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**GaP/GaN<sub>P</sub> Heterojunctions for Efficient Solar-Driven Water Oxidation**

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We report the growth and characterization of an n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction synthesized using a gas-source molecular beam epitaxy (MBE) method, and its application for efficient solar-driven water oxidation. Although n-GaP can be a promising material for the solar water oxidation due to its bandgap, it cannot provide a high-efficiency performance due to its indirect bandgap and low absorption coefficient. Herein, a direct bandgap semiconductor with a high absorption coefficient is made by adding a small amount of N to GaP to result in GaNP, which also exhibits a smaller bandgap. Making a heterojunction of GaP/GaNP with a buried junction on the top, the TiO<sub>2</sub>/Ni passivated n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction provides much higher photoanodic performance in 1 M KOH solution than the TiO<sub>2</sub>/Ni-coated n-GaP substrate, leading to much lower onset potential and much higher photocurrent. There is a significant photoanodic potential shift of 764 mV at a photocurrent of 0.34 mA/cm<sup>2</sup>, leading to an onset potential of ~0.4 V versus reversible hydrogen electrode (RHE) at 0.34 mA/cm<sup>2</sup> for the heterojunction. The photocurrent at the water oxidation potential (1.23 V versus RHE) is 1.46 and 7.26 mA/cm<sup>2</sup> for the coated n-GaP

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and n-GaP/i-GaNP/p<sup>+</sup>-GaP photoanodes, respectively. The passivated heterojunction offers a maximum applied bias photon-to-current efficiency (ABPE) of 1.9% while the ABPE of the coated n-GaP sample is almost zero. Furthermore, the coated n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction photoanode provides a broad absorption spectrum up to ~620 nm with incident photon-to-current efficiencies (IPCEs) of over 40% from ~400 nm to ~560 nm. The high low-bias performance and broad absorption of the wide-bandgap GaP/GaNP heterojunctions render them as a promising photoanode material for tandem photoelectrochemical (PEC) cells to carry out overall solar water splitting.

Hydrogen, a clean and sustainable energy carrier, is considered as a promising approach to meet the growing energy demands.<sup>[1-3]</sup> A promising method for the production of hydrogen is solar-driven water splitting using photoelectrochemical (PEC) cells,<sup>[4-9]</sup> which can offer high solar-to-hydrogen (STH) efficiencies of over 28%.<sup>[10]</sup> A key step in the PEC cells is solar-driven oxidation of water to oxygen. In fact, the solar water oxidation is more challenging than the solar water reduction due to the nature of its reaction and the fact that it requires four electron transfer steps compared to two electron transfer steps needed for the water reduction. The low STH efficiency of the reported tandem PEC cells for overall solar water splitting is mainly due to inefficient photoanodes, which are unable to offer high solar water oxidation performance at low biasing potentials with a low onset potential and a high photocurrent.<sup>[11-15]</sup> As such, developing photoanodes with high performance at low biasing potentials is necessary to make efficient tandem PEC cells for high-efficiency solar hydrogen production.

Protected III-V photoanode materials have shown promising performances for the solar water oxidation owing to their unique properties.<sup>[9, 16-19]</sup> In particular, n-GaP with a bandgap of 2.26 eV can be a promising photoanode material.<sup>[16, 20, 21]</sup> GaP has a proper bandgap to provide a high photovoltage, a relatively suitable energy band alignment for the solar water oxidation,<sup>[1]</sup> and a high carrier mobility.<sup>[22, 23]</sup> Additionally, GaP is a mature semiconductor material widely used in light emitting diodes (LEDs).<sup>[24, 25]</sup> P-GaP is considered as one of the most promising photocathode materials for the solar-driven water reduction due to its high conduction band edge and its large photovoltage.<sup>[26-32]</sup> However, n-GaP with an indirect bandgap and a low absorption coefficient (absorption coefficient in the range of  $10^2$ - $10^3$  cm<sup>-1</sup> above the band edge)<sup>[33]</sup> cannot provide a high-efficiency solar water oxidation performance.<sup>[16]</sup> A direct bandgap semiconductor with a tunable bandgap and an absorption coefficient of around  $10^4$  cm<sup>-1</sup> above the band edge can be made by adding a small amount of N to GaP to result in gallium nitride phosphide, GaNP.<sup>[34, 35]</sup> Moreover, formation of a GaP p-n junction within the photoanode material can increase the photovoltage assisting to further improve the solar conversion efficiency.<sup>[36]</sup>

Herein, we report a novel GaP photoanode material; n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction, consisting of direct bandgap GaNP with a smaller bandgap on the top of GaP forming a GaP/GaNP heterojunction and a buried top junction, fabricated using a gas-source molecular beam epitaxy (MBE) technique for efficient solar water oxidation. The morphology and structure of the n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction is characterized in detail using scanning and transmission electron microscopies. The TiO<sub>2</sub>/Ni passivated n-

GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction provides much higher photoanodic performance in 1 M KOH electrolyte than the TiO<sub>2</sub>/Ni-coated n-GaP substrate, resulting in much lower onset potential and much higher photocurrent. The coated heterojunction provides a maximum applied bias photon-to-current efficiency (ABPE) of 1.9% while the passivated n-GaP ABPE is nearly zero. The coated n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction photoanode also offers a wide absorption spectrum. The mechanism of performance improvement is studied using optical absorption property and energy band diagram.

**Figure 1a** shows a schematic representation of the n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction substrate in which an i-GaNP layer with a thickness of 800 nm and a top p<sup>+</sup>-GaP layer with a thickness of 100 nm were grown on the n-GaP planar substrate (see Experimental Section for the details). Scanning electron microscopy (SEM) image (Figure 1b) exhibits the uniform growth of i-GaNP layer on the n-GaP substrate. The boundary between the n-GaP substrate and i-GaNP layer can clearly be realized from the contrast change shown in Figure 1c.

Transmission electron microscopy (TEM) images of the n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrate is shown in Figure 1d-k. The low-magnification cross-sectional TEM images (Figure 1d and e) exhibit the stacking of three layers in which the boundary between n-GaP and i-GaNP can clearly be realized (Figure 1d) as also shown in Figure 1c. The interface between n-GaP and i-GaNP is a defective interface (as can be seen from the clearly visible defect contrast at the interface in Figure 1d) with misfit defects leading to misfit dislocation.<sup>[34]</sup> The

boundary between i-GaNP and p<sup>+</sup>-GaP is hard to clearly observe (Figure 1e) possibly due to a very small lattice mismatch, which will be discussed in the following. The grown i-GaNP and p<sup>+</sup>-GaP layers are single crystalline as shown in high-resolution TEM (HRTEM) images (Figure 1f and g) revealing formation of epitaxial layers. The single crystallinity further confirms with the fast Fourier transform (FFT) pattern (insets of Figure 1f and g), which also indicates a growth direction of [001]. There is a very small difference in the calculated lattice spacing of i-GaNP and p<sup>+</sup>-GaP layers (0.312 nm versus 0.314 nm (Figure 1f and g)) indicating a minimal lattice mismatch. The minimal lattice mismatch is due to the incorporation of a small amount of N into the GaP ([N] ~ 1.8%<sup>[34]</sup>). The crystal structure, however, remains unchanged with such a small incorporation of N (see Figure S1). The energy dispersive X-ray spectroscopy (EDS) spectrum (Figure 1h) confirms the formation of GaNP with a small amount of N. The surface structure of the n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrate is rough exhibiting a textured surface with a texture size of several nanometers (Figure 1i-k). The facets of such a rough surface are identified and shown in Figure S2. The reason for the formation of rough surface is not totally clear at this point though it may be due to post-growth heating or introduction of dopants. High temperature of the growth may be another reason for the formation of GaP rough surface.<sup>[37]</sup>

**Figure 2** exhibits the optical absorption spectra of the n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrates in which the n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction shows higher absorption than the n-GaP. For wavelengths below ~525 nm, the difference in the optical absorption is not that significant (Figure 2 inset) while for higher wavelengths, the

difference is much higher. For wavelengths below  $\sim 525$  nm, the higher absorption may be due to the textured surface of the n-GaP/i-GaNP/p<sup>+</sup>-GaP substrate (Figure 1i-k), and for higher wavelengths, it can be mostly because of the GaNP layer with a smaller bandgap ( $\sim 2.05$  eV<sup>[34]</sup>) absorbing a broader spectrum (see Figure 3e).

The n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction sample is not stable during the PEC operation. Its surface was then passivated with a thin atomic layer-deposited TiO<sub>2</sub> layer accompanied with a Ni nanoparticle cocatalyst coating (see Experimental Section for the details). The PEC performance (linear sweep voltammetry (LSV) measurement) of the TiO<sub>2</sub>/Ni-coated n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP photoanodes in 1 M KOH solution is shown in **Figure 3a** (see Figure S3 for cyclic voltammetry (CV) measurement) in which the n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction exhibits much higher photoanodic performance than the n-GaP substrate resulting in a much lower onset potential and a much higher photocurrent. There is a significant potential shift of 764 mV at a photocurrent of 0.34 mA/cm<sup>2</sup>. The onset potential of the heterojunction is  $\sim 0.4$  V versus reversible hydrogen electrode (RHE) at the 0.34 mA/cm<sup>2</sup> photocurrent. The photocurrent at 1.23 V versus RHE (equilibrium potential for the water oxidation; the dotted line in Figure 3a) is 1.46 and 7.26 mA/cm<sup>2</sup> for the TiO<sub>2</sub>/Ni-coated n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP photoanodes, respectively. The saturation photocurrent of the n-GaP/i-GaNP/p<sup>+</sup>-GaP sample is over one and a half times larger than that of the n-GaP sample. The dark current of both samples is around zero. The enhanced photoanodic performance of the n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction is due to (i) broader absorption spectrum (see Figure 3e), (ii) enhanced charge separation and collection (see Figure 3b), (iii)

increased reaction surface area coming from the textured surface discussed earlier, and (iv) improved optical absorption (as shown in Figure 2). As shown in the energy band diagram (Figure 3b), the i-GaNP layer forms a junction with the n-GaP substrate and there is a junction between the i-GaNP and p<sup>+</sup>-GaP layers. Due to a very low doping of the i-GaNP layer (around 10<sup>15</sup> cm<sup>-3</sup>), the depletion layer extends across its whole width. Although there is a very small barrier for the holes in the i-GaNP/p<sup>+</sup>-GaP junction (Figure 3c), the holes can thermionically be emitted and eventually transport into the electrolyte. As a result of the two junctions, the charge separation significantly improves. The separated charges then collect efficiently through the grown thin i-GaNP and p<sup>+</sup>-GaP layers. The energy band diagram of the TiO<sub>2</sub>-coated n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP substrates is shown in Figure S4, highlighting the significant effect of the heterojunction in the enhanced charge separation and collection compared to that of the bare n-GaP. Low-bias performance (onset potential and photocurrent at low biasing potentials) of the n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction can further be improved by using a nanostructure morphology such as nanodome array.<sup>[38]</sup> The TiO<sub>2</sub>/Ni-coated n-GaP/i-GaNP/p<sup>+</sup>-GaP sample offers a maximum ABPE of 1.9% while the ABPE of the TiO<sub>2</sub>/Ni-coated n-GaP sample is almost zero (Figure 3d).

The incident photon-to-current efficiency (IPCE) of the TiO<sub>2</sub>/Ni-coated n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP samples at 1.4 V versus RHE is shown in Figure 3e. The n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction provides a broader spectrum up to around 620 nm while the n-GaP substrate only covers up to around 520 nm. The wider spectrum is due to the i-GaNP



layer with a smaller bandgap ( $\sim 2.05$  eV). The n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction offers efficiencies of over 40% from around 400 nm to around 560 nm, while the n-GaP substrate provides comparable efficiencies from about 340 nm to around 440 nm. The high efficiencies of both samples are comparable confirming the small optical absorption improvement of the n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction (Figure 2).

In conclusion, we demonstrated the growth and characterization of the n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction fabricated using the gas-source MBE, and its application for efficient solar-driven water oxidation. The epitaxially-grown i-GaNP and p<sup>+</sup>-GaP layers were single crystalline with a minimal lattice mismatch. The TiO<sub>2</sub>/Ni-passivated n-GaP/i-GaNP/p<sup>+</sup>-GaP heterojunction photoanode provided much higher PEC performance than the TiO<sub>2</sub>/Ni-coated n-GaP substrate in 1 M KOH electrolyte, resulting in a significant potential shift of 764 mV at a photocurrent of 0.34 mA/cm<sup>2</sup> (onset potential of  $\sim 0.4$  V versus RHE at 0.34 mA/cm<sup>2</sup> for the heterojunction) and a high photocurrent of 7.26 mA/cm<sup>2</sup> at 1.23 V versus RHE. The passivated heterojunction offers a maximum ABPE of 1.9%. Moreover, the coated n-GaP/i-GaNP/p<sup>+</sup>-GaP photoanode offered a wide absorption spectrum up to  $\sim 620$  nm with the IPCEs of over 40% from  $\sim 400$  nm to  $\sim 560$  nm. The high low-bias performance and broad absorption of the coated wide-bandgap GaP/GaNP heterojunctions reveal their promising application for the tandem PEC cells to handle overall solar-driven water splitting in an alkaline electrolyte.

## Experimental Section

*Fabrication of TiO<sub>2</sub>/Ni-coated n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP samples:* All the samples reported in this work were grown on n-type ( $6 \times 10^{17} \text{ cm}^{-3}$ ) GaP (001) substrate using a Varian Gen-II molecular beam epitaxy (MBE) system modified to handle gas sources. Thermally cracked PH<sub>3</sub> at 1000°C and radio frequency (RF) N plasma excited at 13.56 MHz were used as P and N sources, respectively. Solid elemental Ga from an effusion cell was used to generate a Ga beam. Prior to the growth, the native oxide was desorbed under P<sub>2</sub> overpressure at 600°C. The substrate temperature was then decreased to 570°C to grow an 800 nm i-GaNP layer. A substrate temperature of 570°C was chosen because it is in the optimal growth temperature range to minimize N-related defects before phase separation in dilute nitride. The following layer was 100 nm p<sup>+</sup>-GaP ( $2 \times 10^{18} \text{ cm}^{-3}$ ) using B as the dopant. All the layers were grown at a rate of 1 μm/h with a V/III incorporation ratio of ~2.5, calibrated by Ga-induced reflection high energy electron diffraction (RHEED) intensity oscillation. The substrate was rotated at 5 RPM during the growth to ensure uniformity.

Bare n-GaP substrates were dipped into aqueous HCl solution (50% v/v) for 30 sec, rinsed with deionized (DI) water, dried with N<sub>2</sub> gas, and transferred to atomic layer deposition (ALD) chamber (Beneq TFS 200 system) along with the n-GaP/i-GaNP/p<sup>+</sup>-GaP substrates. Note that we did not perform any cleaning for the n-GaP/i-GaNP/p<sup>+</sup>-GaP substrates right before the ALD deposition. A thin TiO<sub>2</sub> layer was then deposited on the substrates using ALD in thermal mode (thermal ALD) at a temperature of 300°C. The number of cycles was 440 giving a thickness of ~20 nm based on a growth rate of 0.454 Å/cycle on planar Si substrate. Note that our applied ALD TiO<sub>2</sub> coating is not the best developed ALD TiO<sub>2</sub> coating for the long-term stability and better coating has been reported elsewhere.<sup>[16]</sup> E-beam evaporation was finally used to deposit nominally 2 nm Ni on the TiO<sub>2</sub>-coated substrates. Samples were then stored before any characterization.

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*Characterization:* Sample morphology was examined using an ultra-high-resolution scanning electron microscopy (UHR SEM, FEI XL30-SFEG) working at an accelerating voltage of 15 kV. A high resolution transmission electron microscopy (JEOL JEM3011, HRTEM) operated at 300 kV was employed for the atomic-scale structural analyses. Energy dispersive X-ray spectroscopy (EDS) was carried out to obtain the elemental information. Cross-sectional thin film specimens for the TEM and HRTEM imagings were prepared by mechanical polishing. Thin films were first glued to the sacrificial silicon with M-Bond 610 (Vishay Precision Group). Then, a single cut piece was placed on a wedge-polishing tool (T-tools, Precision TEM, Inc.), thinned, and fine-polished against diamond lapping papers (Southbay Technology, Inc.) of varying grit sizes before being glued with a molybdenum ring (Structure Probe, Inc.) with M-Bond 610 epoxy. The polished cross-sectional pieces were then ion-milled under Ar gas for polishing using a Precision Ion Polishing System (Gatan model 695). The ion milling stops as the hole formed in silicon upon fine thinning reaches the film side.

Optical absorption measurements were achieved using a 150 mm integrating sphere connected to a LAMBDA 1050 UV/Vis/NIR spectrophotometer. The absorption ( $A$ ) was calculated using  $A(\%) = 100 - R - T(\%)$ , in which  $R$  is reflectance and  $T$  is transmittance. Energy band diagram was simulated using SCAPS (version 3.1.02) numerical simulation software. The considered thickness of the n-GaP, i-GaNP, and p<sup>+</sup>-GaP layers were 1  $\mu\text{m}$ , 800 nm, and 100 nm, respectively. The doping concentration of the n-GaP, i-GaNP, and p<sup>+</sup>-GaP layers were considered as  $10^{17}$ ,  $10^{15}$  and  $10^{18} \text{ cm}^{-3}$ , respectively. The bandgap of n-GaP, i-GaNP, and p<sup>+</sup>-GaP layers were considered as 2.26, 2.05, and 2.26 eV, respectively.<sup>[34]</sup>

*Photoelectrochemical (PEC) and IPCE measurements:* Ohmic contact was made to the GaP backside by scratching the backside with a diamond tip scribe, soldering indium on the back, annealing the

sample at 400°C for 10 mins under forming gas, and finally attaching a coated Cu wire to the annealed contact with another indium soldering. The backside and edges of sample were then sealed using a Hysol 615 epoxy. Current density measurements were carried out in an aqueous solution of 1 M KOH (Fisher Chemical, 88.5%) at pH = 13.7 (DI water resistivity; 18.2 MΩ-cm) with a three-electrode configuration, including sample as working electrode (WE), Pt gauze as counter electrode (CE), and Hg/HgO (1 M NaOH) or Ag/AgCl (1 M KCl) as reference electrode (RE). A light power intensity of 100 mW/cm<sup>2</sup> was adjusted at the sample position using a solar simulator (Newport 66905) with a xenon lamp equipped with the 1.5 AM filter. The current density measurements were collected using a potentiostat (Digi-Ivy, DY2300). A scan rate of 10 mV/s was employed for the linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements. During the measurements, a mild agitation was used and the electrolyte was constantly purged with a small flow of N<sub>2</sub> gas. The electrolyte was also purged with N<sub>2</sub> flow for about 30 mins before the measurements. The applied potentials versus Hg/HgO ( $E_{\text{Hg/HgO}}$ ) or Ag/AgCl ( $E_{\text{Ag/AgCl}}$ ) RE were converted to the potentials versus reversible hydrogen electrode (RHE),  $E_{\text{RHE}}$ , using the Nernst equation as;

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098 \quad (\text{V}) \quad (1)$$

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.222 \quad (\text{V}) \quad (2)$$

where pH is the electrolyte pH. Applied bias photon-to-current efficiency (ABPE) is calculated using;<sup>[39]</sup>

$$\text{ABPE (\%)} = \frac{(J_{\text{light}} - J_{\text{dark}}) \times (1.23 - E_{\text{RHE}})}{P_{\text{light}}} \times 100\% \quad (3)$$

where  $J_{\text{light}}$  and  $J_{\text{dark}}$  are the measured current density ( $\text{mA}/\text{cm}^2$ ) under illumination and at dark, respectively at each biasing potential (Figure 3a),  $E_{\text{RHE}}$  is the applied potential (V) versus RHE, and  $P_{\text{light}}$  is the incident light power density ( $\text{mW}/\text{cm}^2$ ) (which is  $100 \text{ mW}/\text{cm}^2$  here). A monochromator (Cornerstone 260) equipped with the solar simulator with the 1.5 AM filter as the light source was used to perform the spectral photoresponse and IPCE measurements. The monochromatic light spectrum was calibrated by a silicon photodiode (Newport 818-UV). Spectral photoresponse and IPCE measurements were carried out in the same three-electrode setup and electrolyte used for the current density measurements without using agitation and  $\text{N}_2$  purging during the tests.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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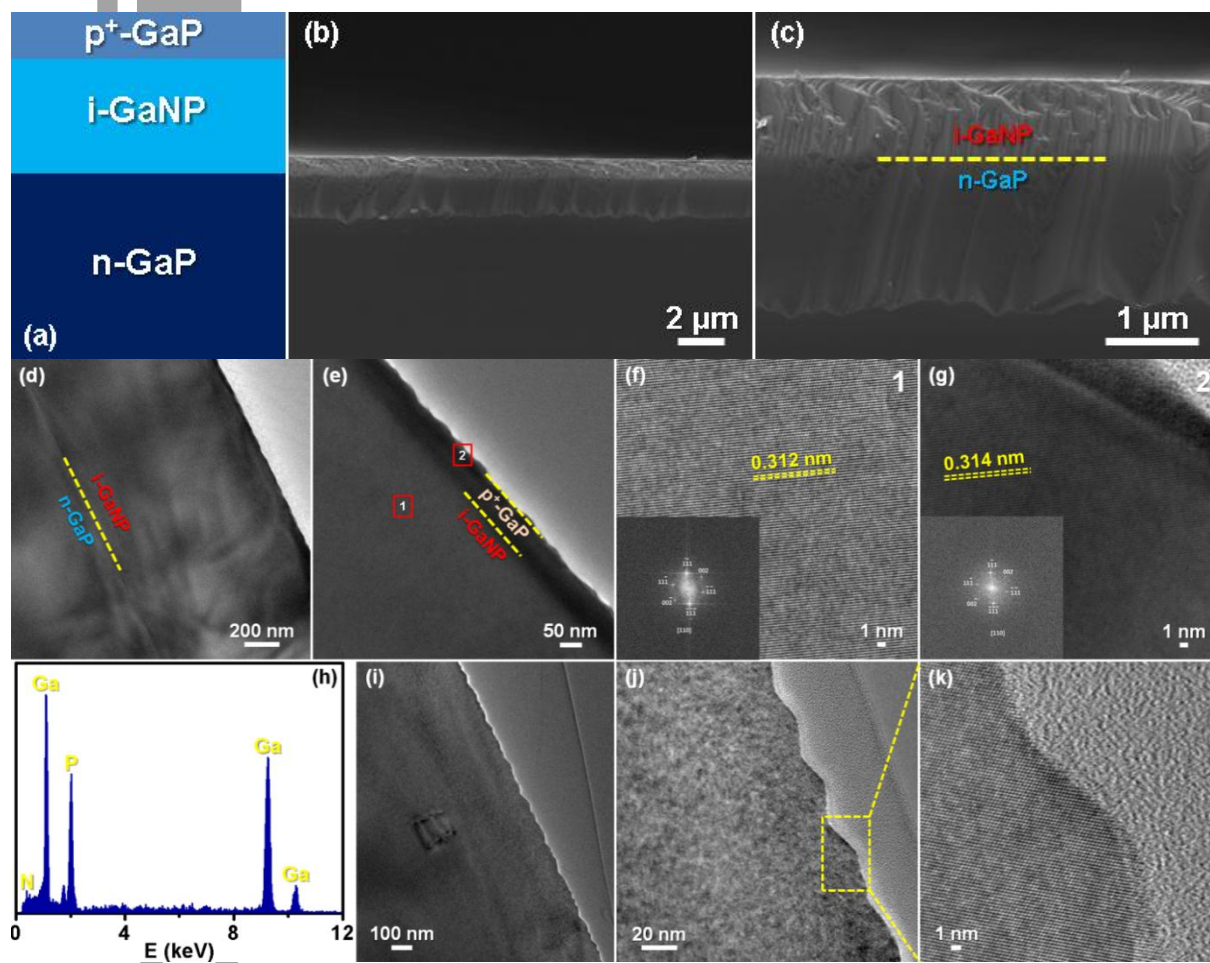
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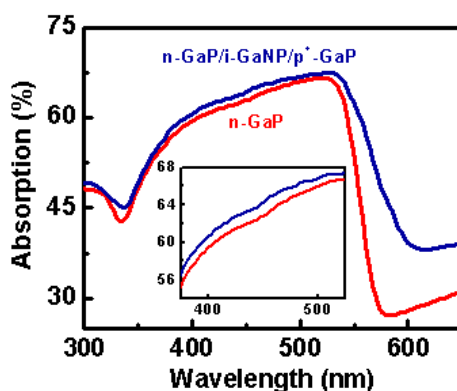
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**Figure 1.** (a) Schematic representation, and (b,c) low- and high-magnification cross-sectional SEM images of n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrate. (d) Low-magnification and (e) higher-magnification cross-sectional TEM images of n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrate. HRTEM image of (f) i-GaNP layer (marked region with “1” in (e)) and (g) p<sup>+</sup>-GaP layer (labelled area with “2” in (e)). Insets are the corresponding FFT patterns. (h) EDS spectrum of i-GaNP layer. (i) Low-magnification TEM, (j) high-magnification TEM, and (k) HRTEM images of surface structure of n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrate.



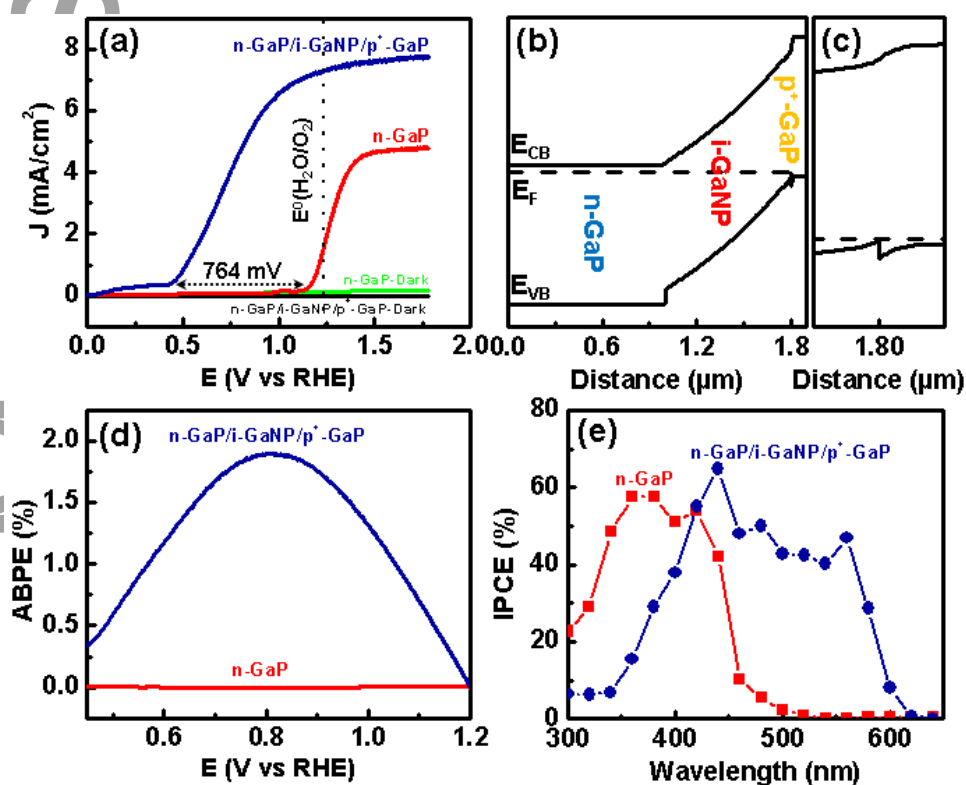
**Figure 2.** Optical absorption spectra of n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction substrates. Inset shows the zoomed-in absorption spectrum from 375 nm to 525 nm.

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**Figure 3.** (a) Linear sweep voltammetry (LSV) measurement at dark and under illumination of the  $\text{TiO}_2/\text{Ni}$ -coated n-GaP and n-GaP/i-GaNP/ $p^+$ -GaP thin film heterojunction substrates collected at a scan rate of 10 mV/s in 1 M KOH solution. (b) Approximate energy band diagram of the n-GaP/i-GaNP/ $p^+$ -GaP heterojunction at equilibrium condition and at dark,

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which was simulated using SCAPS (version 3.1.02) numerical simulation software. (c) Zoomed-in energy band diagram around i-GaNp and p<sup>+</sup>-GaP junction. (d) Applied bias photon-to-current efficiency (ABPE) of the corresponding samples in (a). (e) Incident photon-to-current efficiency (IPCE) of the TiO<sub>2</sub>/Ni-coated n-GaP and n-GaP/i-GaNp/p<sup>+</sup>-GaP thin film heterojunction substrates at 1.4 V versus RHE recorded in 1 M KOH electrolyte.

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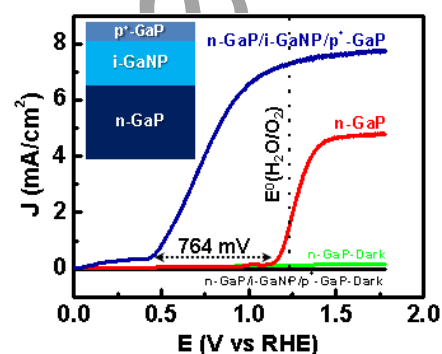
An n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction is synthesized using a molecular beam epitaxy method, and applied for efficient solar-driven water oxidation. The TiO<sub>2</sub>/Ni-coated n-GaP/i-GaNP/p<sup>+</sup>-GaP photoanode provides a high performance in 1 M KOH solution with an onset potential of ~0.4 V versus RHE, a photocurrent of 7.26 mA/cm<sup>2</sup> at 1.23 V versus RHE, a maximum applied bias photon-to-current efficiency of 1.9%, and a broad absorption spectrum up to ~620 nm.

**Keywords:** GaP, GaNP, thin film heterojunction, solar-driven water oxidation, alkaline electrolyte

Alireza Kargar, Supanee Sukrittanon, Chang Zhou, Yun Goo Ro, Xiaoqing Pan, Shadi A. Dayeh, Charles W. Tu,\* and Sungho Jin\*

### GaP/GaNP Heterojunctions for Efficient Solar-Driven Water Oxidation

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Supporting Information

**GaP/GaNP Heterojunctions for Efficient Solar-Driven Water Oxidation**

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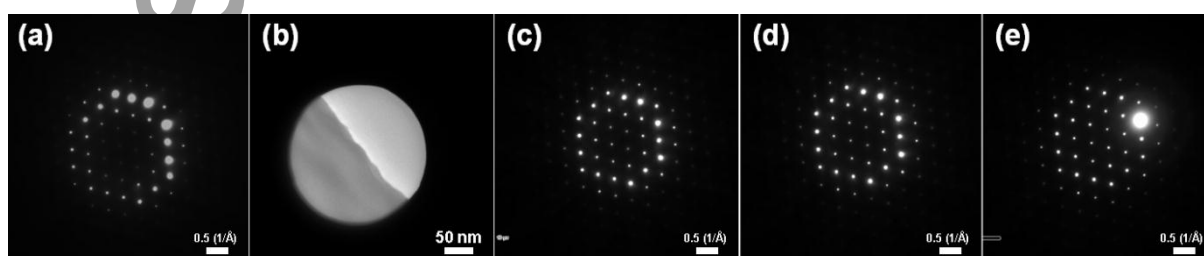
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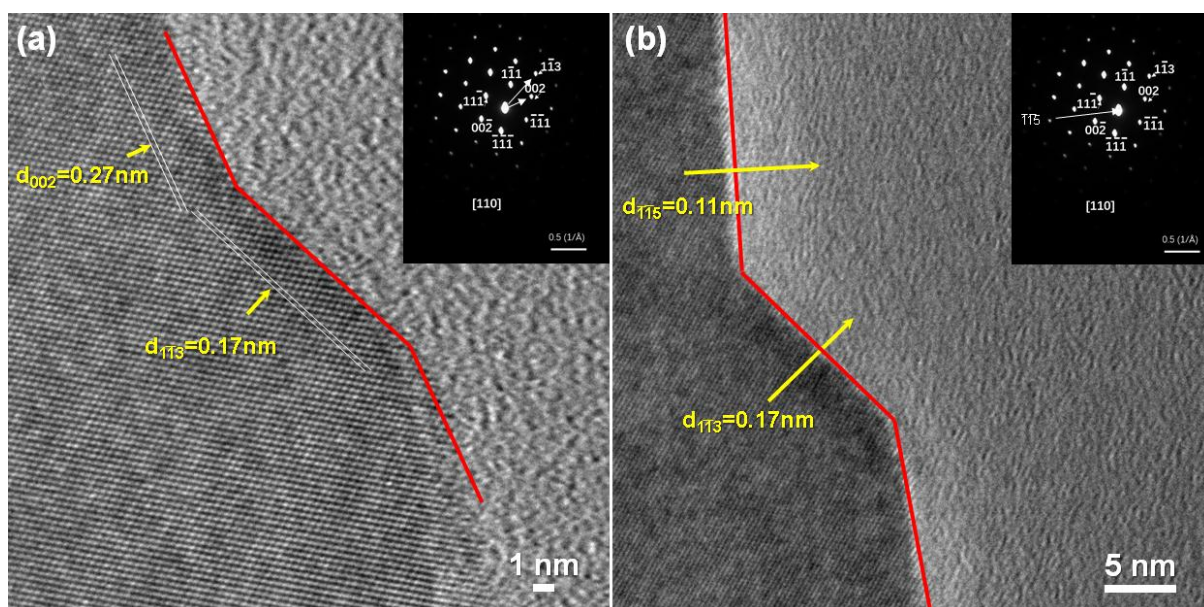
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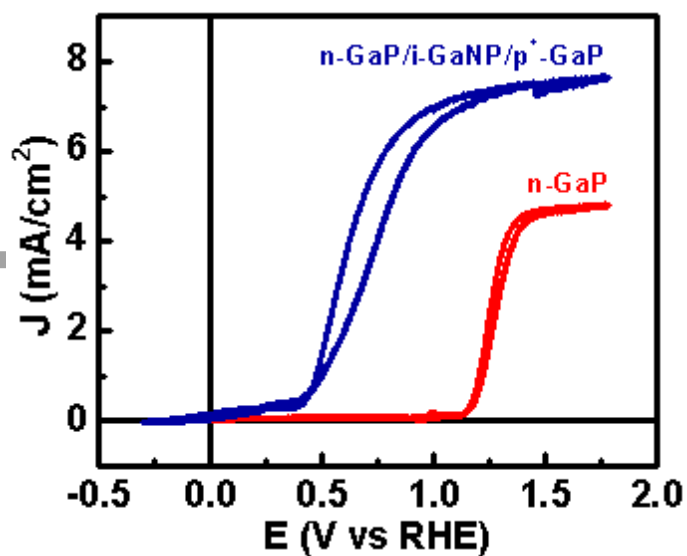
**Figure S1.** Selected area electron diffraction (SAED) pattern of (a) an area of n-GaP, (c) an area including both i-GaNP and p<sup>+</sup>-GaP layers (TEM image of selected region is shown in (b)), and (d) i-GaNP and (e) p<sup>+</sup>-GaP of selected areas in (b). The combined SAED pattern (Figure S1c) is very similar to the SAED pattern of i-GaNP (Figure S1d) and p<sup>+</sup>-GaP (Figure S1e).



**Figure S2.** (a,b) HRTEM images of surface structure of n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film substrate with the identified facets.

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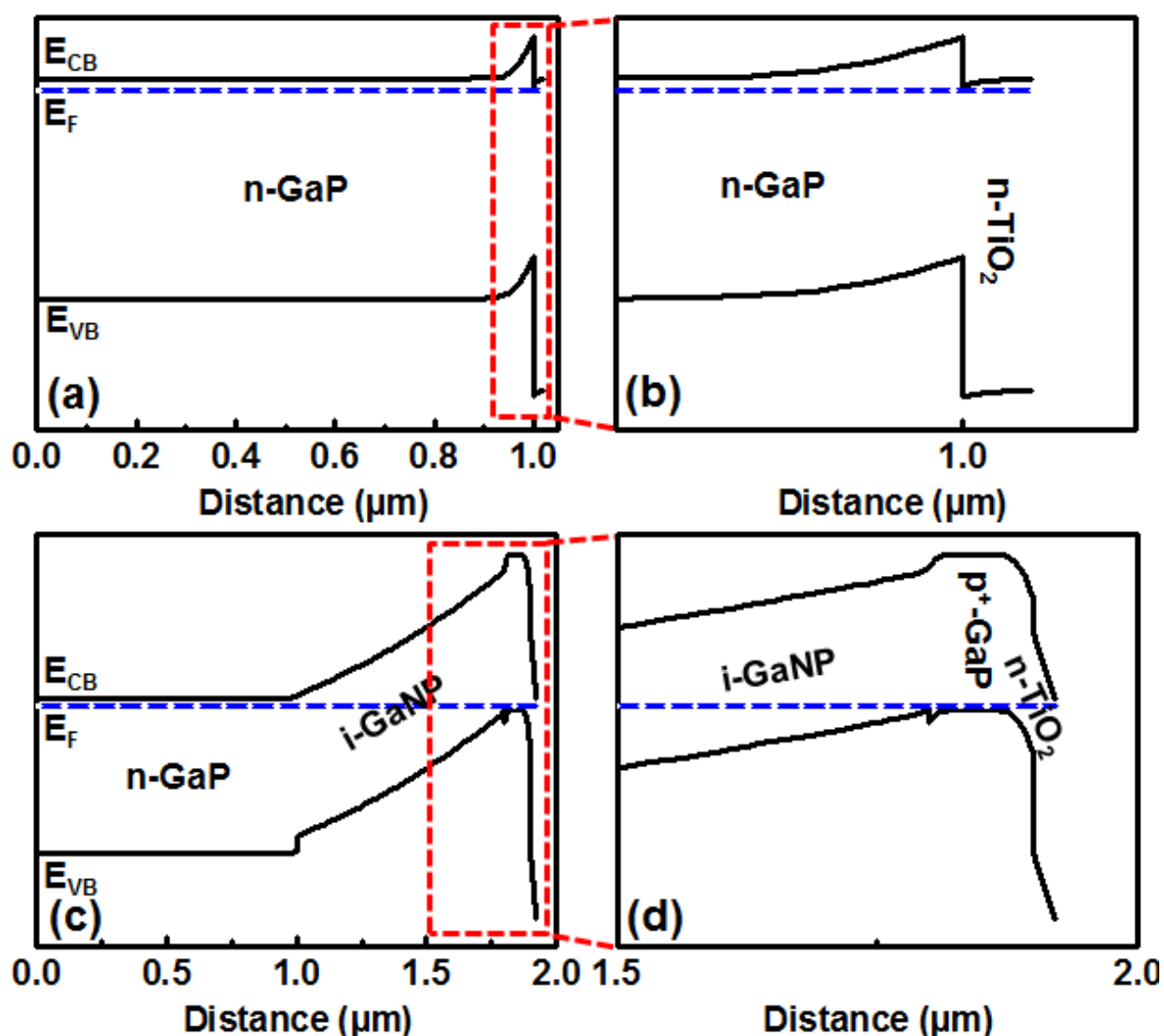


**Figure S3.** Cyclic voltammetry (CV) measurement under illumination of the TiO<sub>2</sub>/Ni-coated n-GaP and n-GaP/i-GaNP/p<sup>+</sup>-GaP thin film heterojunction substrates recorded at a scan rate of 10 mV/s in 1 M KOH electrolyte.

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**Figure S4.** Approximate energy band diagram of the TiO<sub>2</sub>-coated (a,b) n-GaP and (c,d) n-GaP/i-GaNP/p<sup>+</sup>-GaP substrates at equilibrium condition and at dark, which was simulated using SCAPS (version 3.1.02) numerical simulation software. The band gap of anatase TiO<sub>2</sub> layer deposited by ALD was considered to be 3.2 eV.<sup>[1,2]</sup> The electron affinity of TiO<sub>2</sub> (anatase and ALD deposited) was considered as ~4.3 eV.<sup>[1,3]</sup> The doping concentration of the ALD-deposited anatase TiO<sub>2</sub> is in the range of 10<sup>17</sup> cm<sup>-3</sup><sup>[4]</sup> (was considered 10<sup>17</sup> in the simulation). The considered TiO<sub>2</sub> thickness was 20 nm based on its deposited thickness.

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