Supplementary Information

Zn-doped p-type Gallium Phosphide Nanowire Photocathodes from a Surfactant-free Solution Synthesis

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Part A. Experiment details.

Chemicals

Triethylgallium (TEGa, min. 97%, Strem), tris(trimethylsilyl)phosphine (TMSP, min. 98%, Strem), diethylzinc (DEZn, min. Zn 52.0 wt.%, Sigma-Aldrich), squalene (99%, Aldrich), toluene (99.9%, Fisher), methanol (99.9%, Fisher), acetone (99.9%, Sigma-Aldrich), hydrochloric acid (1 M volumetric solution, J. T. Baker), potassium chloride (KCl, 99,99%, Sigma-Aldrich), sodium acetate anhydrous (NaAc, ≥99.0%, Sigma-Aldrich), acetic acid (HAc, ≥99.7%, Sigma-Aldrich), and gallium-indium (Ga-Zn) eutectic (Sigma-Aldrich) were purchased and used as received, except that squalene was vacuum-dried under 140°C to remove moisture. Hydrochloric acid (≥37%, *Trace*Select[®], Fluka), Nitirc acid (≥69.0%, *Trace*Select[®], Fluka), and water (*Trace*Select[®], Fluka) were used for elemental analysis of dopant concentrations.

Synthesis of the GaP nanowires

Surfactant-free gallium phosphide nanowires were synthesized following our previous report via the solution-liquid-solid mechanism¹. In a typical synthesis, 0.15 mmol/g TEGa-TMSP solution was prepared by dissolving TEGa-TMSP adduct in vacuum-dried squalene. Using standard Schlenk line techniques, 150ml vacuumdried squalene was thermally stabilized at ~295 °C in a NaNO₃/KNO₃ salt bath (46/54% by weight) under constant stirring (800 rpm). Then 5 g of TEM-TMSP squalene solution was injected into the reactor. The stirring was stopped 30 sec after the injection, which resulted in GaP nanowires of ~25 nm diameter. Prolonged stirring after injection yielded GaP nanowires of larger diameters. The reaction medium first turned yellow to form Ga droplets and then brown as the nanowires started growing. The reaction flask was held at this temperature for 15 min, then withdrawn from the salt bath and allowed to cool. For the Zn-doped GaP nanowires, calculated amounts of DEZn were added to the squalene solution of TEGa-TMSP, followed by the same process as described above.

Nanowire purification and removal of the Ga droplets

GaP nanowires capped with Ga droplets were separated from the reaction mixture and washed with toluene five times. Then these nanowires were washed in methanol, filtered through a polyvinylidene fluoride (PVDF) filter membrane (pore size 0.22 μ m), and dried under ambient conditions. After drying, nanowires were redispersed in 1 M hydrochloric acid. Constant stirring and occasional sonication were applied to dissolve the Ga droplets. The nanowires were then washed with deionized water several times and filtered through a PVDF membrane (pore size 0.22 μ m). GaP nanowires were stored in an N₂ box after drying in the ambient environment.

Elemental analysis of dopant concentration in GaP nanowires

To measure the Zn dopant concentration in the synthesized GaP nanowires, inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer 5300 DV) was applied. About 5 mg of GaP nanowires was dissolved in high purity aqua regia, then prepared as a 10.00 ml solution in a volumetric flask. After measuring the elemental emission spectra in ICP-AES, the concentration ratio of Zn vs. Ga was obtained. The doping concentration of Zn in GaP nanowires was then calculated. Since Zn is a common impurity even in high purity chemicals, a blank control experiment was also performed to subtract the background. The signal-tonoise ratio was at least ten.

Single-nanowire field effect transistor (FET) measurements

In general, to measure the electrical properties of GaP nanowires, top-gated singlenanowire FET devices were fabricated. GaP nanowires were dispersed via drop casting onto heavily doped silicon substrates with 300 nm thermal oxide. With electron beam lithography, two separated Ti/Au electrodes were patterned to bridge a single GaP nanowire, serving as source and drain electrodes. Then 40 nm of Al₂O₃ was deposited over the GaP nanowire by a home-built atomic layer deposition system at 200°C as a dielectric layer for the FET devices. Finally, another Ti/Au metal electrode was patterned on top of the GaP nanowire as a top-gate electrode. The FET devices were loaded into a probe station, and the characteristics of the single-nanowire GaP FET devices were measured using a source-measure unit (Keithley, SMU 236) and power supply.

Preparation of the photoelectrodes

GaP nanowires were freshly washed in 1M hydrochloric acid for one hour and rinsed three times in water/acetone mixed solvent to remove any salt. Then these washed nanowires were redispersed in acetone with a concentration of 1 mg/ml. Indium tin oxide coated glass ($1.3 \times 1.3 \text{ cm}^2$) was cleaned, and 5 nm of In metal was thermally evaporated onto the substrate. Then the acetone dispersion (~40 µL) of GaP nanowires was drop cast onto the substrate and dried slowly under a controlled acetone vapor pressure. This process was repeated until the desirable loading amount was achieved. After drop casting, the substrate was annealed in Ar at 150 °C for 10min to ensure good electric contact. For a control experiment, a Zn-doped GaP single crystalline wafer ($6 \times 10^{17} \text{ cm}^{-3}$, AXT inc.) was used. The ohmic contact for the planar electrode was realized by applying Ga-In eutectic to the back of the wafer and annealing the substrate in Ar at 400°C for 10min.

Photoelectrochemical measurements

The photoelectrochemical properties of the GaP nanowires were tested under a standard three-electrode setup, with Pt foil as the counter electrode and a Ag/AgCl electrode (3.5M KCl) as the reference electrode. In all cases, the aqueous electrolyte used was 0.1M pH 5.2 HAc-NaAc buffer, containing 0.5M KCl. To convert the measured voltage into the voltage vs. the reversible hydrogen electrode (RHE), the following calculation was performed: V vs RHE = V vs AgCl/Ag + 0.5052 volt During all measurements, the electrochemical cell was purged with Ar under constant stirring. All experiments were measured using a Gamry Reference 600 potentiostat.

For *I-V* measurements, the scan rate was set as 10 mV/sec, and chopped light was applied. The light source used was a 300W xenon arc lamp (Newport) equipped with an AM1.5G filter. The power density of the illumination was calibrated to be 100mW/cm² using a standardized photodiode (Hamamatsu, S1787-04).

For photovoltage measurement, the same experiment setup as the *I-V* measurement of the GaP photocathode was applied. The photovoltage measured is calculated as the difference of open-circuit potential of the electrode between dark and 1 sun illumination (AM 1.5G). Light intensity measurement indicates that this light intensity is close but not exact at flat-band condition based on the fact that less than 10 mV increase of photovoltage could be gained for intensity up to 500 mW/cm². For incident photon-to-current efficiency (IPCE, η_{IPCE}) measurements, a monochromomater (Newport) was applied to provide incident light of variable wavelength, and the photocurrent was recorded at a constant bias (0.1 V vs. RHE) with a spectral step of 10 nm. The bandwidth of the light delivered from the monochromator was about 15 nm at full-width half maximum. The measured photocurrent was converted to IPCE by normalizing it to the incident light as measured using a photodiode with known quantum efficiency.

To obtain the absorbed photon-to-current conversion efficiency (APCE, η_{APCE}) spectrum, the absorption of the GaP electrode (A_{GaP}) was measured according to previously reported method². The electrode was placed inside a custom 4-in. diameter integration sphere (Gigahertz Optik UPK-100-L coated with ODM98), and a Newport 300W xenon arc lamp was applied as broadband light source. Signals were sent to a liquid N₂ cooled CCD/spectrometer (Princeton Instruments, Acton) via an optical fiber. The difference of spectrum measured in the CCD with and without the electrode was the amount of light absorbed by the electrode. For nanowire electrode, the absorption of thermally evaporated 5 nm indium metal on indium tin oxide coated glass was also measured to subtract the absorption from underlying substrate. The APCE spectrum was obtained from the following equation: $\eta_{APCE} = \eta_{IPCE} / A_{GaP}$.

For the Mott-Schottky measurements, the capacitance of the semiconductorelectrolyte interface was collected at 500Hz, with 10 mV AC voltage amplitude, in the same setup for *I-V* measurement.

To measure the Faradic efficiency of the photoelectrode, the electrochemical cell was sealed as a batch reactor and connected to an online gas chromatograph (GC, SRI Instrument Inc.) via a gas circulation pump (Micropump Inc.). The GC was equipped with a molecular sieve 13X packed column and a helium ionization detector. During the measurement at constant bias (0.1 V vs. RHE), the photocurrent was measured under simulated one-sun illumination (AM 1.5G). The amount of evolved hydrogen gas was measured after 24 h operation. Faradic efficiency was calculated based on the amount of hydrogen gas evolved and the amount of charge passed through the electrode. Part B. Supplementary Figures.



Supporting Figure 1. TEM images of GaP nanowires of varying diameters. Tapering of the nanowires is more prominent as the diameter increases, along with increased polydispersity of the Ga seeds and GaP nanowires (~20% standard deviation).



Supporting Figure 2. IPCE and APCE spectra of both planar and nanowire GaP photocathodes. The GaP nanowires used here were doped with 0.98 at% Zn vs. Ga, and the spectra were measured at 0.1 V vs. RHE under simulated one-sun conditions (AM1.5G).



Supporting Figure 3. SEM image of a Zn-doped GaP nanowire photoelectrode with 5.4 μ g/cm² nanowire loading amount, indicating that the photoelectrode at this loading amount contains less than a monolayer of GaP nanowires.

References:

1. Sun, J.; Liu, C.; Yang, P., Surfactant-Free, Large-Scale, Solution-Liquid-Solid Growth of Gallium Phosphide Nanowires and Their Use for Visible-Light-Driven Hydrogen Production from Water Reduction. *J. Am. Chem. Soc.* **2011**, *133* (48), 19306-19309.

2. Gargas, D. J.; Gao, H.; Wang, H.; Yang, P., High Quantum Efficiency of Band-Edge Emission from ZnO Nanowires. *Nano Lett.* **2011**, *11* (9), 3792-3796.