

## Supplementary Information

### A synergistic interaction between isolated Au nanoparticles with oxygen vacancies in amorphous black TiO<sub>2</sub> nanoporous film: toward enhanced photoelectrochemical water splitting

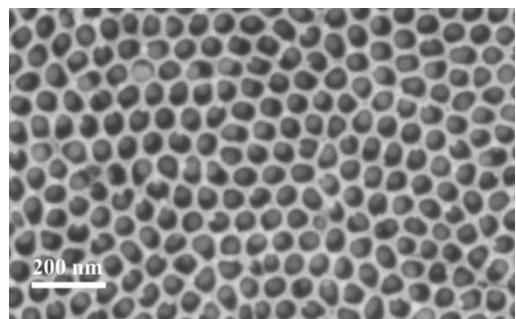
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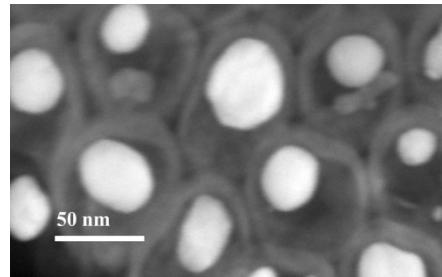
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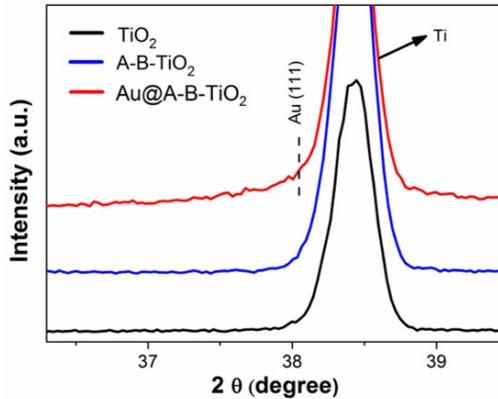
\*E-mail: [Yang.Yang@ucf.edu](mailto:Yang.Yang@ucf.edu)



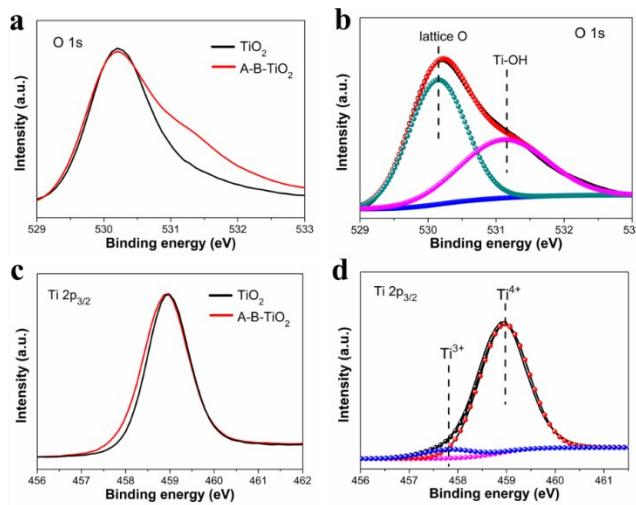
**Figure S1.** SEM image of the Au@TiO<sub>2</sub> nanoporous film.



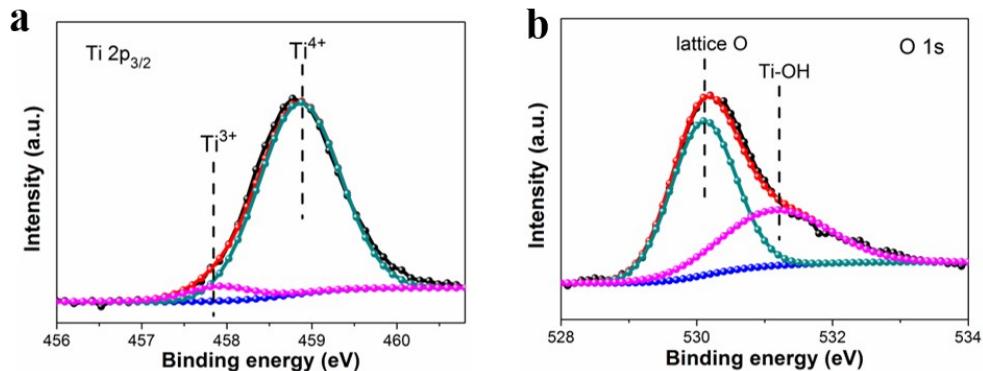
**Figure S2.** STEM image of the Au@A-B-TiO<sub>2</sub> nanoporous film.



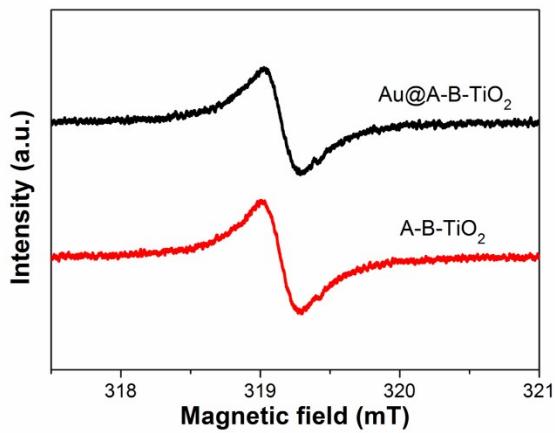
**Figure S3.** Magnified XRD patterns of TiO<sub>2</sub> nanoporous film, A-B-TiO<sub>2</sub> nanoporous film and Au@A-B-TiO<sub>2</sub> nanoporous film.



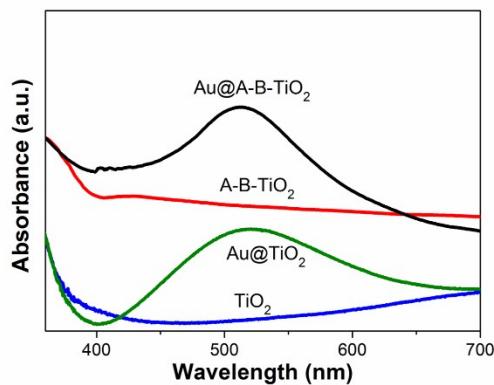
**Figure S4.** (a) High-resolution XPS O 1s peaks of TiO<sub>2</sub> and A-B-TiO<sub>2</sub>. (b) High-resolution XPS O 1s peak of A-B-TiO<sub>2</sub>. (c) High-resolution XPS Ti 2p<sub>3/2</sub> peaks of TiO<sub>2</sub> and A-B-TiO<sub>2</sub>. (d) High-resolution XPS Ti 2p<sub>3/2</sub> peak of A-B-TiO<sub>2</sub>.



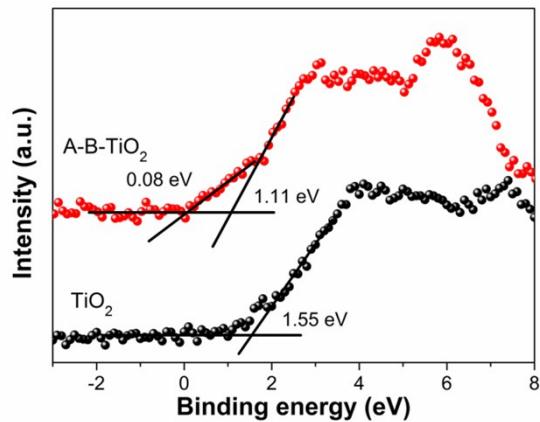
**Figure S5.** High-resolution XPS (a) Ti 2p<sub>3/2</sub> peak and (b) O 1s peak of Au@A-B-TiO<sub>2</sub>.



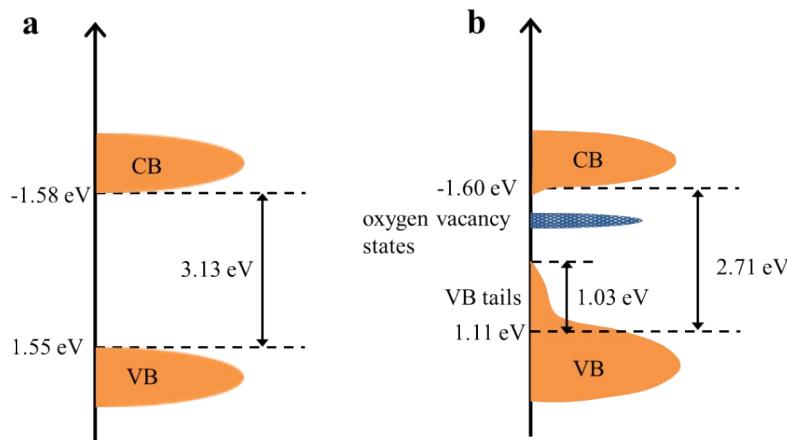
**Figure S6.** ESR spectra of A-B-TiO<sub>2</sub> and Au@A-B-TiO<sub>2</sub>.



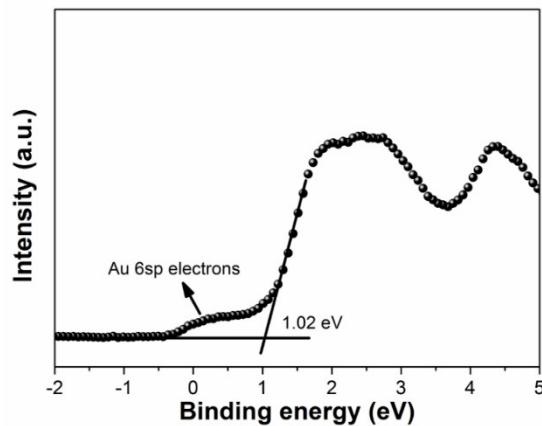
**Figure S7.** UV-vis absorption spectra of TiO<sub>2</sub>, Au@TiO<sub>2</sub>, A-B-TiO<sub>2</sub>, and Au@A-B-TiO<sub>2</sub>.



**Figure S8.** VB-XPS spectra of TiO<sub>2</sub> and A-B-TiO<sub>2</sub>.

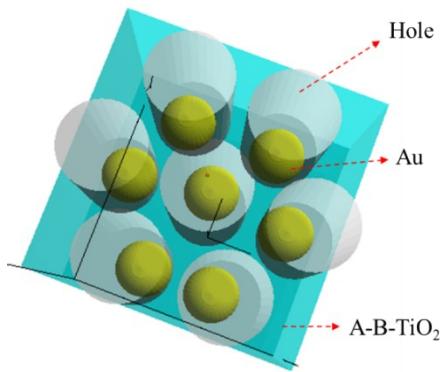


**Figure S9.** Band energy diagram of (a) TiO<sub>2</sub> and (b) A-B-TiO<sub>2</sub>.

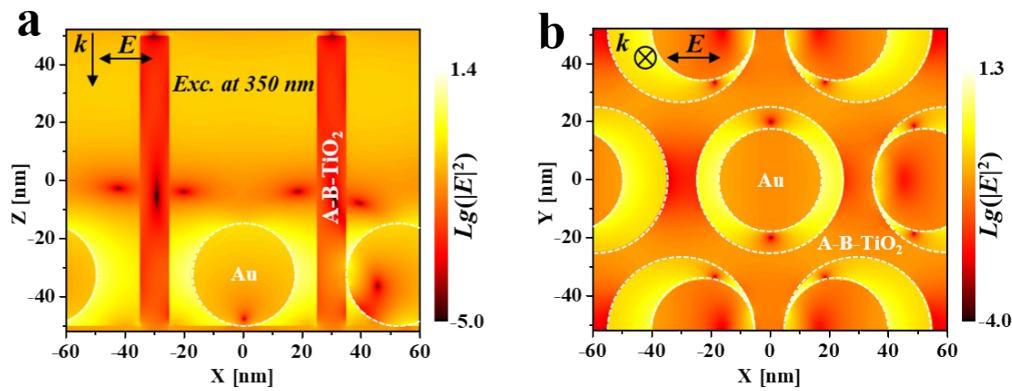


**Figure S10.** VB-XPS spectra of Au@A-B-TiO<sub>2</sub>.

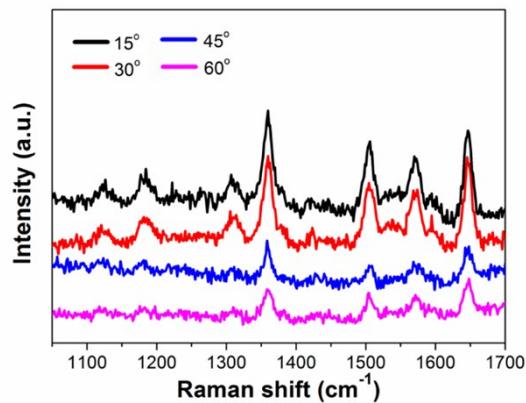
Because Au@A-B-TiO<sub>2</sub> is a composite material, the VB-XPS spectrum of Au@A-B-TiO<sub>2</sub> can give the information of both Au and A-B-TiO<sub>2</sub>. The binding energy near the Fermi levels can be attributed to Au 6sp electrons. And the binding energy at 1.02 eV is related to the VB of A-B-TiO<sub>2</sub>. The slight difference of VB between A-B-TiO<sub>2</sub> in Au@A-B-TiO<sub>2</sub> (1.02 eV) and bare A-B-TiO<sub>2</sub> (1.11 eV) may be due to the slight band bending and alignment of Fermi levels after formation of hybrid structure. It is difficult to determine the band tail of A-B-TiO<sub>2</sub> in Au@A-B-TiO<sub>2</sub> from the VB-XPS spectra because it will overlap the Au 6sp electrons.



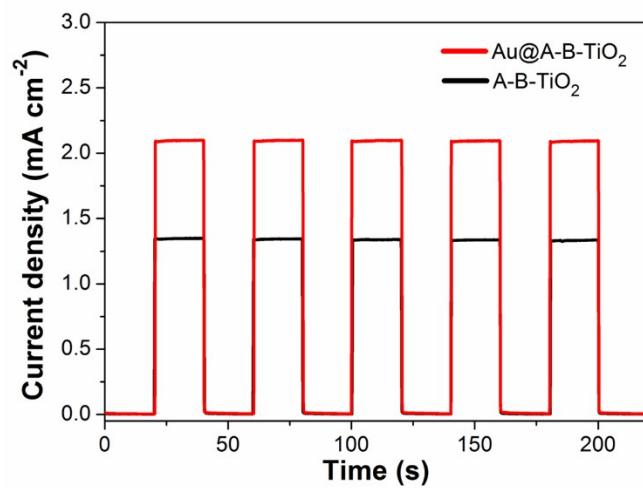
**Figure S11.** Structure model of Au@A-B-TiO<sub>2</sub> heterostructure for the FDTD simulation.



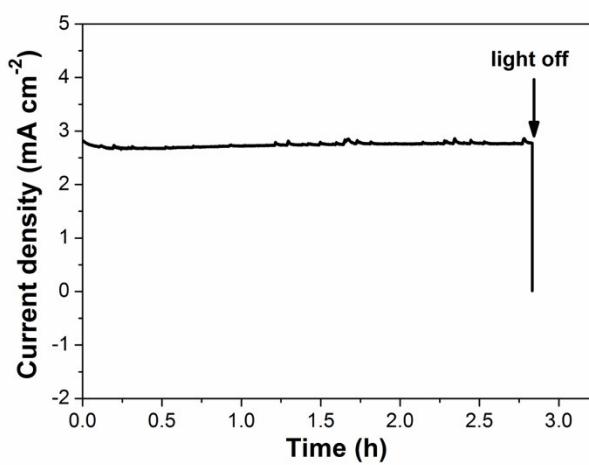
**Figure S12.** Spatial distribution of the enhancement of electromagnetic field intensity at wavelengths of 350.



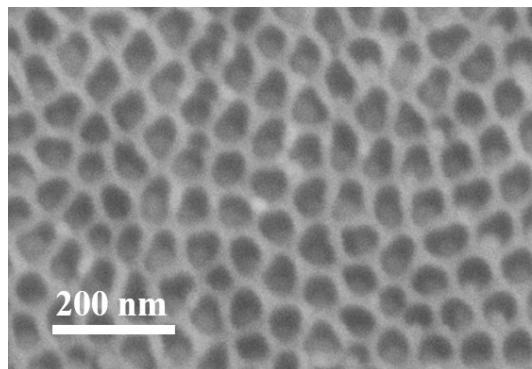
**Figure S13.** Angle-resolved SERS spectra of Au@A-B-TiO<sub>2</sub>.



**Figure S14.** Transient photocurrent responses of A-B-TiO<sub>2</sub> and Au@A-B-TiO<sub>2</sub> photoelectrodes measured at 1.23 V vs RHE under UV light.



**Figure S15.** Longtime photocurrent of  $\text{Au@A-B-TiO}_2$  measured at 1.23 V vs RHE under AM 1.5G illumination.



**Figure S16.** SEM image of  $\text{Au@A-B-TiO}_2$  after long time photocurrent measurement.

**Table S1.** PEC water splitting performance comparison of different Au-TiO<sub>2</sub> based photoanodes.

Photoelectrodes	Electrolyte / Light source	Photocurrent at 1.23 V vs RHE / maximum photoconversion efficiency	Reference
<b>Au@A-B-TiO<sub>2</sub></b>	<b>1 M KOH aqueous solution / AM 1.5G</b>	<b>2.82 mA cm<sup>-2</sup> / 1.27%</b>	<b>This work</b>
Au/TiO <sub>2</sub> NTPC	1 M KOH aqueous solution / AM 1.5G	2.25 mA cm <sup>-2</sup> / 1.1%	1
Au/TiO <sub>2</sub> NRPCs	1 M KOH aqueous solution / AM 1.5G	~1.6 mA cm <sup>-2</sup> / 0.7%	2
Au -decorated TiO <sub>2</sub>	1 M KOH aqueous solution / AM 1.5G	~1.7 mA cm <sup>-2</sup>	3
Au/TiO <sub>2</sub> BNRs	1 M KOH aqueous solution / AM 1.5G	~2.32 mA cm <sup>-2</sup> / 1.2%	4
Au NR/TiO <sub>2</sub>	1 M potassium borate / AM 1.5G	0.15 mA cm <sup>-2</sup> at 0.6 V vs RHE	5
LE-Au/TNTs	1 M KOH aqueous solution / AM 1.5G	1.48 mA cm <sup>-2</sup> / 0.81%	6
Au/H-TiO <sub>2</sub>	1 M KOH aqueous solution / AM 1.5G	1.99 mA cm <sup>-2</sup> / 0.687%	7
AuNP/GQD@TNR	1 M NaOH aqueous solution / AM 1.5G	1.75 mA cm <sup>-2</sup>	8
AZO/TiO <sub>2</sub> /Au NCA	0.1 M Na <sub>2</sub> SO <sub>4</sub> solution / AM 1.5G	~1.0 mA cm <sup>-2</sup> / 0.7%	9
TONT-Al <sub>2</sub> O <sub>3</sub> -Au	1 M KOH aqueous solution / AM 1.5G	~0.7 mA cm <sup>-2</sup>	10
Au/B-TiO <sub>2</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub> solution / 500 W Xe lamp	~2.5 mA cm <sup>-2</sup> / 0.6%	11

## References

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