

# Supporting Information

## Spatially separated bimetallic cocatalysts over hollow-structured TiO<sub>2</sub> for photocatalytic hydrogen generation

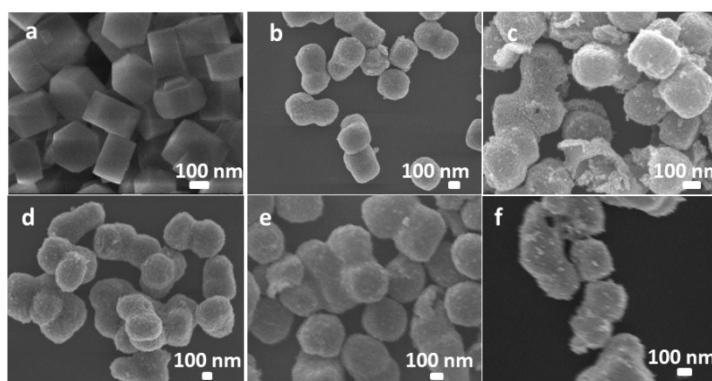
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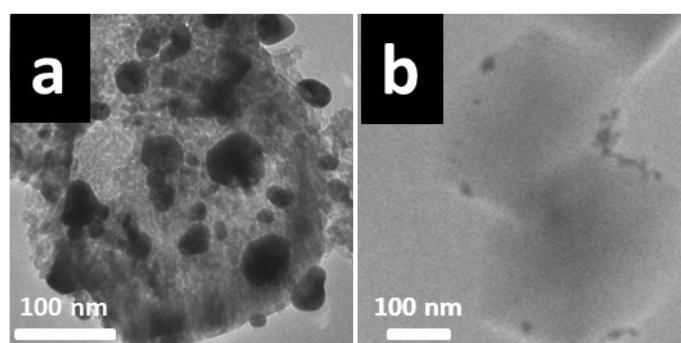
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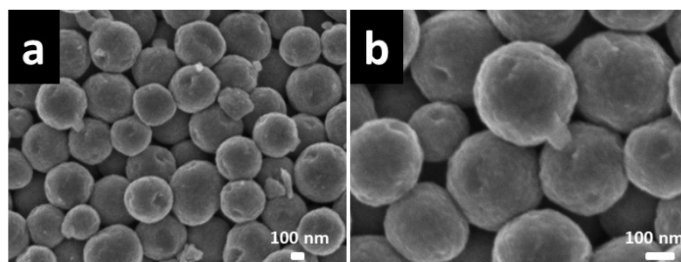
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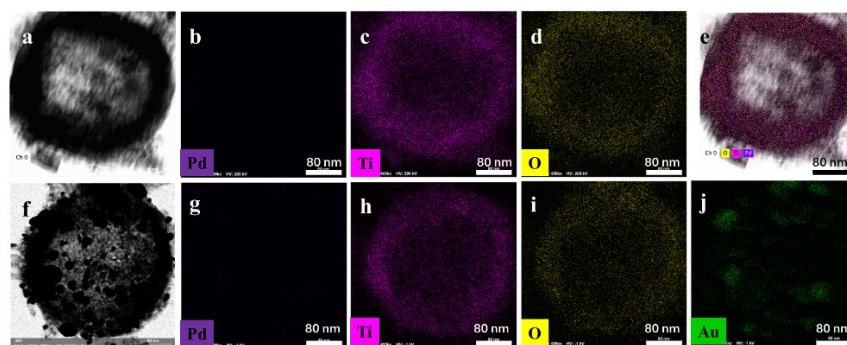
**Fig. S1.** SEM images of S1 (a), S1@TiO<sub>2</sub> (b), hollow TiO<sub>2</sub> (c), Pd@S1@TiO<sub>2</sub> (d), Pd@TiO<sub>2</sub> (e) and Pd@TiO<sub>2</sub>@Au (f) in low magnification.



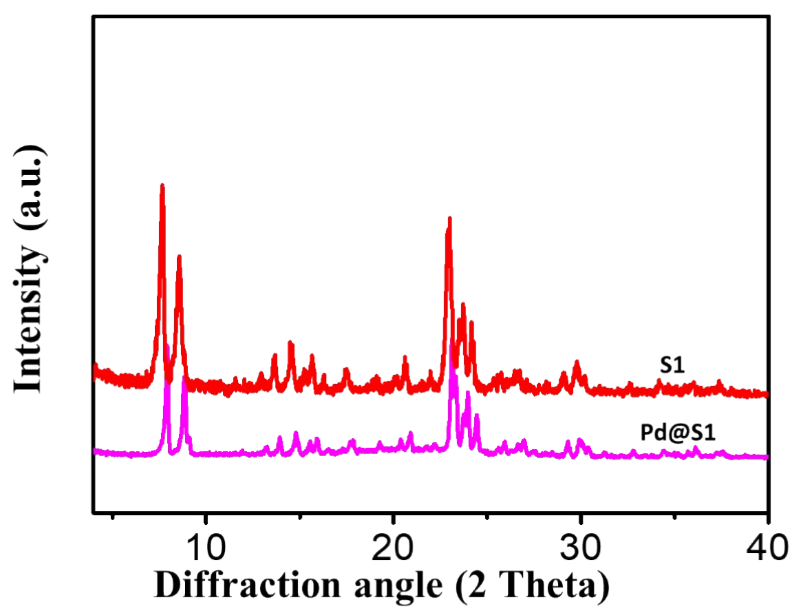
**Fig. S2.** TEM images of hollow TiO<sub>2</sub>@Au (a) and Au-im/Pd@S1 (b).



**Fig. S3.** SEM images of  $\text{TiO}_2$  nanoparticles. (b) enlarged image of (a).



**Fig. S4.** Elemental mapping images of  $\text{Pd@TiO}_2$  (a-e) and sandwiched-like  $\text{Pd@TiO}_2\text{@Au}$  (f-j)



**Fig. S5.** XRD profiles of S1 and  $\text{Pd@S1}$ .

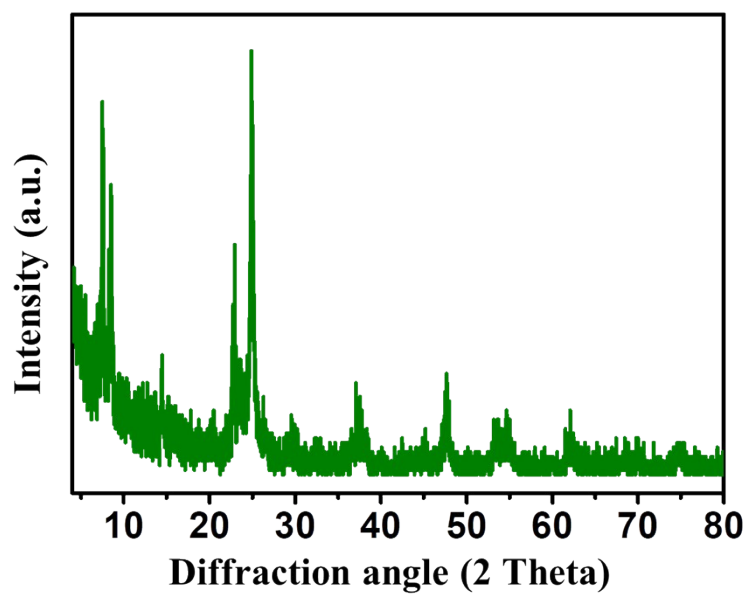


Fig. S6. XRD profiles of Pd@S1@TiO<sub>2</sub>.

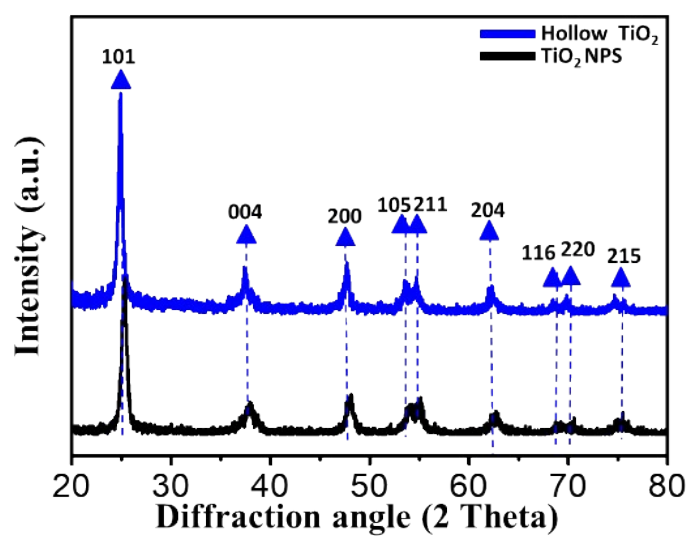
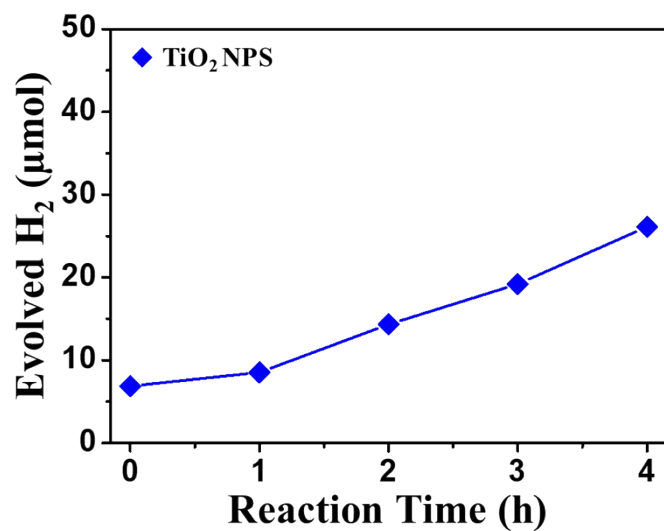
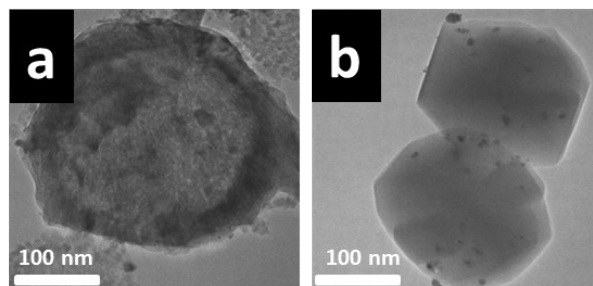


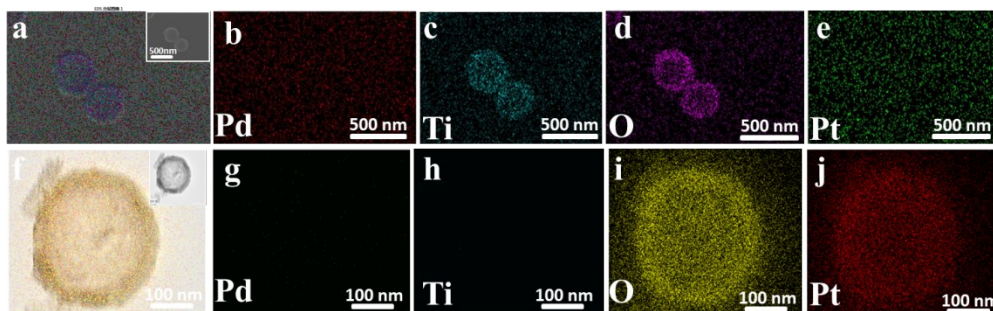
Fig. S7. XRD profiles of TiO<sub>2</sub> NPs and hollow TiO<sub>2</sub>.



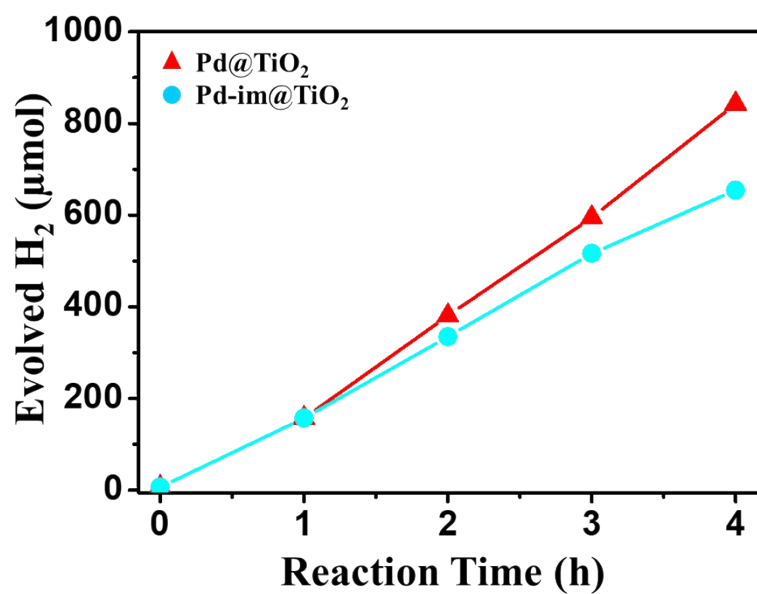
**Fig. S8.** Photocatalytic H<sub>2</sub> evolution by TiO<sub>2</sub> NPs.



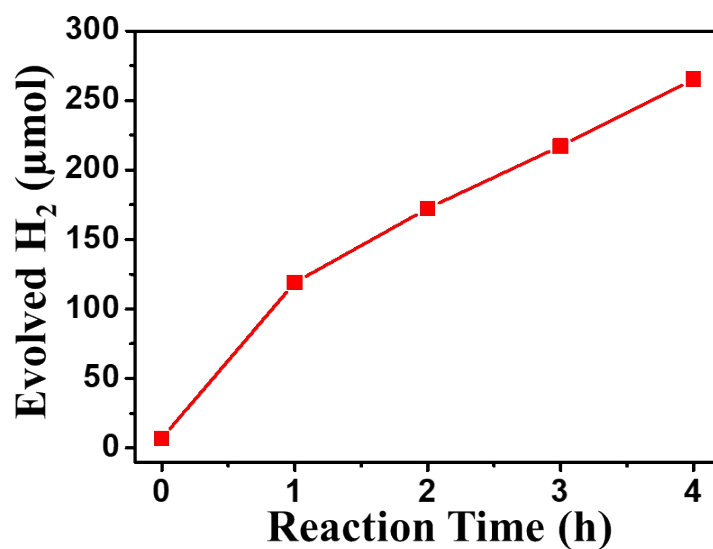
**Fig. S9.** TEM images of hollow TiO<sub>2</sub>@Pt (a) and Pt-im/Pd@S1 (b).



**Fig. S10.** Elemental mapping images of Pd@TiO<sub>2</sub>@Pt: (a) and (f) the corresponding mixed elemental mapping of SEM and TEM images. The insets are the corresponding SEM and TEM images; (b, g) Pd mapping images; (c, h) Ti mapping images; (d, i) O mapping images; (e, j) Pt mapping images.



**Fig. S11.** Photocatalytic H<sub>2</sub> generation over Pd@TiO<sub>2</sub> and Pd-im@TiO<sub>2</sub>.



**Fig. S12.** Time courses of H<sub>2</sub> generation over Pd@TiO<sub>2</sub>@Au catalyst. Catalytic condition: catalysts: (10 mg), light source: Xenon lamp (300W) with a bandpass filter ( $\lambda$  =380 nm).

**Table S1.** Summary of the photocatalytic hydrogen generation properties of TiO<sub>2</sub> based photocatalysts reported in this work and recent literature works.

| Photocatalyst                                        | H <sub>2</sub> evolution rate<br>( $\mu\text{mol g}^{-1} \text{h}^{-1}$ ) | Photocatalytic condition<br>(irradiation range, sacrificial reagent, light source) | Ref.             |
|------------------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------|
| <b>Pd@TiO<sub>2</sub>@Au</b>                         | <b>27231</b>                                                              | <b>(<math>\lambda</math>=200-1100 nm, methanol, 250 mW/cm<sup>2</sup>)</b>         | <b>This work</b> |
| <b>Pd@TiO<sub>2</sub>@Pt</b>                         | <b>64859</b>                                                              | <b>(<math>\lambda</math>=200-1100 nm, methanol, 250 mW/cm<sup>2</sup>)</b>         | <b>This work</b> |
| RuO <sub>2</sub> @TiO <sub>2</sub> @Pt               | 4100                                                                      | ( $\lambda$ = 365 nm, methanol)                                                    | [S1]             |
| Au@TiO <sub>2</sub>                                  | 4900                                                                      | ( $\lambda$ =200-1100 nm, methanol, 300 W Xe-lamp)                                 | [S2]             |
| Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /Pt | 625                                                                       | ( $\lambda$ > 420 nm, triethylamine, 450 W Xe-lamp)                                | [S3]             |
| Janus Au-TiO <sub>2</sub>                            | 2.0 mL min <sup>-1</sup>                                                  | ( $\lambda$ > 400 nm, isopropyl alcohol, 500 W tungsten halogen lamp)              | [S4]             |
| CoO <sub>x</sub> /TiO <sub>2</sub> /Pt               | 7883                                                                      | (UV light, methanol, 300 W Xe lamp)                                                | [S5]             |
| Mg-TiO <sub>2</sub>                                  | 666                                                                       | (300-W xenon lamp, pure water)                                                     | [S6]             |
| TiO <sub>2</sub> -C <sub>3</sub> N <sub>4</sub>      | 770                                                                       | ( $\lambda$ =200-2500 nm, triethanolamine,150 W Xe lamp)                           | [S7]             |
| NiO/rGO/TiO <sub>2</sub>                             | 240                                                                       | (300-W xenon lamp, methanol,100 mW/cm <sup>2</sup> )                               | [S8]             |
| Pt/TiO <sub>2</sub> /rGO                             | 1076                                                                      | (A full spectrum solar simulator, triethanolamine, 1 sun power by CELS500)         | [S9]             |

## References

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