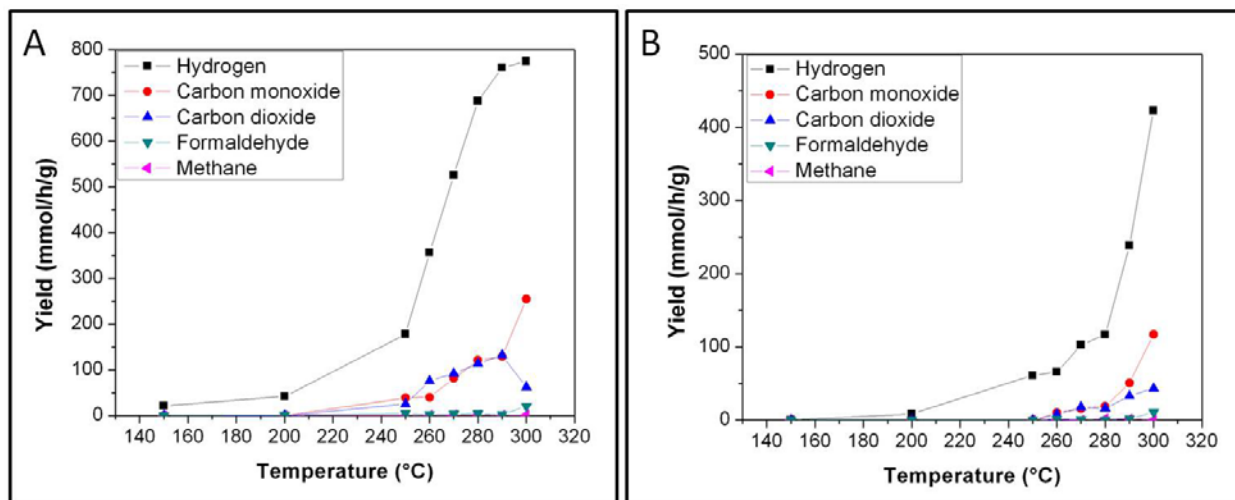


Fig. S2. Product yield vs reaction temperature for catalytic hydrogen production from H₂O with methanol (30%, as a sacrificial agent) over black Pt/TiO₂ catalyst dispersed on light-diffuse-reflection-surface of a SiO₂ substrate with AM 1.5 global sunlight illumination (A) and without AM 1.5 global sunlight illumination (B).

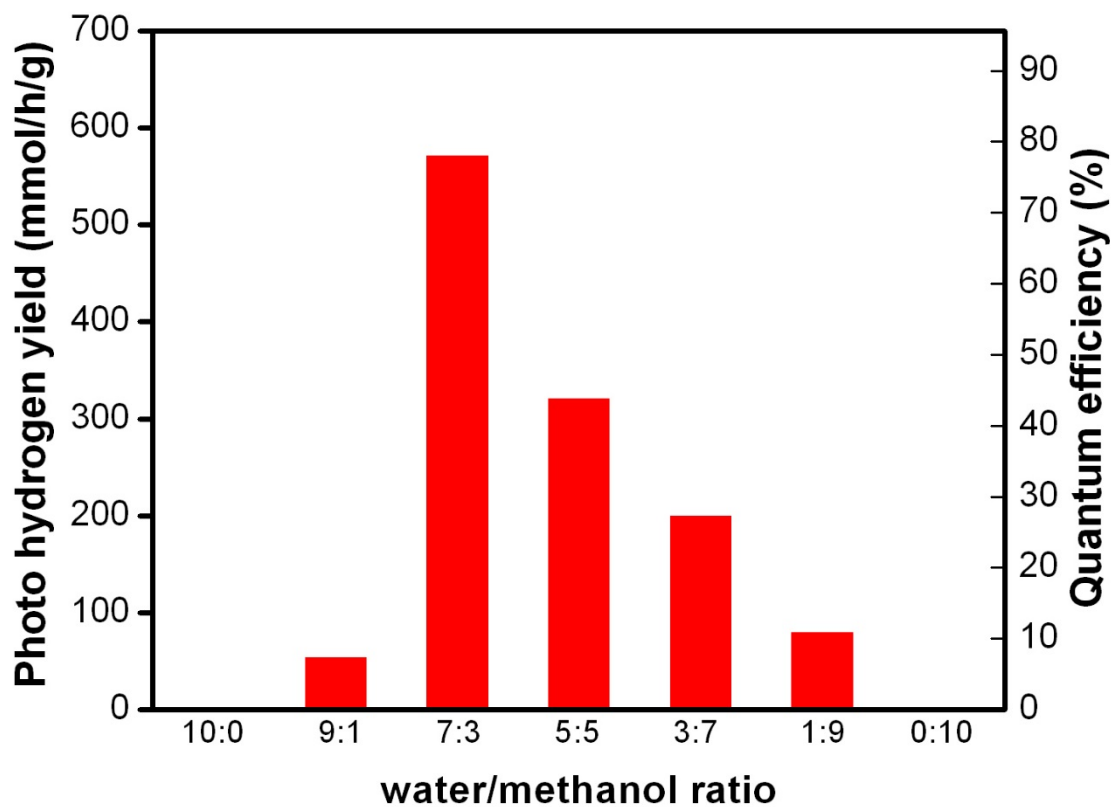


Fig. S3. Photocatalytic hydrogen production from H₂O with methanol as a sacrificial agent over black Pt/TiO₂ catalyst dispersed on the light-diffuse-reflection-surface of SiO₂ substrate under AM 1.5 global sunlight illumination at 280 °C. Photo-hydrogen yield (equal to the difference of hydrogen yields with and without light irradiation) and apparent quantum efficiency increase with decreasing water/methanol ratio and then decreases. The maximum values can be obtained at water/methanol ratio of 7/3.

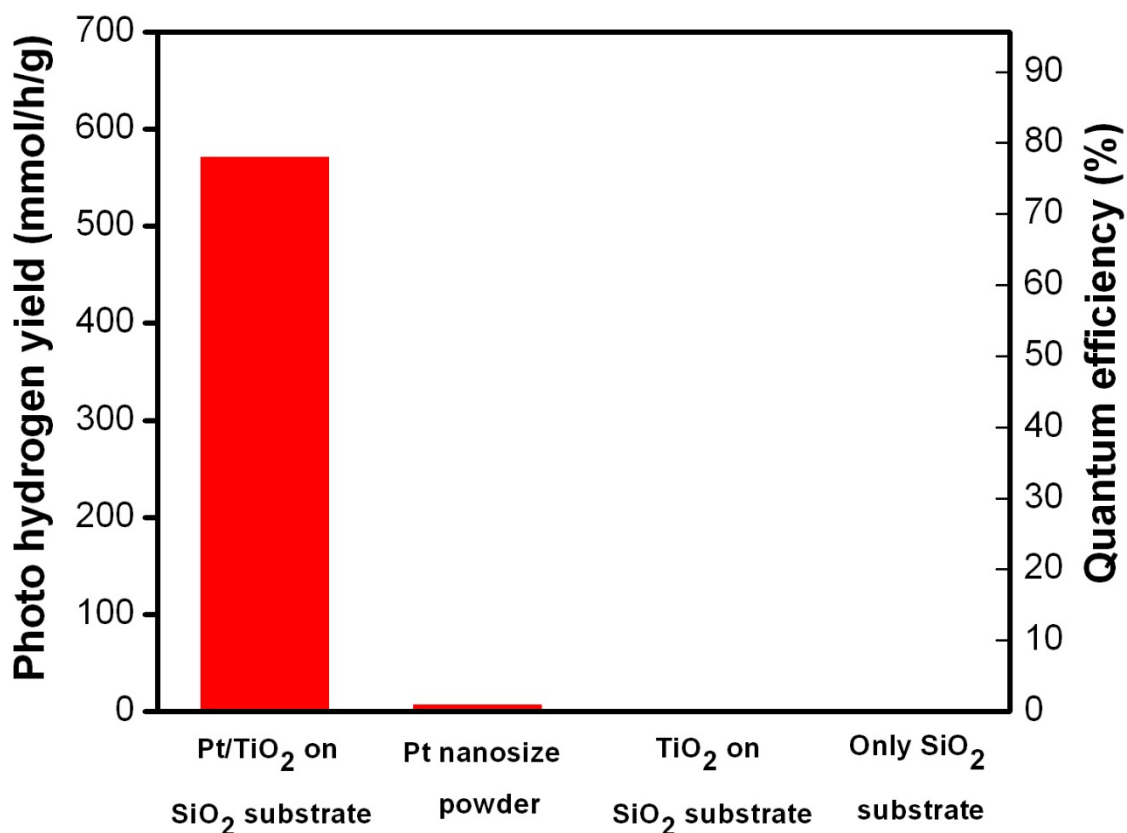


Fig. S4. Photocatalytic hydrogen production from H₂O with 30% methanol as a sacrificial agent under AM 1.5 global sunlight illumination at 280 °C. Either SiO₂ substrate or TiO₂ on SiO₂ substrate doesn't exhibit photocatalytic activity. The photo-hydrogen yield and apparent quantum efficiency are negligible for Pt dispersed on SiO₂ substrate. Only black Pt/TiO₂ catalyst dispersed on SiO₂ substrate exhibits an excellent photo-hydrogen yield (571 mmol/h/gcat) with a high apparent quantum efficiency (78.0%).

2. SUPPLEMENTARY MOVIE

A movie was recorded for the impressive photocatalytic hydrogen production process from water with 30% methanol as a sacrificial agent over black Pt/TiO₂ catalyst dispersed on the light-diffuse-reflection-surface of SiO₂ substrate under 1.5 AM global sunlight illumination at room temperature (please watch *Supplementary Movie S1*).

3. REFERENCES

S1. Xing, M.; Zhang, J.; Chen, F.; Tian, B. An Economic Method to Prepare Vacuum Activated Photocatalysts with High Photo-activities and Photosensitivities, *Chem. Commun.* **2011**, 47, 4947-4949.