Supporting Information

Surface plasmon assisted high-performance photodetectors based on hybrid TiO_2@GaO_xN_y-Ag heterostructure

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EXPERIMENTAL SECTION

Fabrication of TiO_2@GaO_xN_y-Ag heterojunction photodetector. TiO_2 nanowires were prepared using the hydrothermal method on the FTO substrate (2 cm × 1 cm). Before the hydrothermal reaction, the substrate was placed in a container filled with the reaction solution and placed in the stainless steel high-pressure reactor, in which the FTO was at an angle of 60° with the lining side wall and the conductive surface facing up. The reaction mixture was composed of 0.25 mL of Ti(OBU), 15 mL of H_2O, and 15 mL of HCl. The temperature of the hydrothermal reaction was 150 °C, and the reaction time was 4 h. The TiO_2 nanowires obtained after the hydrothermal reaction were repeatedly washed with C_2H_5OH and H_2O, and then dried for use. TiO_2 nanowires were placed in the PE-ALD cavity, and the GaO_xN_y film was deposited through the optimal ALD process to form the TiO_2@GaO_xN_y core-shell nanowire heterojunction. Finally, the prepared TiO_2@GaO_xN_y heterojunction nanowire array was placed in 0.1 M $AgNO_3$ solution and irradiated under 22 W UV for 0.5 h to undergo the photodecomposition reaction. Subsequently, the samples were washed with deionised water and blow dried with N_2 to obtain the heterojunction nanowire array of TiO_2@GaO_xN_y-Ag ternary system.

Characterization and measurement. SEM (Sigma HD, Zeiss), TEM (FEI, TECNAI G2 F20) and HRTEM (Talos, F200X) were used to characterize the morphology and microstructure of the prepared films in this work. EDX (EDX-700, Shimadzu) was used to characterize the existing elements and content. XPS (ESCALAB, 250Xi) measurements were performed via a SPECS XPS system equipped with a monochromatic Al Kα source ($h\nu$ = 1486.6 eV). A continuous light source (HPS-2000, Ocean) was used for photodetector performance measurements, which can output light in the wavelength range of 185-2000 nm. The device electrodes of Cr/Au (10 nm/70 nm) were patterned by standard optical lithography and grown by electron-beam evaporation, and followed by a lift-off process. The electrical properties were measured with a semiconductor device analyzer (Keysight 1500A) using Tungsten probe tips in the air at room temperature.

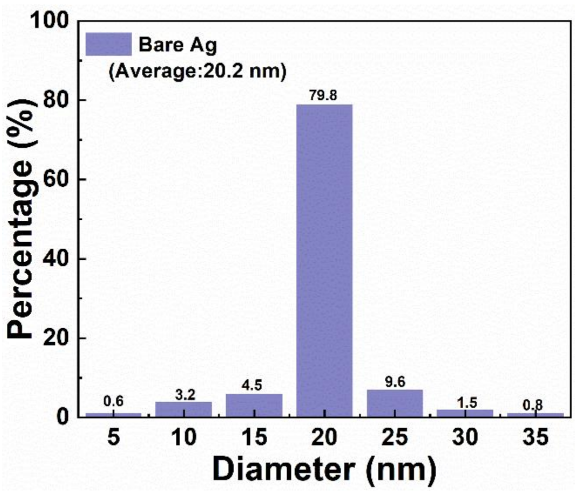

Fig. S1. Statistical diagram of size distribution of Ag particles.

The results of Spectroscopic Ellipsometry (SE) characterization for 200-cycles GaO_xN_y layers deposited by PE-ALD were shown in Figure S3**,** which were consistent with the growth rate and physical characteristics of GaO_xN_y film. The thickness of GaO_xN_y is 10 nm, which is consistent with the growth rate of 0.05 nm/cyc mentioned before. At the wavelength of 632.8 nm, the refractive index (n) and extinction coefficient (k) of the GaO_xN_y layers are 1.740 and 6.51×10^{-3}, which was consistent with literature reports.[1,2]

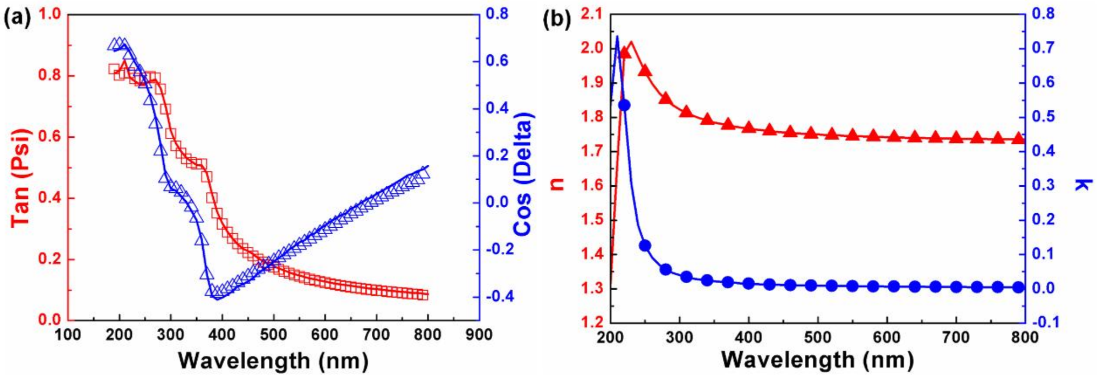

Fig. S2. (a) Changes of Tan(Psi) and Cos(Delat) of GaO_xN_y layers with wavelength during SE measurement and fitting. (b) The variation of n and k with wavelength of GaO_xN_y layers.

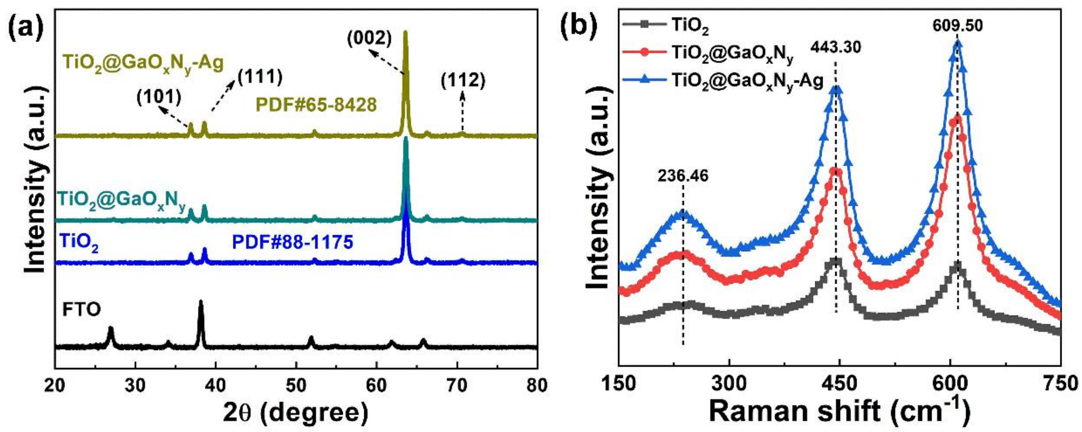

Fig. S3. (a) XRD spectra and (b) Raman spectra of TiO_2, TiO_2@GaO_xN_y, and TiO_2@GaO_xN_y-Ag.

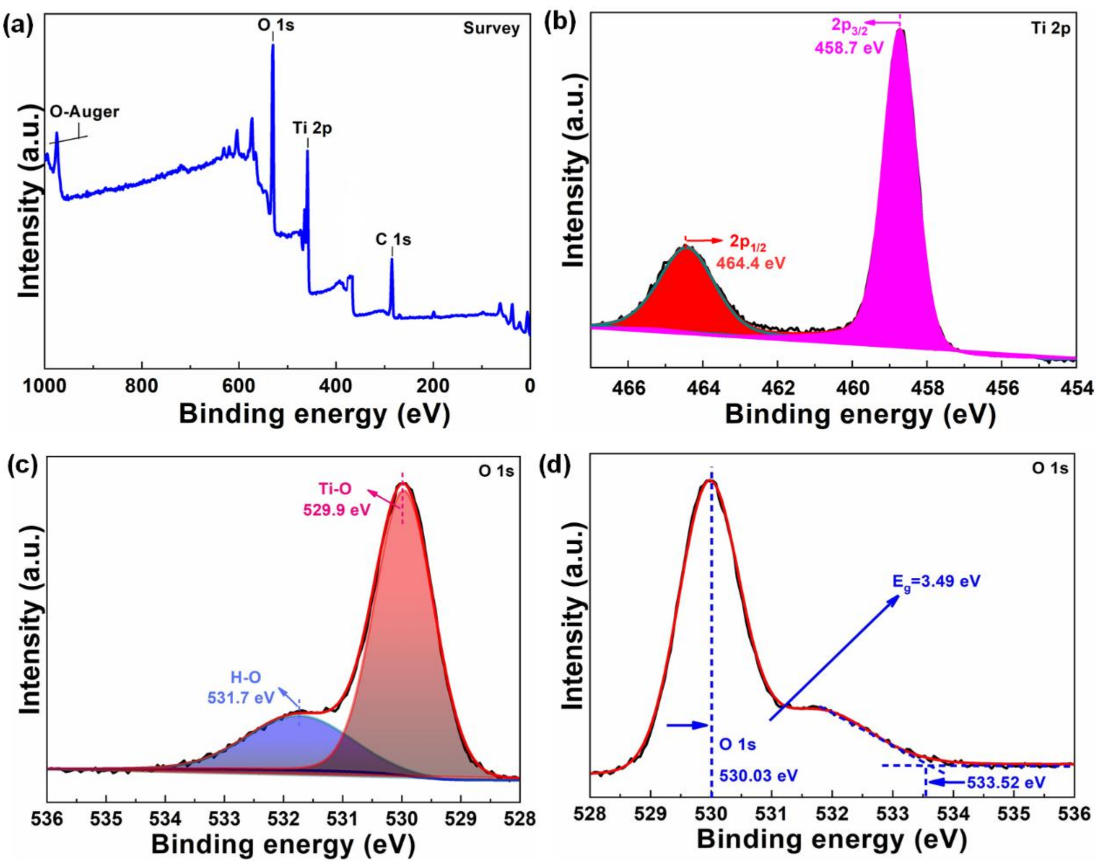

Fig. S4. XPS specturm of TiO_2 (a) survey spectrum, (b) Ti 2p, (c)Ti-O and H-O, (d) O 1s.

SIMULATION SECTION

Simulation. The modelling was implemented using the commercial FDTD software. A 3D simulation domain with perfectly matched layer boundary condition (along the x-, y-, and z-direction)[3] were used to simulate TiO_2@GaO_xN_y-Ag heterostructure. In this simulation model, the Ag particles are defined as cubes with an edge length of 20 nm, and the thicknesses of the FTO, TiO_2, and GaO_xN_y are 5, 200, and 15 nm, respectively. It should be noted that TiO_2 is completely coated with 10 nm thick GaO_xN_y. A total field scattered field (TSFS) light source with propagation along the z-axis and electric field polarized along the x-axis was used as the excitation source above the Ag particles. The scattering (B) and absorption (A) monitors are placed as shown in the schematic diagram in Figure 5a, and the relationship between extinction power and absorption and scattering is extinction = absorption + scattering. When simulating the electric field distribution of Ag particles, the electric field distribution monitor was kept at a height above 5 nm of the interface of Ag particles and GaO_xN_y. The simulated boundary conditions are set to a perfectly matched layer (PML) with a spacing from the nanostructure greater than half the maximum incident wavelength. In addition, the grid size in the x, y, z directions are all set to 3 nm, while the duration of the simulation, the temperature of the simulation, and the auto-off level are all set to default. The complex refractive index of Ag is derived from Palik's model in the FDTD material library. Similarly, the composite refractive indices of the FTO layer and the TiO_2 layer are referenced to Abdullahi's model[4] and Siefke's model[5], respectively. Differently, the composite refractive index of the GaO_xN_y layer is derived from the results of ellipsometric measurements (see S2 for detailed data). The absorption spectra were recorded in the range from 350 to 610 nm.

References

[1]. Ozgit-Akgun C, Goldenberg E, Okyay A K, et al. Hollow cathode plasma-assisted atomic layer deposition of crystalline AlN, GaN and $Al_xGa_{1-x}N$ thin films at low temperatures. J Mater Chem C 2014, 2, 2123

[2]. Ramachandran R K, Dendooven J, Botterman J, et al. Plasma enhanced atomic layer deposition of Ga_2O_3 thin films. J Mater Chem A 2014, 2, 19232

[3]. Kunwar S, Pandit S, Kulkarni R, et al. Hybrid device architecture using plasmonic nanoparticles, graphene quantum dots, and titanium dioxide for UV photodetectors. ACS Appl Mater Interfaces 2020, 13, 3408

[4]. Abdullahi S, Moreh A U, Hamza B, et al. Optical characterization of fluorine doped tin oxide (FTO) thin films deposited by spray pyrolysis technique and annealed under nitrogen atmosphere. Int J Innov Appl Stud 2014, 9, 947

[5]. Kroker T S, Pfeiffer K, Puffky O, et al. Materials pushing the application limits of wire grid polarizers further into the deep ultraviolet spectral range. Adv Opt Mater 2016, 4, 1780