Supporting Information for:

**Surfactant-Free, Large-Scale, Solution-Liquid-Solid (SLS) Growth of Gallium Phosphide Nanowires and Their Use for Visible-Light-Driven Hydrogen Production from Water Reduction**

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Experimental details:

**Chemicals.** Triethylgallium (TEG, min. 97%, Strem), tris(trimethylsilyl)phosphine (TMSP, min. 98%, Strem), squalane (99%, Aldrich), tri-\(n\)-octylphosphine oxide (TOPO, 99%, Aldrich), toluene (99.9%, Fisher), methanol (99.9%, Fisher), hydrochloric acid (1 M volumetric solution, J. T. Baker) were purchased and used as received for the syntheses and purification of GaP nanowires. Water (ultrapure, spectrophotometric grade, Alfa Aesar) and methanol (≥ 99.9%, spectrophotometric grade, Sigma-Aldrich) were purchased and used as received for the photocatalytic water reduction measurements using gas chromatography.

**Preparation of a stock 0.15 mmol/g TEG-TMSP solution.** Squalane was degassed and dried at ~140 °C under vacuum for ~ 2 h and stored in a glove box filled with dry N\(_2\). The precursor TEG-TMSP solution was prepared in the glove box by mixing TEG (2.354 g, 15 mmol) with TMSP (3.758 g, 15 mmol), followed by adding squalane (93.888 g). When TEG was mixed with TMSP, white precipitate was observed immediately, indicating that a TEG-TMSP adduct was formed. Under continuous stirring of the mixture, the white precipitate dissolved in squalane to form a clear solution, which was stored in the glove box for use.

**Synthesis of GaP nanowires in squalane.** All procedures were conducted under dry N\(_2\) using standard Schlenk technique. In a typical preparation, squalane (150 ml) was loaded into a reaction flask, degassed and dried at ~100 °C under vacuum. After back-filled with dry N\(_2\), the flask was inserted into a preheated salt bath (NaNO\(_3\)/KNO\(_3\), 46/54 by weight) at 290 °C. The reaction mixture was allowed to equilibrate to the salt bath temperature for at least 30 min. Then the TEG-TMSP stock solution (5 g) was transferred into a syringe and quickly injected into the flask under vigorous stirring (800 rpm). After 30 s, stirring was stopped and the color of the reaction mixture changed to yellow at ~45-50 s, indicating formation of Ga nanoparticles, and
then quickly to brown as the nanowires grew. The reaction flask was withdrawn from the salt bath 15 min after the precursor injection and allowed to cool.

**Isolation and purification of GaP nanowires.** The GaP nanowires were separated from the reaction mixture by centrifugation (6000 rpm). The precipitated wires were redispersed in toluene (~100 mL), sonicated for a few minutes, and recollected by centrifugation (6000 rpm). This step was repeated 5 times to remove unreacted precursors, by-products, and squalane. The recollected wires were redispersed in toluene (~200 mL) and filtered through a PVDF filter membrane (pore size 0.22 μm), followed by washing with methanol (~250 mL) and DI water (~250 mL) and drying under ambient conditions.

**Removal of Ga nanoparticles.** The purified GaP nanowires having Ga nanoparticle tips were dispersed in 1 M hydrochloric acid (~25 mL). The mixture was stirred for 5 h with occasional sonication. During this process, bubbles were observed due to hydrogen generation by the reaction between Ga nanoparticles and hydrochloric acid. Along with time, the wires aggregated and precipitated. After 5 h, the precipitate was collected by centrifugation (2000 rpm). The collected wires were dispersed in DI water (~25 mL), sonicated for a few minutes, and recollected by centrifugation (2000 rpm). This step was repeated a few times until the wires could be well dispersed in DI water. Then the recollected wires were redispersed in DI water (~200 mL). Any wires that floated on the water surface were removed. The aqueous dispersion of GaP nanowires was then filtered through a PVDF filter membrane (pore size 0.22 μm), followed by washing with DI water (~1 L) and drying under ambient conditions.
**Figure S1.** Representative TEM image of GaP nanowires synthesized using a surfactant-free self-seeded SLS method at unoptimized conditions.
**Figure S2.** TEM image of a whole GaP nanowire with a Ga nanoparticle tip, showing that the wire is tapered at the nanoparticle-free end.
Figure S3. Pt 4f X-ray photoelectron spectrum of Pt-loaded (2 wt.% ) GaP nanowires.