Electronic Supplementary Material (ESI) for Nanoscale.

Plasmon-induced Electron Injection into the Large Negative Potential Conduction Band of Ga_2O_3 for Coupling with Water Oxidation

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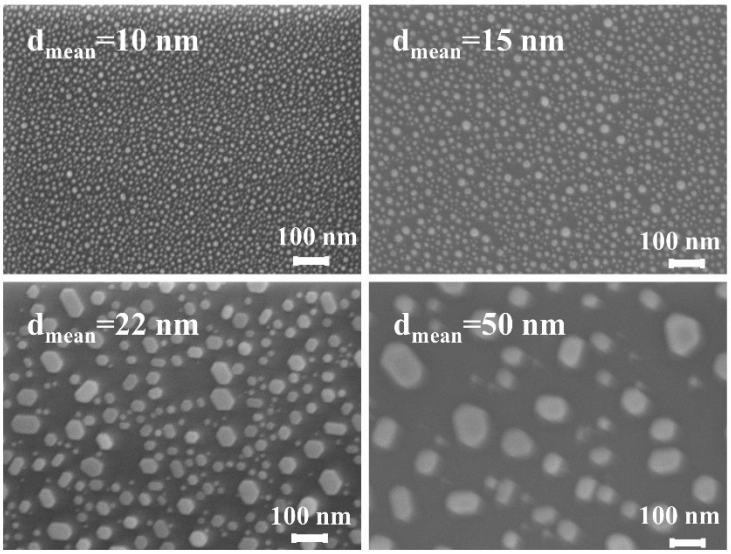

Fig. S1 Top-view SEM images showing surface morphology of samples fabricated by annealing Au film with different thickness.

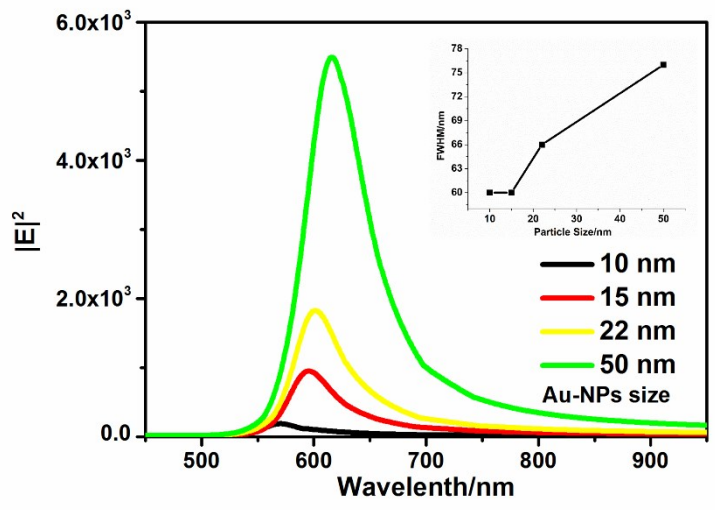

Fig. S2 Near-field spectra on Au-NPs/Ga_2O_3 interface with different Au-NPs size simulated by the FDTD method. Inset: FWHMs of the spectra.

In Fig. S2, full-field electromagnetic wave simulations were performed using the finite-difference time-domain method solver (FDTD Solutions, Lumerical). The ellipsoid sphere with various diameters of 10 nm, 15 nm, 22 nm and 50 nm in the x and y directions were used to model the Au-NPs. Accordingly, the z direction was set as 7 nm, 10 nm, 13 nm and 24 nm. The investigated structure was simulated using perfectly matched layers along z-direction and periodic boundary conditions along x-and y-directions with period of 15, 20, 35 and 80 nm, respectively. In the simulation, the refractive index was taken from the optical constants of Johnson and Christy. Ga_2O_3 was treated as dielectric materials with refractive index of 1.8.

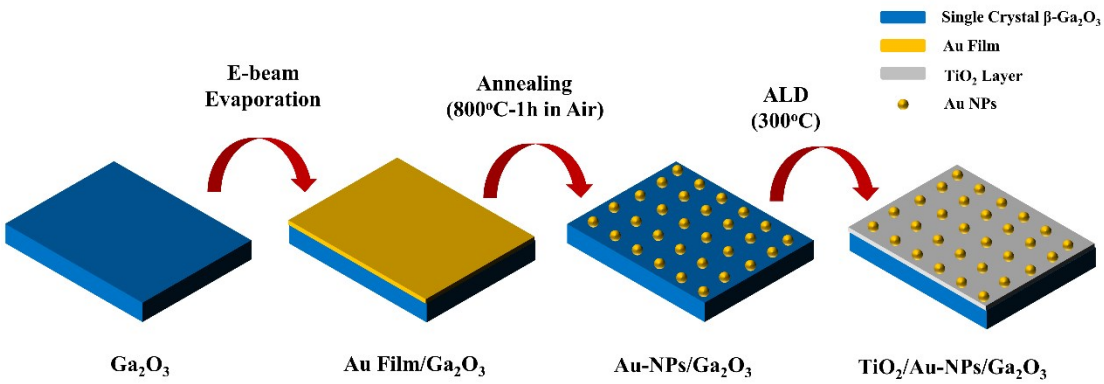

Fig. S3 Schematics of the fabrication procedure for the TiO_2/Au-NPs/Ga_2O_3 photoelectrode.

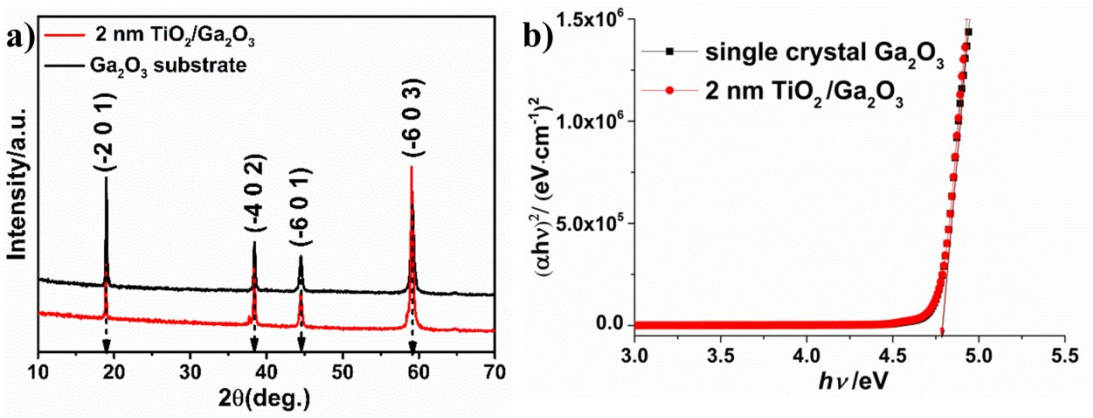

Fig. S4 (a) XRD of single crystal Ga_2O_3 with and without TiO_2 (2 nm). (b) Tauc plots of single crystal Ga_2O_3 with and without TiO_2 (2 nm) calculated from the UV-Vis spectra.

All the peaks in XRD are attributed to the diffraction peaks of β-Ga_2O_3. No peaks shift and broadening of Ga_2O_3 were observed after the deposition of TiO_2. Figure S4b shows the profile of $(\alpha hv)^2$ versus hv for the single crystal Ga_2O_3 with and without TiO_2 (2 nm) which is related to the equation:

$$\alpha hv = A(hv - E_g)^n$$

where A is a constant, n=1/2 for direct band gap semiconductor, α is the absorption coefficient, h is the Planck constant, v is the light frequency. The bandgap energies (E_g) were estimated from the x-intercept of Fig. S4b.

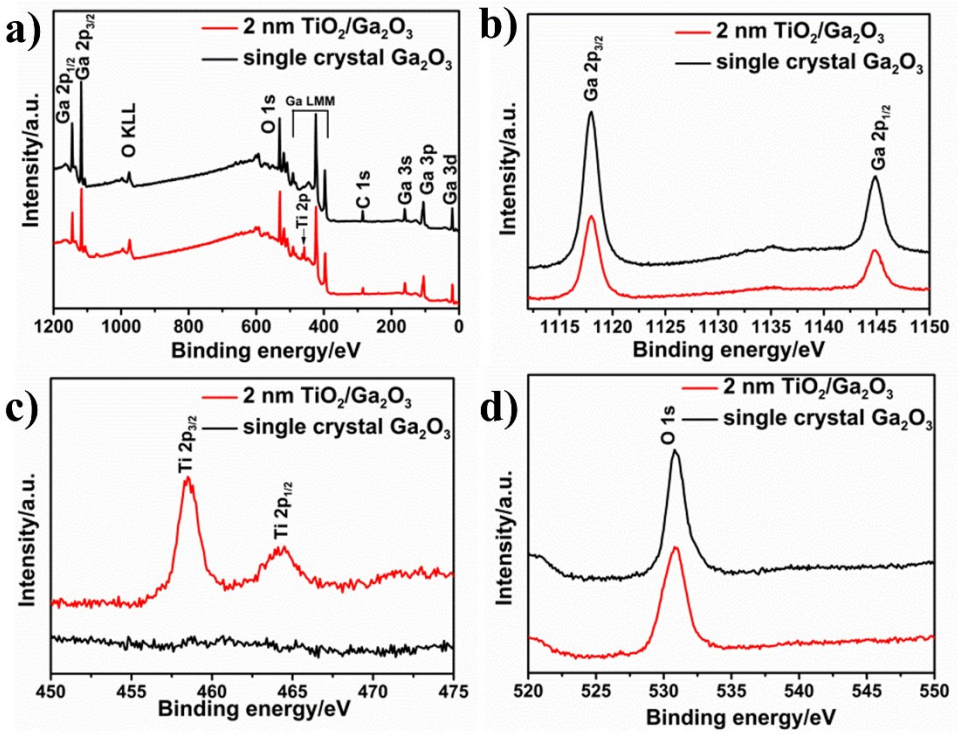

Fig. S5 XPS spectra of single crystal Ga_2O_3 with and without TiO_2 (2 nm): (a) full survey spectra; (b) core level spectra for Ga 2p; (c) core level spectra for Ti 2p; (d) core level spectra for O 1s.

Two symmetrical peaks of Ga $2p_{1/2}$ (1144.5 eV) and Ga $2p_{3/2}$ (1117.9 eV) were attributed to the Ga^{3+} in Ga_2O_3.[1] After the deposition of TiO_2, peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at binding energies of 458.6 eV and 464.4 eV appeared indicating the presence of Ti^{4+} in TiO_2. The binding energy of O 1s peak of Ga_2O_3 was observed at 530.7 eV. After TiO_2 deposition, the binding energy of O 1s peak shows slightly broadening at the lower energy side rather than peak energy shift, which is ascribed to the presence of O 1s peak of Ti-O (529.8 eV).[2]

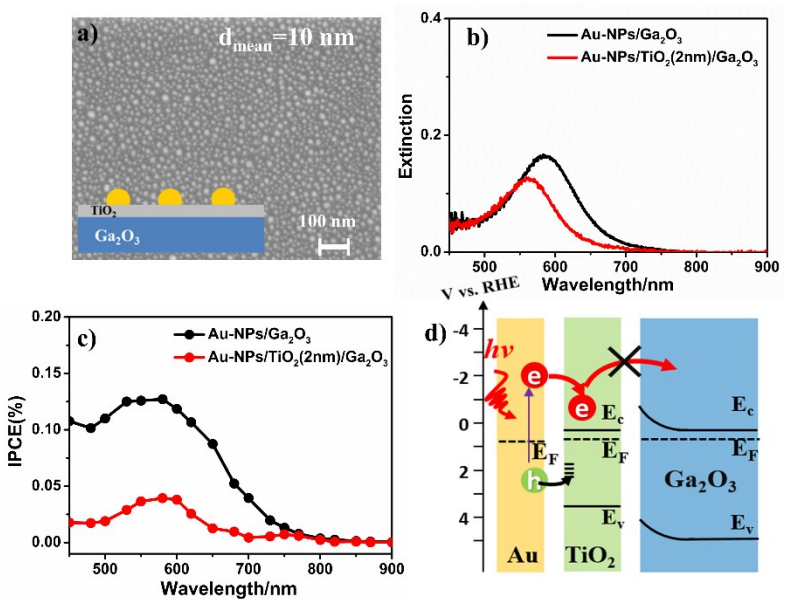

Fig. S6 (a) The top-view SEM image of Au-NPs/TiO_2 (2 nm)/Ga_2O_3. Inset: schematic of Au-NPs/TiO_2/Ga_2O_3 structure. (b) Extinction spectra and (c) IPCE action spectra of Au-NPs/Ga_2O_3 and Au-NPs/TiO_2 (2 nm)/Ga_2O_3 . (d) Schematic diagram of charges transfer in Au-NPs/TiO_2/Ga_2O_3.

TiO_2 is deposited on the surface of Ga_2O_3 before the annealing process as shown in the inset in Fig. S6a (Au-NPs/TiO_2/Ga_2O_3). Au-NPs/TiO_2/Ga_2O_3 had a blue shift of LSPR peak and weaker LSPR intensity compared with Au-NPs/Ga_2O_3 as shown in Fig. S6b due to the smaller particle size of Au-NPs (d_{mean}~10 nm). However, the application of the TiO_2 layer between Au-NPs and Ga_2O_3 dramatically decreases the IPCE to one-third of the value without TiO_2 as shown in Fig. S6c. The hot electrons generated by the photoirradiation would first be transferred to the TiO_2 layer adjacent to Au-NP. The electron transfer from CB of TiO_2 to the more negative CB of Ga_2O_3 is difficult as shown in Fig. S6d. This unfavorable electron transfer process and weaker LSPR effect lead to the IPCE decrease.

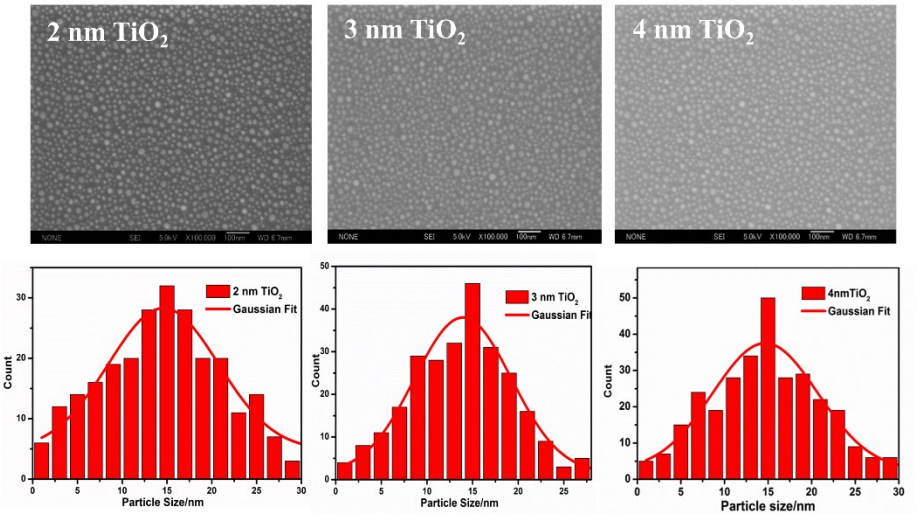

Fig. S7 Top-view SEM images (upper) and the particle size distributions (lower) of x-nm-TiO_2/Au-NPs/Ga_2O_3 (x=2-4).

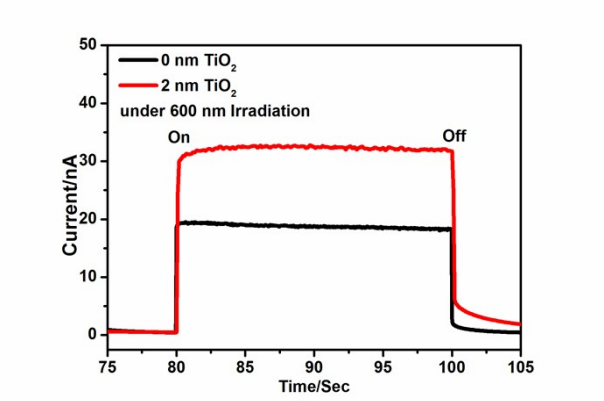

Fig. S8 *I-t* characteristics Au-NPs/Ga_2O_3 with 0 and 2 nm TiO_2 under 600 nm irradiation.

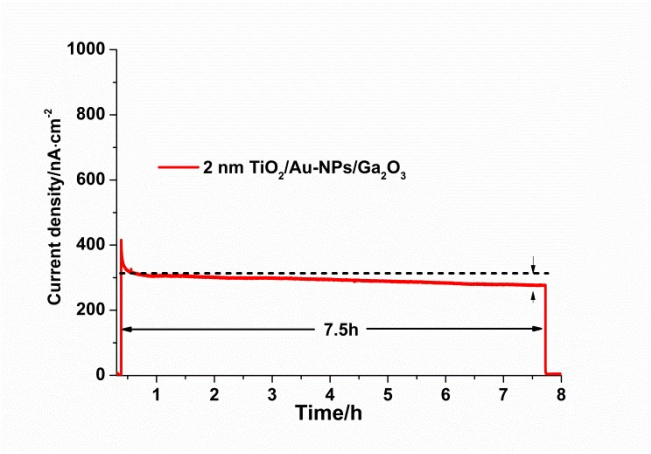

Fig. S9 Current density-time curve of 2-nm-TiO_2/Au-NPs/Ga_2O_3 under 600 nm light irradiation. The measurement conditions were identical to the photocurrent measurements in the manuscript. The dash line meant the initial value of quasi-steady current density.

After 3 minutes irradiation, quasi-steady photocurrent density was obtained as 310 nA/cm^2 as shown in Fig. S9. The photocurrent density after 7.5 hours was 280 nA/cm^2 which showed long-time stability.

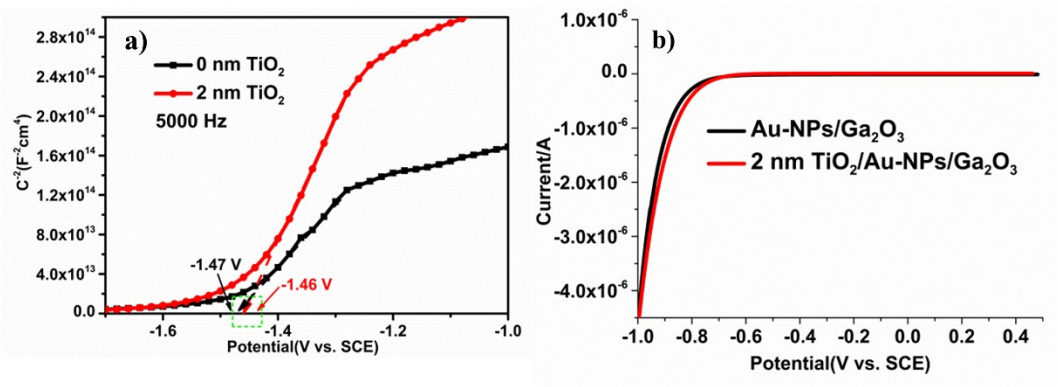

Fig. S10 (a) A typical Mott–Schottky plot of Au-NPs/Ga_2O_3 without TiO_2 modification. (b) *I-V* characteristics of 2-nm-TiO_2 / Au-NPs/Ga_2O_3 and Au-NPs/Ga_2O_3 measured in dark condition.

According to the Mott-Schottky measurement in Fig. S10a, the flat-band potential of Au-NPs/Ga_2O_3 is estimated to be -1.47 V (vs. SCE at pH 7). Thus, the flat-band potential of Au-NPs loaded Ga_2O_3 could be concluded to be -0.81 V (vs. RHE) by the following formula:

$$E(\text{RHE}) = E(\text{SCE}) + 0.244 + 0.059 \times \text{pH}.$$

After the deposition of TiO_2, the flat-band potential shows a further positive shift to -0.80 V vs. RHE which is consistent with the onset potential shift in I-V result shown in Fig. S10b. The energy barrier of 2.03 eV is calculated between flat-band potential of 2-nm-TiO_2/Au-NPs/Ga_2O_3 and the oxidation potential of water (+1.23 V vs. RHE).

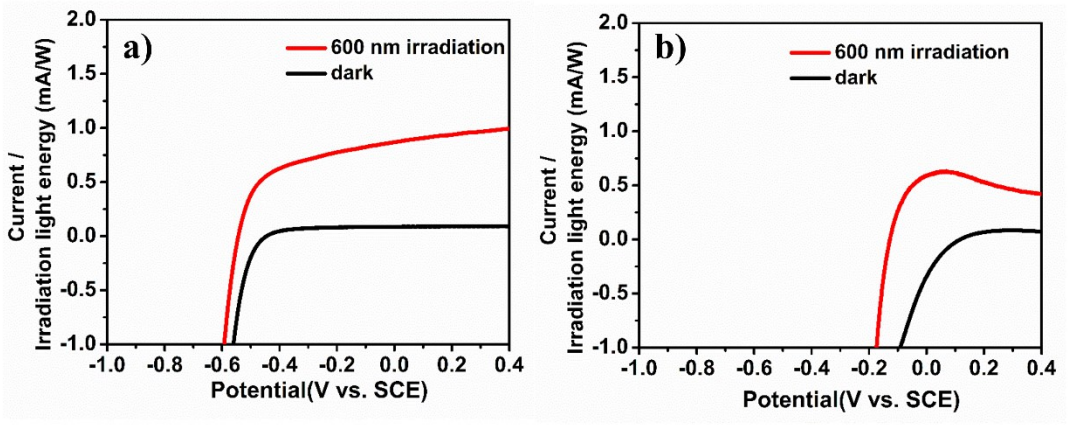

Fig. S11 *I-V* characteristics of (a) 2-nm-TiO_2/Au-NPs/Ga_2O_3 and (b) Au-NPs on TiO_2 thin film with a thickness of 54 nm with and without light irradiation of the wavelength of 600 nm. The current is normalized by the irradiation light energy.

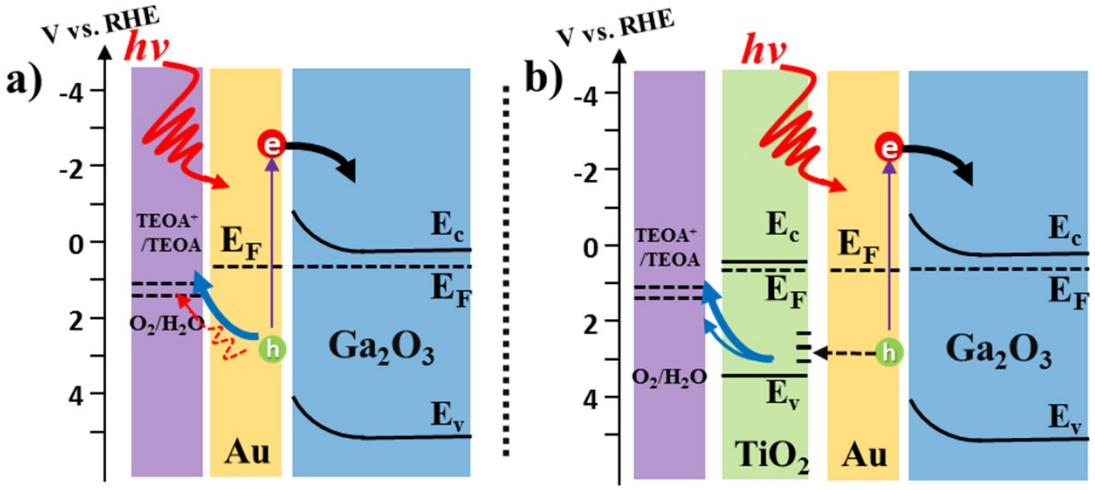

Fig. S12 Schematics of plasmon-induced charges transfer of (a) Au-NPs/Ga_2O_3 and (b) 2 nm-TiO_2/Au-NPs/Ga_2O_3. e and h indicate the electrons and holes, respectively.

Reference

1. W. Mi, X. Du, C. Luan, H. Xiao and J. Ma, *RSC Adv.,* 2014, 4, 30579-30583.
2. B. Bharti , S. Kumar , H. Lee and R. Kumar, *Sci. Rep.* 2016, 6, 32355.