

GaP/GaPN core/shell nanowire array on silicon for enhanced photoelectrochemical hydrogen production

Guancai Xie ^{a,b,†}, Saad Ullah Jan ^{a,b,†}, Zejian Dong ^{a,b}, Yawen Dai ^{a,b}, Rajender Boddula ^a, Yuxuan Wei ^{a,b}, Chang Zhao ^{a,b}, Qi Xin ^a, Jiao-Na Wang ^c, Yinfang Du ^c, Lan Ma ^c, Beidou Guo ^{a,b,#}, Jian Ru Gong ^{a,b,*}

^a Chinese Academy of Sciences (CAS) Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchy Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China

^b University of CAS, Beijing 100049, China

^c Beijing Institute of Fashion Technology, Beijing 100029, China

* Corresponding author. Tel: +86-10-82545649; Fax: +86-10-62656765; E-mail: gongjr@nanoctr.cn

Corresponding author. Tel: +86-10-82545649; Fax: +86-10-62656765; E-mail: guobd@nanoctr.cn

[†] These authors contributed equally to this paper.

I. Growth of GaP NWs on the p-Si substrate (p-Si-NW)

The boron doped p-Si (100) substrates with resistivity of 0.2–0.8 Ω cm were cut into small slices of the size of 1 cm \times 1 cm and washed thoroughly through sonication in acetone, isopropyl alcohol, and water for 15 min in each solvent. After blow-drying with N₂ gas, Si substrates were transferred into an ion sputtering instrument (Hitachi E-101 Ion sputter). Au NPs (~25 nm) (Fig. S1) were sputtered on the Si substrates to form a thin layer at a working current of ~10 mA for duration of 30 s.

GaP (99.99% metal basis, Aladdin) was grinded to powder and used as a precursor without further treatment or purification. About 15 mg of GaP was loaded in the upstream (center of Zone 1) while the Au coated p-Si (100) substrate was mounted ~21.5 cm downstream to the precursor boat. High purity Ar was used as a carrier gas to transport the evaporated precursor to the substrate. Zone 1 was heated to 950 °C at an average rate of 38 °C per minute and then kept at this temperature for the next 30 min while Zone 2 was heated to 630 °C at an average rate of 42 °C per minute and maintained for 45 min. Prior to heating, O₂ was purged out by Ar flow at 500 sccm for several minutes. The carrier gas was reduced to 100 sccm when the temperature of Zone 1 reached 600 °C, and kept it until the furnace cooldown to room temperature (Fig. S2).

II. Remove the Au NP before annealing in NH₃

The Au catalyst NP on the top of each NW was removed by immersing the sample into the gold etching solution, which was prepared by dissolving 4 g of KI and 1 g of I₂ in 40 mL deionized water followed by addition of 4.5 mL HCl for better etching result. After removal of the Au NPs from NW tips, the sample was rinsed with deionized water and blow-dried with N₂ gas.

The reason for the Au NP removal was that samples with the Au NP lead to the formation of cotton-like structure (Fig. S3 (d)) at the top of NWs upon annealing in the NH₃ atmosphere.

The XRD data peaks (Fig. S4, green line) show the appearance of extra peaks labeled with steric (*) related to the GaN (PDF#50-0792) which is absent in the XRD data (Fig. S4, blue line) of the Au etched samples. From these results it is concluded that the absorbed Ga in the Au NP during the crystallization of the NWs through VLS mechanism, upon annealing in the N rich environment at high temperature reacts with the N leading to the formation of GaN.

Annealing of GaP NWs sample in NH₃ environment

The as synthesized sample (p-Si-NW) was positioned in the center of Zone 1 and heated the furnace up to 750 °C at an average rate of 38 °C per minute. The furnace was evacuated with the aid of Ar gas having a flow rate of 500 sccm. After furnace evacuation the Ar flow was stopped while continuous supply of NH₃ gas as a source of N was started and maintained till the reaction was completed. The flow of NH₃ was immediately stopped upon the reaction completion while opening the Ar gas flow to keep the sample under inert environment inside the furnace (Fig. S5). Once the furnace cools down to room temperature naturally, the sample was brought out for further analysis.

Since the p-Si-cs-NW photocathode showed a high limited current compared to p-Si, its stability was tested at voltage -0.7 V versus RHE on which the J-V curve reaches the saturation current density (Fig. S9). As in this case the GaPN is acting as a protective layer [S1] so the p-Si-cs-NW photocathode was found very stable for a long period of time. Initially the fluctuation in photocurrent was caused by accumulation of hydrogen gas bubbles on the surface of photocathode and its sequential sudden release. Surprisingly, shortly after starting the stability test, the photocurrent of the p-Si-cs-NW increases to approximately -17 mA cm⁻², and shows no obvious decrease in 10 h. Based on the literature [S2], we suspect the influence of the Pt counter electrode in the PEC system. Since all the related lit works have been using Pt as the counter electrode, it will be difficult to compare with other reported results if other counter electrode materials are used. A detailed investigation of the electrode stability and addition

of suitable electrocatalysts are still under process.

III. Photoelectrode fabrication

The backside of the Si substrate was scratched with a diamond scribe to remove the native thick SiO₂ layer and an ohmic contact was formed by embedding a Cu wire in a Ga/In eutectic alloy onto the scratched Si surface. After drying, the Cu lead was passed into a nylon tube, and the Si electrode and Cu wire were encased in silica gel (Type 704, Nanda).

IV. Characterization of samples

The morphology of the samples were studied by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) at 10 kV accelerating voltage. A field-emission transmission electron microscope (FEI Technai F20) operated at 200 kV was used to capture TEM images and EDS elemental mapping images. X-ray diffraction (XRD) patterns were recorded using X'pert Powder diffractometer with working voltage of 40 kV and 40 mA current. Raman spectra were recorded on a Renishaw InVia Plus laser Raman spectrometer at room temperature using the 514 nm line of an Ar⁺-ion laser as the excitation source. X-ray photoelectron spectra (XPS) spectra measurements were carried out using (Thermo Scientific Escalab 167 250Xi) in an ultrahigh vacuum which was equipped with a multi-channel detector. Ultraviolet-visible (UV-Vis) transmittance and reflectance spectra were recorded

using a UV-Vis spectrophotometer (UV-2600) equipped with an external diffuse reflectance accessory (DRA-2500). The absorption (A) was calculated through formula $A=1-T-R$, where T is the total transmittance and R is the total reflectance.

V. Electrochemical Measurements

Electrochemical measurements of the fabricated electrode were performed in a three-electrode cell configuration using HClO₄ (1mol L⁻¹, pH≈0) as an electrolyte. The Pt foil was used as a counter electrode while Ag/AgCl as a reference electrode. A home-made electrochemical cell was used for all of the electrochemical measurements. During the measurement, the electrolyte was agitated with a magnetic stir bar driven by a magnetic stirring apparatus. I-V and stability test were carried out using an electrochemical workstation (Zahner Zennium, Germany). For the current density-potential (J-V) plots, the photocathodes were scanned at 11 mV s⁻¹ between -1500 mV and -200 mV vs. the saturated Ag/AgCl electrode and illuminated with standard simulated AM 1.5G sunlight (100 mW cm⁻²), which was generated from a 500 W Xenon lamp and filtered by an AM 1.5G filter (CEL-S500, Aulight, Beijing, China). For the IPCE test, the same three-electrode configuration was illuminated under a 150 W xenon lamp (Crowntech., CT-XE-150). A Si photodiode with known IPCEs was also test as reference. A source meter (Keithley 2400) was used to measure the photocurrents of the Si photodiode and the photocathodes.

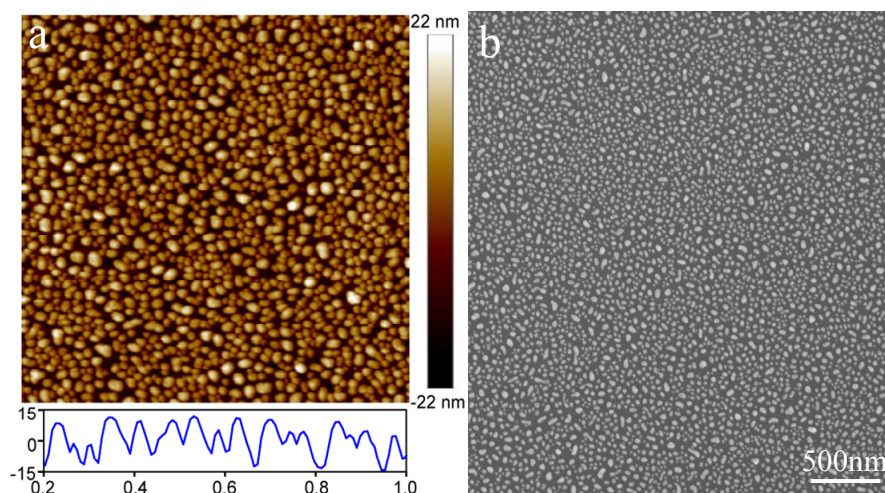


Fig. S1. (a) AFM and (b) SEM image of Au NPs.

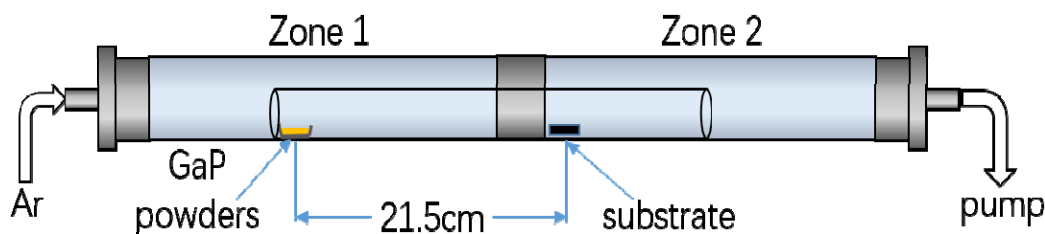


Fig. S2. Schematic diagram of the GaP NW growth setup.

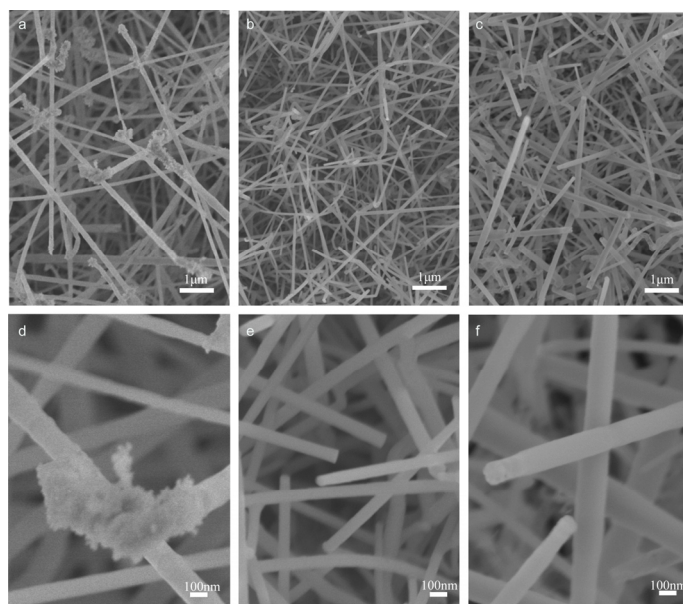


Fig. S3. (a) p-Si-cs-NW without removing Au NP. (b) p-Si-NWs after removing Au NP. (c) p-Si-cs-NW after removing Au NP. (d-f) Magnified images of the area in the rectangle of (a-c), respectively.

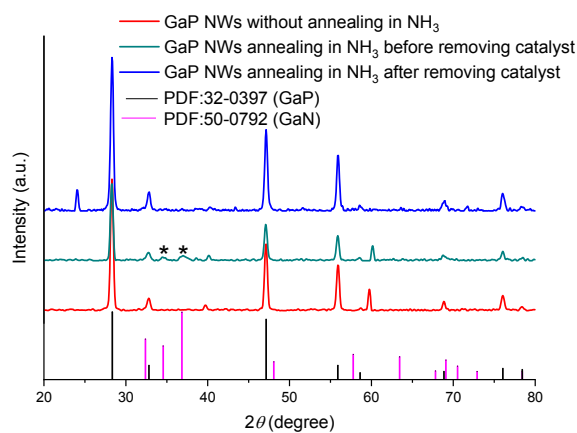


Fig. S4. XRD data of samples under different synthesis conditions.

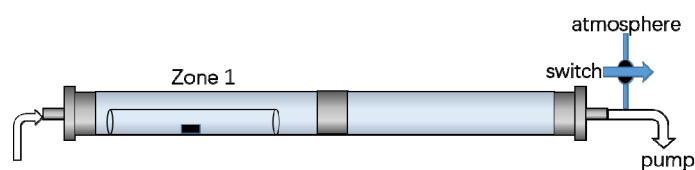


Fig. S5. Schematic diagram of the NH_3 annealing step.

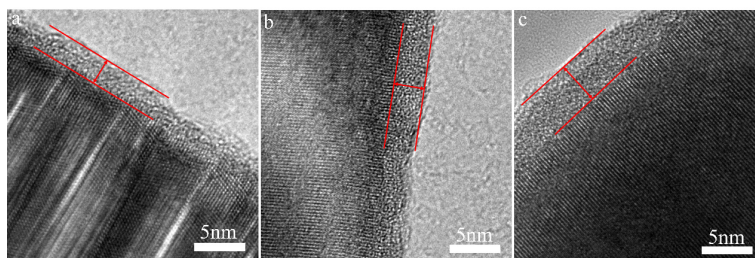


Fig. S6. HRTEM images of p-Si-cs-NWs annealed in NH_3 for (a) 1 h, (b) 2 h, (c) 4 h with respective thickness of 2.7, 3.01, and 4.2 nm.

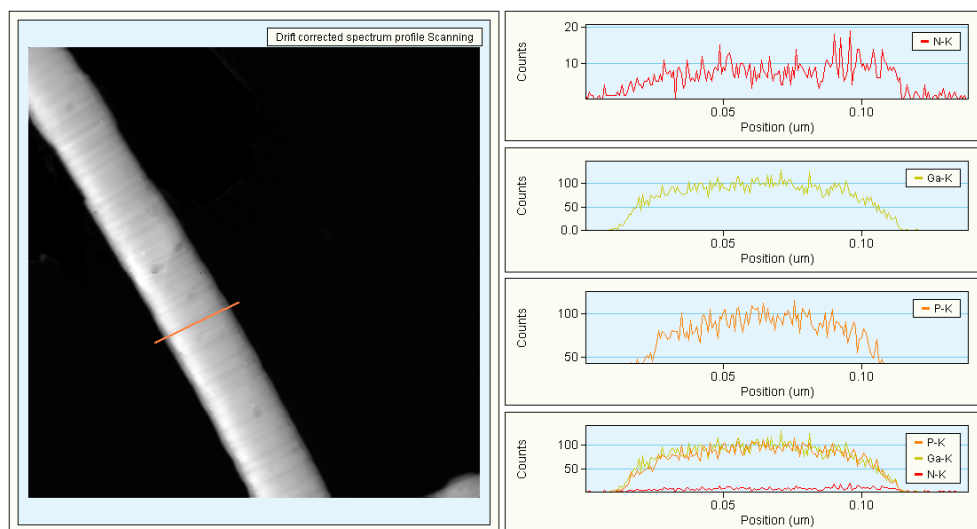


Fig. S7. EDS line scan of p-Si-cs-NW.

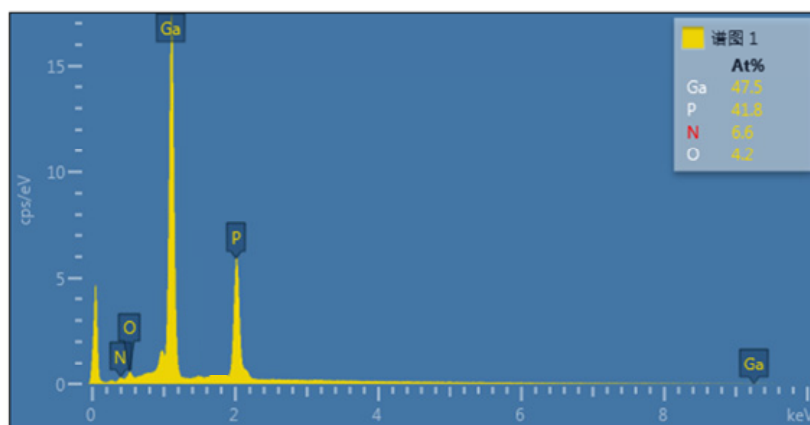


Fig. S8. EDX spectrum of the p-Si-cs-NWs.

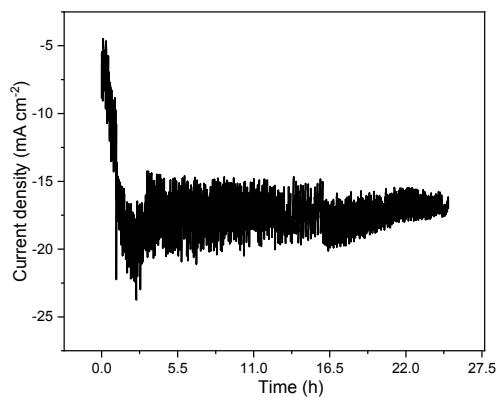


Fig. S9. Stability test of the p-Si-cs-NWs.

References

- [1] T. G. Deutsch, C. A. Koval, J. A. Turner, *J. Phys. Chem. B*, **2006**, 110, 25297–25307.
- [2] R. Wei, M. Fang, G. Dong, J. C. Ho, *Sci. Bull.*, **2017**, 62, 971–973.