Electronic Supplementary Material (ESI) for Nanoscale Advances.

Improved water splitting efficiency of Au-NP-loaded Ga_2O_3 thin films in the visible region under strong coupling conditions

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Supplmentary Data

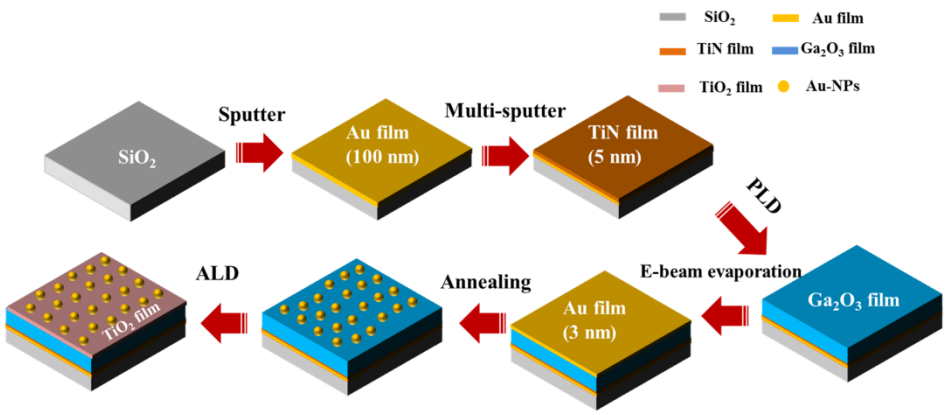

Fig. S1 Schematic of TAGA fabrication

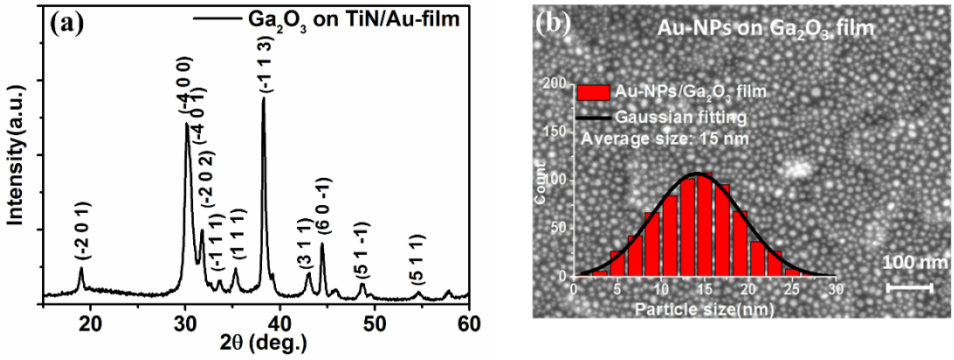

Fig. S2 (a) XRD of Ga_2O_3 film on TiN/Au-film. (b) Top-view SEM image of the Au-NPs on Ga_2O_3 and the size analysis by ImageJ.

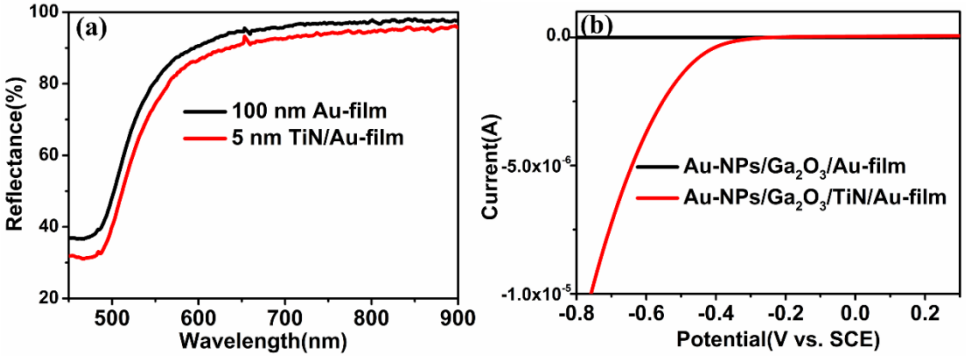

Fig. S3 (a) Reflectance spectra of Au film on SiO_2 with and without TiN film. (b) I-V curves of Au-NPs/Ga_2O_3/Au-film with and without TiN measured under dark conditions.

When Ga_2O_3 was deposited directly on the Au film, poor semiconductor properties of Ga_2O_3 film on Au-film were observed, as shown by the black line in Fig. S3b. After the addition of the TiN layer, the resulting I-V curve showed obvious semiconductor characteristics with a very low dark current under a positive potential. The current of Au-NPs/Ga_2O_3/TiN/Au-film generated at a negative potential range under dark conditions indicated a better electron transfer due to the superior semiconductor properties of Ga_2O_3 film on TiN/Au-film.

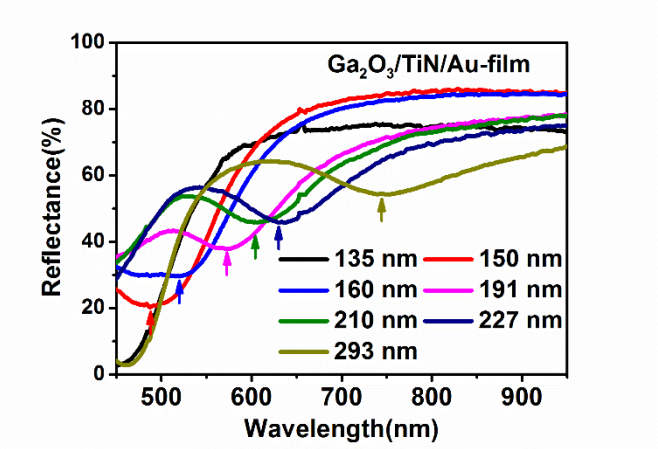

Fig. S4 Reflection spectra of Ga_2O_3/TiN/Au-film with different thicknesses of Ga_2O_3 film. Corresponding colorful arrows mark the cavity modes.

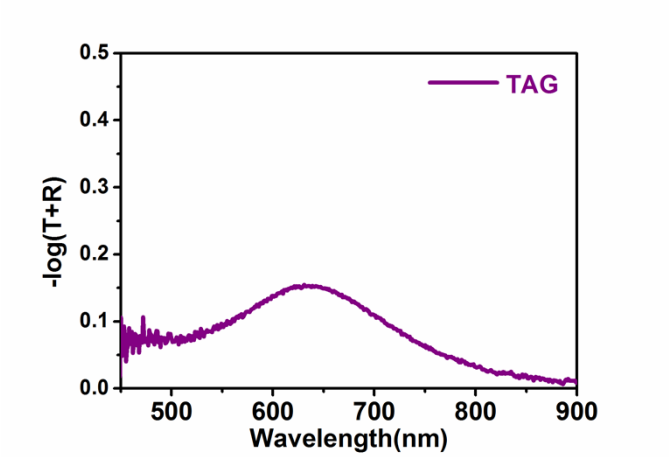

Fig. S5 (a) Absorption spectra of TAG. The thickness of TiO_2 was 4 nm.

When the Ga_2O_3 film was deposited on sapphire, only the LSPR mode existed in the structure of TiO_2/Au-NPs/Ga_2O_3/sapphire (TAG) without a cavity mode because of the similar refractive index between Ga_2O_3 (n=1.90) and sapphire (n=1.77).

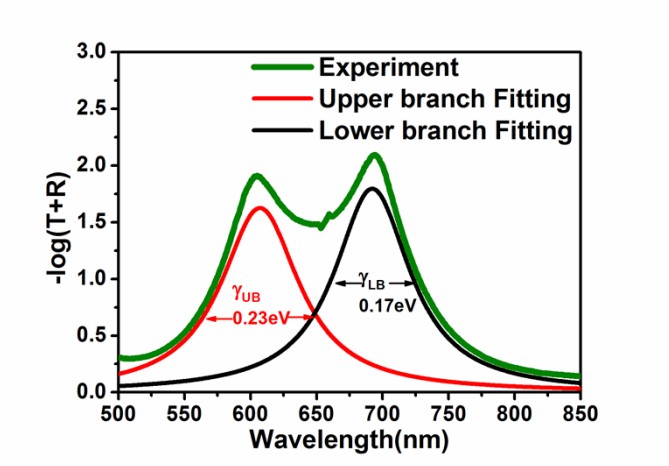

Fig. S6 Spectral separation of the absorption spectrum of TAGA with a tuning structure by Lorentz fitting.

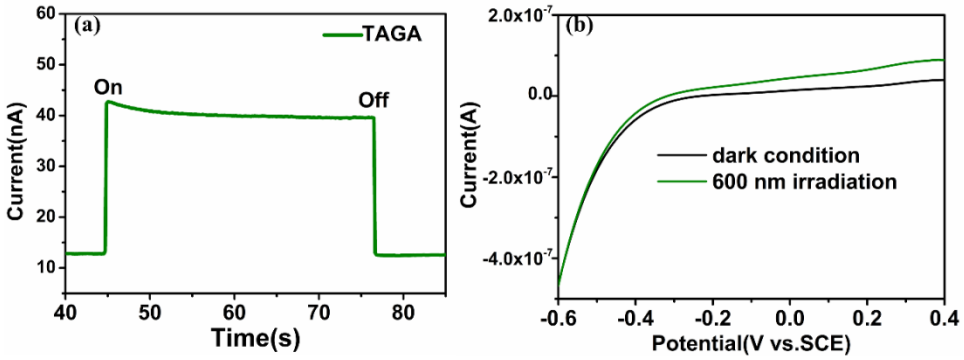

Fig. S7 (a) I-t curve of TAGA under 600 nm irradiation. A bias potential was applied as + 0.3 V vs. SCE. (b) I-V curve of TAGA samples measured in 0.1 mol/L KOH solution under dark conditions and 600 nm irradiation.

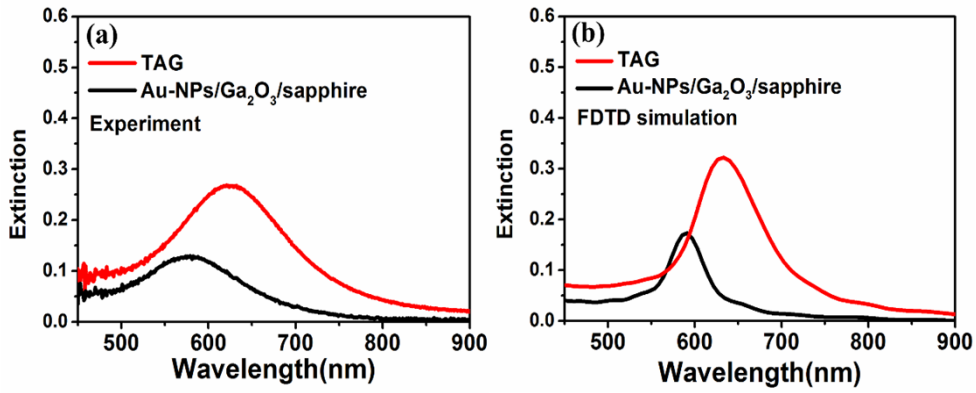

Fig. S8 (a) Experimental extinction spectra of TAG and Au-NPs/Ga_2O_3/sapphire. (b) FDTD simulation of extinction spectra of TAG and Au-NPs/Ga_2O_3/sapphire. The thickness of Ga_2O_3 was 210 nm.

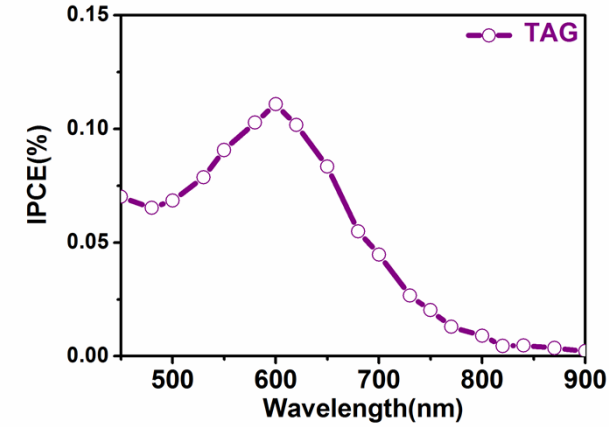

Fig. S9 IPCE of TAG measured in 0.1 mol/L KOH solution. The applied bias potential was + 0.3 V vs. SCE.

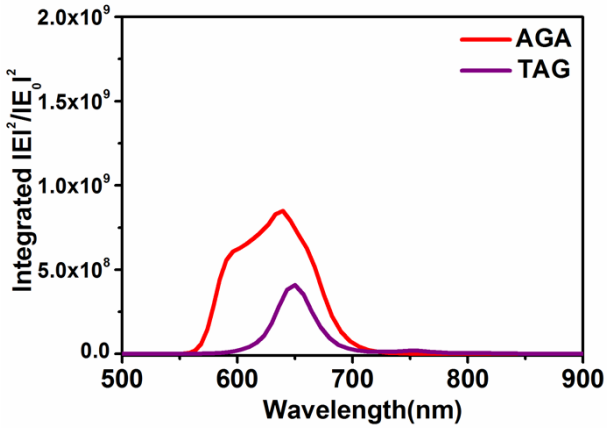

Fig. S10 FDTD simulation of the near-field spectra at the interface of the Au-NPs/Ga_2O_3 in AGA and TAG. The monitor position (black line) is 1 nm above the Au-NPs/Ga_2O_3 interface.

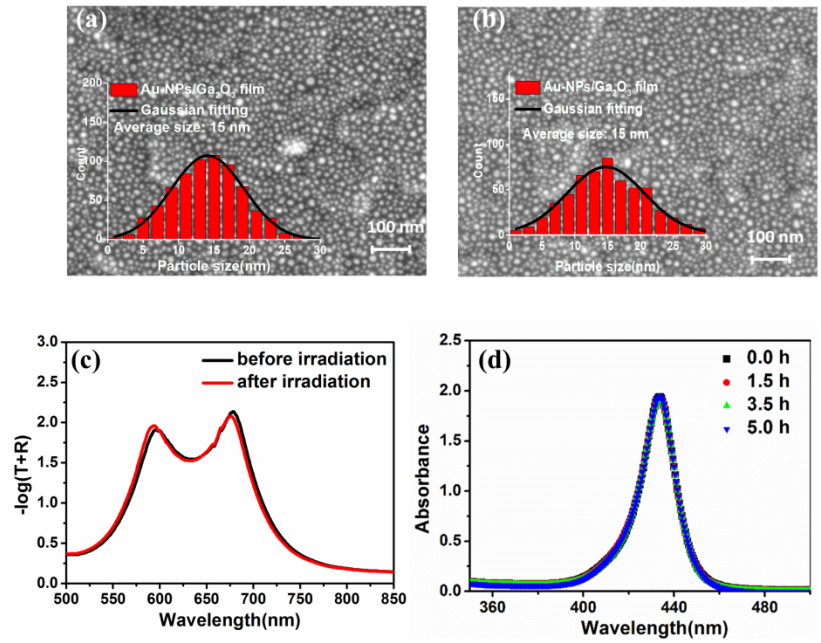

Fig. S11 Top-view SEM images and the size analysis of the Au-NPs on TAGA (a) before and (b) after 6 h irradiation under visible light; (c) Absorption spectra of TAGA before and after 6 h irradiation under visible light; (d) Absorbance spectra of $TiO(tpypH_4)^{4+}$ solution after the addition of electrolyte for O_2 evolution using TAGA photoanode under visible light. The legend indicates the irradiation time.

Fig. S11a and b showed the SEM image of Au-NPs and surface morphology on TAGA and the analyzed particle distribution before and after irradiation. No apparent differences in surface morphology and particle size distribution were observed. In addition, after 6 h irradiation under visible light, the absorption spectra of TAGA shown in Fig. S11c were almost the same before and after irradiation, indicating that no self-oxidation of the photoanode occurred during the measurement.

Since no sacrificial electron donor or acceptor was used in our experiment, the main possible side reaction product is H_2O_2, as reported in our previous paper.[1] To examine this possible side reaction product of H_2O_2, as shown in Fig. S11d, a spectrophotometric analysis using a Ti-porphyrin reagent was applied to detect the formation of H_2O_2 during water oxidation.[2] $TiO(tpypH_4)^{4+}$ solution (5.0×10^{-5} mol/L) was prepared by dissolving [Oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV)] in hydrochloric acid solution. During the measurement, 100 µL electrolyte for O_2 evolution using TAGA after different irradiation time was added into 300 µL $TiO(tpypH_4)^{4+}$ solution. However, according to the absorbance result in Fig. S11d, no H_2O_2 was detected after irradiation. It meant this side reaction did not occur during water oxidation.

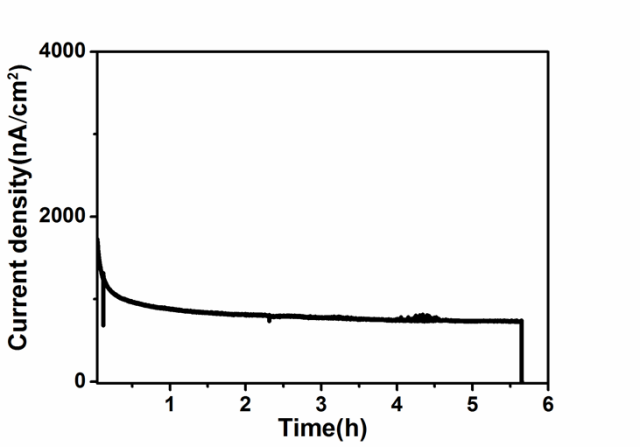

Fig. S12 Photocurrent density of TAGA under the same experimental condition for oxygen evolution.

Reference

1. Y. Nishijima, K. Ueno, Y. Kotake, K. Murakoshi, H. Inoue and H. Misawa, *J. Phys. Chem. Lett.*, 2012, **3**, 1248-1252.

2. C. Matsubara, N. Kawamoto and K. Takamura, *Analyst*, 1992, **117,** 1781-1784.