Electronic Supplementary Information

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2. Experimental

2.1 Preparation

2.1.1 Preparation of Ti^{3+}TiO$_2$ orderly nanoarrays/FTO: Firstly, the FTO substrates were washed by acetone, alcohol and deionized water for 15 min (2 times), and dried by an oven. Dropping 15 ml HCL (36%) into 15 ml deionized water, then, adding 500 ul tetrabutyl titanate dropwise, and stirring until it is clear. Subsequently, the FTO and precursor solution were transferred into an inner tank of reaction kettle, which was maintained at 130 °C for 5 h. After reaction, the TiO$_2$ orderly nanoarrays were cleaned with deionized water and dried at 60 °C in air. Secondly, CaH$_2$ is dispersed in dimethylformamide of 0.02M, 0.04M, 0.06M and 0.08M. Taking 100 uL as-prepared solution and dropping it on the TiO$_2$ orderly nanoarrays. Then, it is heated

at 550 °C for 1h in argon atmosphere by tubular furnace. After the reaction is completed, adding anhydrous ethanol and ultrasound for 15 min to remove impurities on the surface.

2.1.2 Preparation of AgInS$_2$ quantum dots: Firstly, Add 0.6279 g glutathione (GSH) into 150 mL deionized water, 1 mL AgNO$_3$ aqueous solution (0.1M) and 4 mL In (NO$_3$)$_3$ aqueous solution (0.2M), mix and fully stir, while adjusting the pH to 7.3 through NaOH solution (0.5M) and fully stir for 10 min. After the color becomes clear, add 8 mL Na$_2$S aqueous solution (0.1M) and keep it in 120 °C oil bath for 2 h. After reaction, adding isopropanol, ethanol and deionized water to centrifugally clean the sample for three times, and then naturally dry after centrifugation to obtain the AgInS$_2$ QDs quantum dot powder. Finally, the as-prepared AgInS$_2$ QDs were dispersed in ethanol as precursor (0.1M)

2.1.3 Preparation of AgInS$_2$ QDs/NiO/Ti^{3+}-TiO$_2$ orderly nanoarrays pn junction: Subsequently, NiO thin films were deposited on the surface of Ti^{3+}-TiO$_2$ orderly nanoarrays by RF magnetron sputtering. The background vacuum, sputtering pressure, sputtering power and sputtering time were 6×10^{-4} Pa, 1.0 Pa, 100 W and 25 min, respectively. The sputtering gas was Ar (40 SCCM). Finally, AgInS$_2$ QDs were introduced on the surface of NiO film. In detail, 10 uL AgInS$_2$ QDs (0.1M) precursor was dropped onto the surface of NiO film and dried naturally. Herein, samples with different solid reduction of CaH$_2$ are labeled as NiO/Ti^{3+}-TiO$_2$-0/1/2/3/4 (0.00/0.02/0.04/0.06/0.08 M), and finally sample is labelled as AIS/NiO/Ti^{3+}-TiO$_2$-3.

2.2 Characterizations

Here, the morphology, microstructure, and thicknesses of as-prepared films and nanoarrays are characterized by a field emission scanning electron microscope (FESEM, Hitachi S-4800) and a transmission electron microscope (TEM JEM-2100). The crystal information and phase purity are analyzed by an X-ray diffraction (XRD, Bruker AXS D8-discover) and a transmission electron microscope (TEM JEM-2100). A UV-vis absorption spectrophotometer (U-3900 Hitachi) is used to record the light transmission spectrum and light absorption spectrum. The chemical states are determined by an X-ray photoelectron spectroscopy (XPS) using the Thermo ESCALAB250 system. The PL spectra of different excitation wavelengths in ultraviolet region are recorded by a FLS1000 spectrophotometer, and the Time-resolved PL are recorded by the Pico Quant Fluo Time 300. The photoelectric performance is measured by an electrochemical workstation (ZAHNER IM6, Germany) with 0 bias voltage at room temperature, a 100 mw/cm^2 xenon lamp is used as the light source. Ag electrode was prepared by RF magnetron sputtering as the working electrode, and the vertical test was carried out. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky curves were studied by ZAHNER IM6 (Germany) via the standard three-electrode configuration, including the Ag/AgCl electrode being used as the reference electrode, Pt electrode as the counter electrode and as-prepared samples as the working electrodes. The Na_2SO_4 (0.1 M) was used as the electrolyte. The exposed functional area was controlled to be 1×1 cm^2. The Keithley 4200 system was used to study the semiconductor characteristics.

2.3 Density functional theory (DFT) calculations

All plane-wave density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) software [1-2]. The generalized gradient approximation by Perdew, Burke and Ernzerhor was used for the exchange-correlation energy. The ionic cores were described by projector-augmented wave potentials [3-4]. The on-site Coulumb repulsion parameter U within the GGA + U approach was included in the calculations with a consistent value of U = 2 eV on Ti ions [5]. The primitive TiO_2 belongs to space group of pnma. To calculate parameters to analyze structural, electronic properties, 3×3×1 super cells were constructed. There are total of 108 atoms in the super cell 3×3×1 of TiO_2. In the models of TiO_2-O_v, we removed two oxygen atoms (O_{2c} and O_{3c}). The kinetic energy cutoff is 500 eV, the convergence criteria were $1×10^{-5}$ eV for energy and 0.03 eV/Å for stress, and the k points grids are 2×2×3 for structure optimization and 6×8×4 for dos calculation.
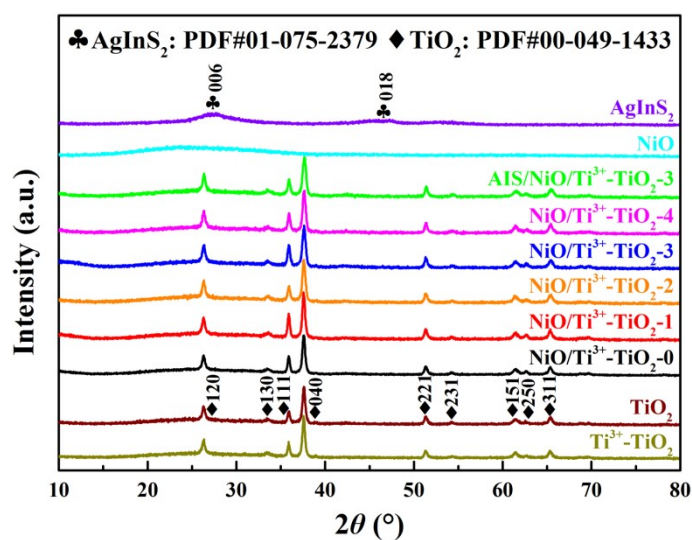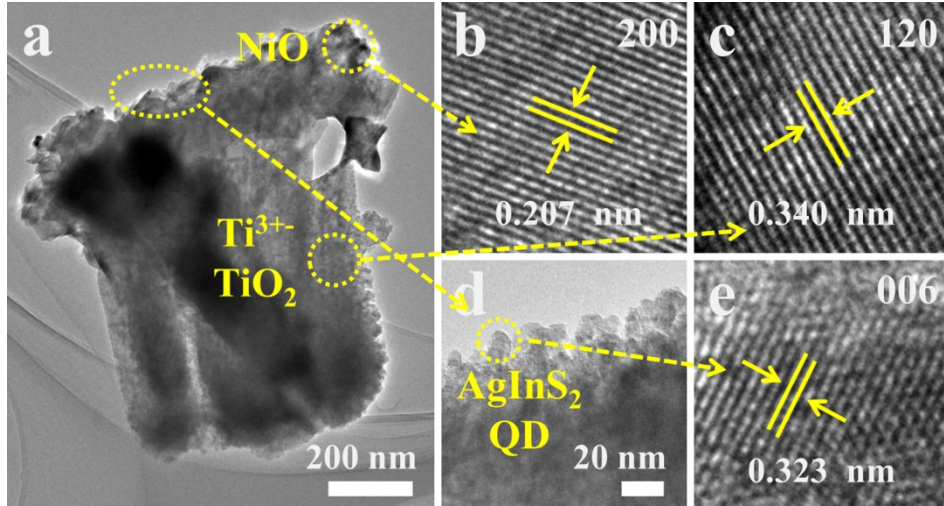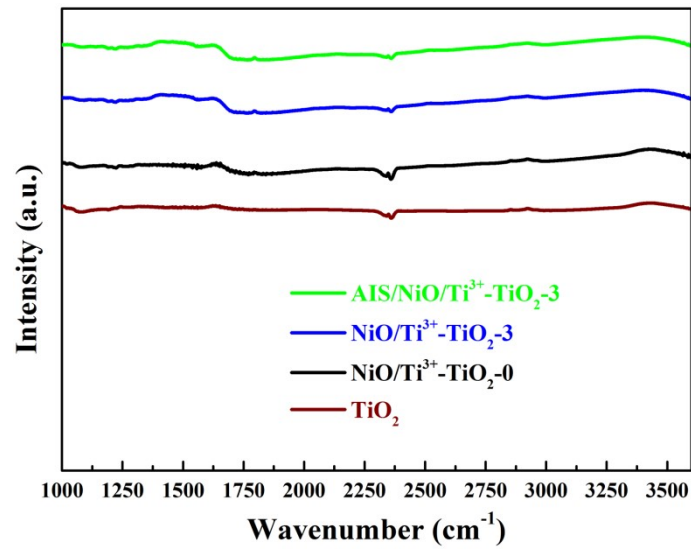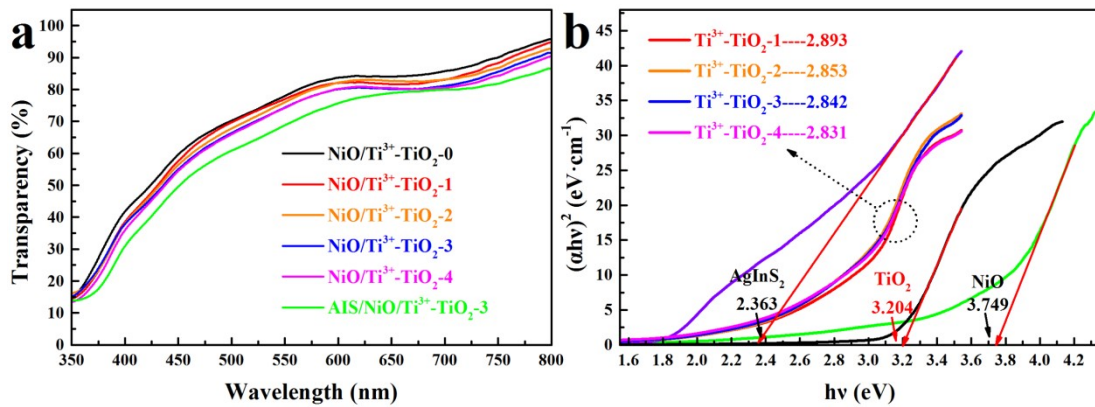
3. Results and discussions

Fig. S1 the XRD for different control groups

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Fig. S2 (a) TEM of AgInS$_2$ QDs/NiO/Ti^{3+}-TiO$_2$ pn junction, HRTEM of (b) NiO and

(c) Ti^{3+}-TiO$_2$, (d) interface of AgInS$_2$ QDs/NiO and (e) HRTEM of AgInS$_2$ QDs

Fig. S3 the FT-IR of different samples

Fig. S4 (a) transmittance of AgInS$_2$ QDs/NiO/Ti^{3+}-TiO$_2$, (b) the corresponding band

gaps of AgInS$_2$ QDs, NiO, TiO$_2$ and different reduced Ti^{3+}-TiO$_2$
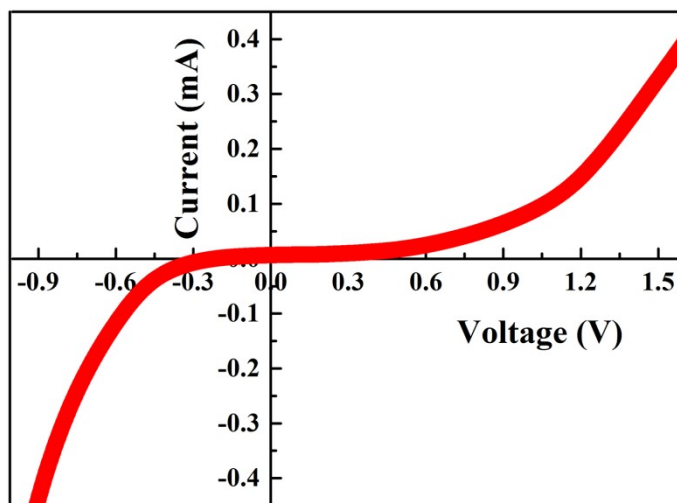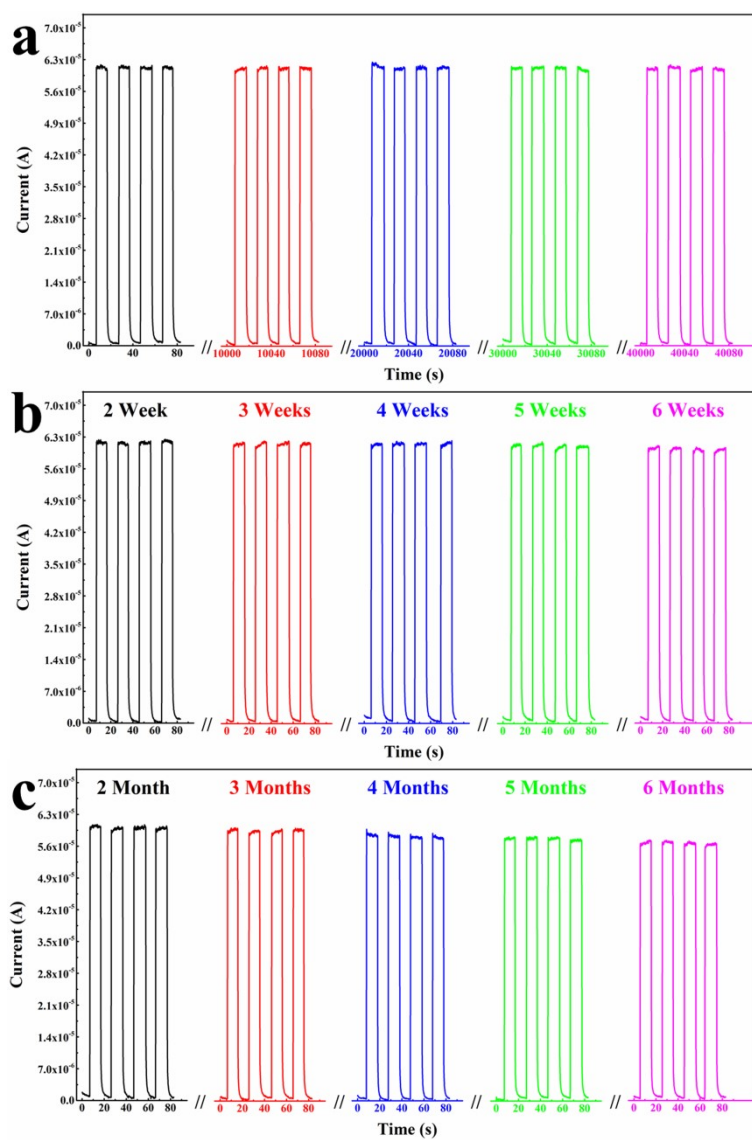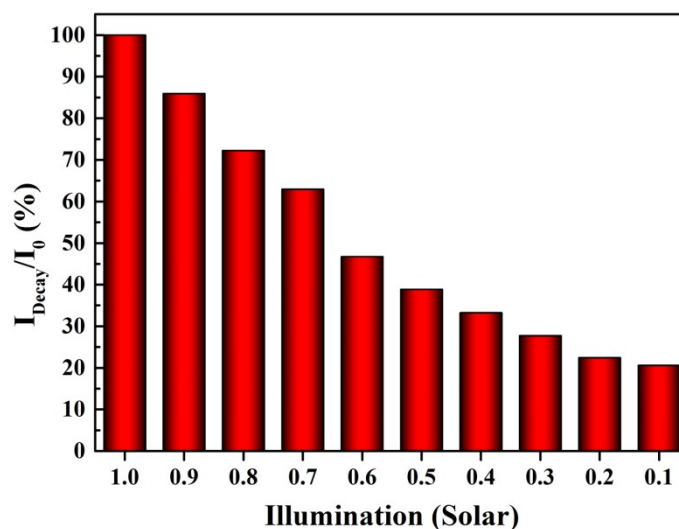

Fig. S5 voltage-current curve of AgInS$_2$ QDs/NiO/Ti^{3+}-TiO$_2$-3

Fig. S6 recycle current-time curve

Fig. S7 photovoltaic response of AgInS$_2$ QDs/NiO/Ti^{3+}-TiO$_2$-3

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