

# Unique Three-Dimensional InP Nanopore Arrays for Improved Photoelectrochemical Hydrogen Production

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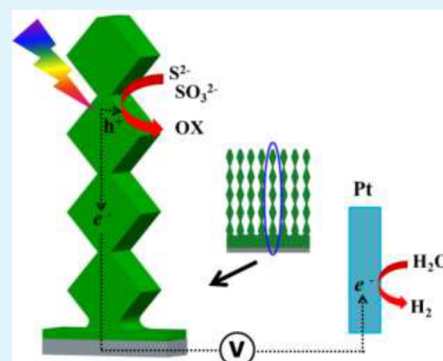
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## S Supporting Information

**ABSTRACT:** Ordered three-dimensional (3D) nanostructure arrays hold promise for high-performance energy harvesting and storage devices. Here, we report the fabrication of InP nanopore arrays (NPs) in unique 3D architectures with excellent light trapping characteristic and large surface areas for use as highly active photoelectrodes in photoelectrochemical (PEC) hydrogen evolution devices. The ordered 3D NPs were scalably synthesized by a facile two-step etching process of (1) anodic etching of InP in neutral 3 M NaCl electrolytes to realize nanoporous structures and (2) wet chemical etching in HCl/H<sub>3</sub>PO<sub>4</sub> (volume ratio of 1:3) solutions for removing the remaining top irregular layer. Importantly, we demonstrated that the use of neutral electrolyte of NaCl instead of other solutions, such as HCl, in anodic etching of InP can significantly passivate the surface states of 3D NPs. As a result, the maximum photoconversion efficiency obtained with ~15.7  $\mu\text{m}$  thick 3D NPs was 0.95%, which was 7.3 and 1.4 times higher than that of planar and 2D NPs. Electrochemical impedance spectroscopy and photoluminescence analyses further clarified that the improved PEC performance was attributed to the enhanced charge transfer across 3D NPs/electrolyte interfaces, the improved charge separation at 3D NPs/electrolyte junction, and the increased PEC active surface areas with our unique 3D NP arrays.

**KEYWORDS:** photoelectrochemical cells, InP, three-dimensional, nanopore arrays, anodic etching



## 1. INTRODUCTION

Photoelectrochemical (PEC) water splitting is a clean and environmentally benign strategy to address the increasing global energy demand by efficient storage of solar energy in hydrogen fuels.<sup>1–5</sup> Since the discovery of water splitting,<sup>6</sup> significant research efforts have been made to develop high-quality photocatalytic materials in functional structures for high solar-to-hydrogen (STH) conversion efficiencies.<sup>7–11</sup> The key factors to realize high efficiency are efficient utilization of solar light, effective transport of photogenerated charges, and fast water splitting reactions.<sup>5,12–14</sup> Therefore, development of highly efficient solar energy conversion devices has been focused largely on engineering the band structure of photoelectrodes, enlarging semiconductor/electrolyte interfacial area, and enabling rapid charge separation, collection, and transport.<sup>15–17</sup> In this regard, 3D ordered nanostructure arrays, such as branched nanowire architectures, are very promising, because they can confine the light within nanostructures for improved light absorption, have an enlarged depletion/bulk ratio in nanowires for fast electron–hole separation, and have largely

enhanced surface areas for improved electrochemical reactions.<sup>5,17</sup>

To achieve high-efficiency PEC hydrogen production, the use of semiconductors that are capable of absorbing a broad spectrum of solar light is desirable. However, most of the metal oxide semiconductors such as TiO<sub>2</sub> and ZnO can only absorb light in the ultraviolet (UV) region due to their relatively large band gap ( $E_g = 3.2$  eV). The narrow band gap metal oxide of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is able to absorb visible light up to 600 nm; however, it suffers from low absorption coefficient and short carrier diffusion length, and therefore poor incident-photocurrent efficiency (IPCE; <10% at 1.23 V vs RHE).<sup>18,19</sup> Nanostructuring ZnO, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> photoanodes, such as fabrication of their nanowire/nanotube array,<sup>20–25</sup> lead to improved STH conversion efficiency; however, the total efficiency is still not satisfactory.

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InP is an important narrow band gap III–V semiconductor ( $\sim 1.34$  eV). It is widely used as photocathodes for PEC hydrogen production attributing to its favorable conduction band position for water reduction and its low surface-recombination velocity.<sup>26–28</sup> Recently, p-InP photocathode has achieved a benchmark solar-to-hydrogen efficiency of approximately 15.8%.<sup>29</sup> The PEC properties of n-type InP has also been intensively studied but mainly using sacrificial-reagent-containing electrolytes due to its poor stability for water oxidation.<sup>30–32</sup> Recently, InP photoanodes with effective protective coatings have shown excellent PEC performances for water oxidation in 1.0 M KOH solution.<sup>33,34</sup> However, most of these studies were conducted with planar InP that has relatively small surface areas. Our group and other groups have demonstrated that 2D InP NP photoanodes exhibited superior PEC performances compared to their planar counterparts.<sup>35,36</sup> However, the photocurrent density is still low mainly attributed to high surface recombination at surface states.<sup>36</sup> Therefore, it is highly desirable yet challenging to find an efficient way to passivate the surface recombination.

Herein, we show that a remarkably enhanced PEC hydrogen production performance is realized with our newly fabricated 3D InP NPs. These ordered 3D InP NPs were synthesized via a facile two-step etching strategy. The unique 3D NPs were systematically characterized with different techniques to understand their structural, optical, and electronic properties. The excellent optical absorption characteristic with the enlarged effective surface area of 3D NPs photoelectrodes largely enhanced the PEC performances. Importantly, we found that 3D NPs fabricated in neutral NaCl electrolytes have effective passivated surfaces compared to 2D NPs prepared in HCl electrolytes. As a result, the maximum photoconversion efficiency reaches 0.95% from  $\sim 15.7$   $\mu\text{m}$  long 3D NPs and is 7.3 and 1.4 times higher than its planar and 2D NPs counterparts.

## 2. EXPERIMENTAL SECTION

**Sample Preparation.** All chemicals used in this study were analytical grade and were used as received without further purification. Deionized water was used in all cases for making solutions. Samples used in this work were Sn-doped n-type InP (100) single crystals, supplied by GRINM. The thickness of the InP wafer was 600  $\mu\text{m}$ , and the concentration was  $(1\text{--}4) \times 10^{18}$   $\text{cm}^{-3}$ . The wafer was first mechanically mirror polished on one side with emery paper and diamond suspension. They were then cleaned ultrasonically in acetone and ethanol followed by rinsing in deionized water. For electrical connections, indium (In) films was sputtered on the back side using magnetron sputtering to form ohmic contacts. Subsequently, the sputtered samples were annealed at 350  $^{\circ}\text{C}$  in  $\text{N}_2$  atmosphere for 1 min. High-purity silver paint was smeared on In films to establish an electrical contact with a copper plate. The copper plate was painted with epoxy to ensure that only the InP sample was in contact with the electrolyte. After cleaning, the sample was pressed against an O-ring in an electrochemical cell leaving 0.48  $\text{cm}^2$  electrode exposed to the electrolyte. Just prior to immersing samples into the electrolyte, the samples were chemically cleaned with HF (49%) and  $\text{H}_2\text{O}$  (1:10) for about 60 s to remove native oxides from the surface.

**Preparation of Well-Aligned 3D InP NPs.** Ordered 3D n-type InP NPs were grown on an InP substrate via a double-step etching procedure. Electrochemical etching was first carried out in 3 M NaCl aqueous solution ( $\text{pH} = 7$ ) in darkness at room temperature. A classical three-electrode configuration of a platinum counter electrode, an Ag/AgCl reference electrode to which all potentials are referenced, and an InP working electrode was used. The morphology of InP nanopore strongly depended on the current density. To obtain well-aligned 3D InP NPs, we applied 180  $\text{mA cm}^{-2}$  of the current density.

After the first electrochemical etching, a nucleation layer was formed on the top surface of the ordered porous layer. The top nucleation layer was then removed by wet chemical etching in HCl and  $\text{H}_3\text{PO}_4$  solution with 1:3 in volume ratio at room temperature for  $\sim 100$  s to obtain highly ordered 3D InP NPs. For comparison, we also prepared 2D InP NPs by anodic etching InP in HCl electrolyte as described in detail in our previous study.<sup>36</sup>

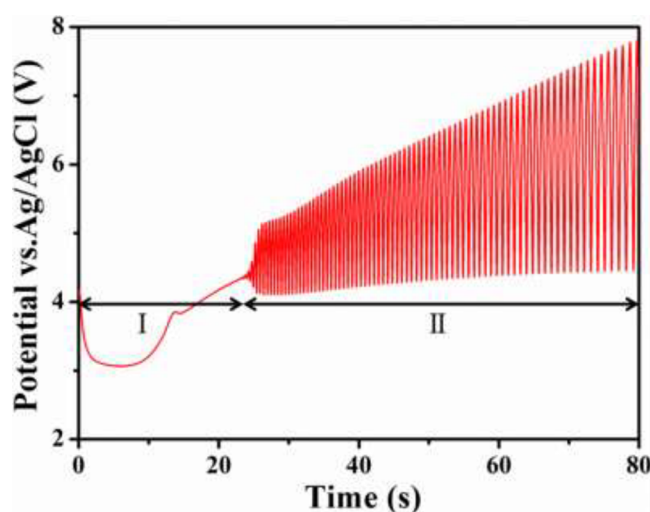
**Materials Characterization.** The morphologies of the as-grown 3D InP nanopores were observed by a field-emission scanning electron microscope (FE-SEM, FEI Sirion 200). The crystalline structure of the as-prepared sample was analyzed using an X-ray diffractometer (XRD; D8 ADVANCE X-ray diffractometer, Bruker, Karlsruhe, Germany) with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm). Surface compositions of the sample were analyzed by X-ray photoelectron spectroscopy (XPS; AXIS ULTRA DLD, Kratos, Hadano, Japan). Reflectance spectra were obtained using a Lambda 750S spectrometer (PerkinElmer) consisting of a deuterium and tungsten–halogen lamp, photomultiplier, and integrating sphere with 60 mm. The room-temperature photoluminescence (PL) spectra of the as-prepared samples were recorded using an excitation wavelength of 514 nm. Raman and PL spectra were obtained using the Jobin Yvon LabRam HR 800 UV system at room temperature. The excitation wavelength was 514.5 nm.

**Photoelectrochemical Measurements.** The PEC performances of photoelectrodes were evaluated in a typical three-electrode electrochemical cell configuration using an electrochemical workstation (PARSTAT 4000) in 0.35 M  $\text{Na}_2\text{S}$  and 0.5 M  $\text{Na}_2\text{SO}_3$  ( $\text{pH} = 13.6$ ) solution. All three electrodes were immersed in a glass cell with a quartz window, through which the working electrode was illuminated by a solar simulator (SOLAR DGE 700) which is equipped with a 300 W xenon arc lamp and an air mass (AM) 1.5 G filter. The incident illumination intensity was adjusted to 100  $\text{mW cm}^{-2}$  by changing the position of the lamp relative to that of the electrochemical cell. Before illumination, high-purity  $\text{N}_2$  was purged into the three-electrode cell for 30 min to remove the dissolved  $\text{O}_2$ . The current density–voltage ( $J$ – $V$ ) curve was measured under chopped simulated solar light illumination (100  $\text{mW cm}^{-2}$ ) with the potential sweeping from negative potential to the positive potential with a scan rate of 10  $\text{mV s}^{-1}$ . The cyclic voltammograms (CVs) were performed between  $-1.2$  and  $-0.5$  V vs Ag/AgCl at a scan rate of 10  $\text{mV s}^{-1}$ . The stability test was evaluated under constant simulated solar light irradiation at a fixed potential of  $-0.7$  V vs Ag/AgCl. Potentials are reported as measured vs Ag/AgCl and as calculated vs RHE using the Nernstian equation of  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.1976$ , where  $E_{\text{RHE}}$  is the converted potential vs RHE and  $E_{\text{Ag/AgCl}}$  is the experimental potential measured against the Ag/AgCl reference electrode.

The flat potential and carrier density ( $N_d$ ) were determined using Mott–Schottky analyses at a fixed frequency of 10 kHz in darkness. The electrochemical impedance spectroscopy (EIS) data were collected under simulated solar light (100  $\text{mW cm}^{-2}$ ) illumination at applied bias of +0.2 V vs OCP (open circuit potential) with AC perturbation amplitude of 10 mV in the frequency range from  $10^5$  to  $10^{-1}$  Hz.

## 3. RESULTS AND DISCUSSION

A typical time-course galvanostatical curve of n-InP electrodes anodized in a 3 M NaCl aqueous solution at 180  $\text{mA cm}^{-2}$  for 80 s is shown in Figure 1. The curve has two different stages. After a smooth increase of the voltage in stage I, a well-defined voltage oscillation curve was formed in stage II. It has been reported that such high-amplitude-voltage oscillations are related to synchronized pore-diameter oscillations.<sup>37</sup> Figure 2 shows the cross-sectional and plan-view SEM images of the as-prepared porous InP obtained under this anodic etching condition with a subsequent wet chemical etching. As can be seen from the cross-sectional SEM image of the sample in Figure 2a, a multilayer structure including an irregular layer on the top (crystal oriented pores, marked as region I) and a nanopore array layer (oriented pores, marked as region II) at



**Figure 1.** Potential vs time curve for anodic etching of n-InP at  $I_p = 180 \text{ mA cm}^{-2}$  in 3 M NaCl solution. The different curves are marked as I and II.

the bottom was formed.<sup>38,39</sup> This corresponds to the voltage evolution in Figure 1, and the regions with different porous structures were marked as I (the top layer) and II (the bottom layer). The crystal oriented pores observed in the I area were magnified in the inset of Figure 2a. The bottom layers of the II area are zoomed in and shown in Figure 2b, showing well-aligned 3D NPs. Obviously, the size of pores is strongly modulated; the maximum diameter is  $\sim 140 \text{ nm}$ , and the minimum value is  $\sim 95 \text{ nm}$  along with the horizontal direction. The observed local increases in the pore diameter were called pore “nodes”,<sup>37</sup> and the size of the “node to node” is  $\sim 150 \text{ nm}$  along with the current-line-oriented pores. Figure 2c shows the top view of the porous InP right after anodic etching; the pores

in the top layer are sparse, with a pore diameter of about  $30 \text{ nm}$ . In contrast, quasi-square pores with diameter in a range of  $\sim 100\text{--}200 \text{ nm}$  were formed after wet chemical etching (Figure 2d). This result indicates that the disordered irregular layers were completely removed after the chemical etching process. Therefore, after two-step etching, highly ordered and vertically oriented 3D InP NPs are obtained.

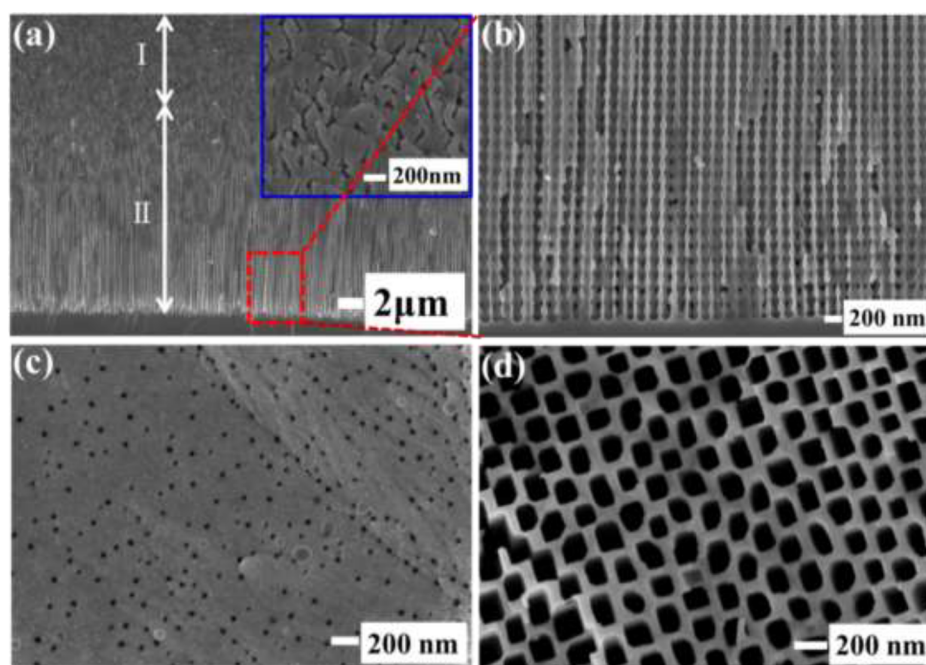
The thickness of the regular 3D NP films can be easily determined by adjusting the anodic oxidation duration (Supporting Information, Figure S1). The thickness of the 3D NP films almost linearly increased to about  $7.2$ ,  $11.4$ ,  $15.7$ , and  $20.5 \mu\text{m}$  at different anodic oxidation times of  $40$ ,  $60$ ,  $80$ , and  $100 \text{ s}$ . The thickness of the NP films ( $d_p$ ) linearly increased with etching time ( $t$ ) at a mean growth rate ( $k$ ) of  $0.19 \mu\text{m/s}$ . From the SEM images (Figure 2), the average values of both pore radius ( $r_p$ ) and wall thickness can be estimated as  $100\text{--}200 \text{ nm}$  and  $50\text{--}100 \text{ nm}$ . The pores density ( $N_p$ ) is roughly  $1.7 \times 10^9 \text{ cm}^{-2}$ . Assuming square pores and the wall of pores made up of a series of cubes, the evolution of the porous area ( $A_p$ ) can be determined from

$$A_p = 4r_p \times \sqrt{2}d_p \times N_p \quad (1)$$

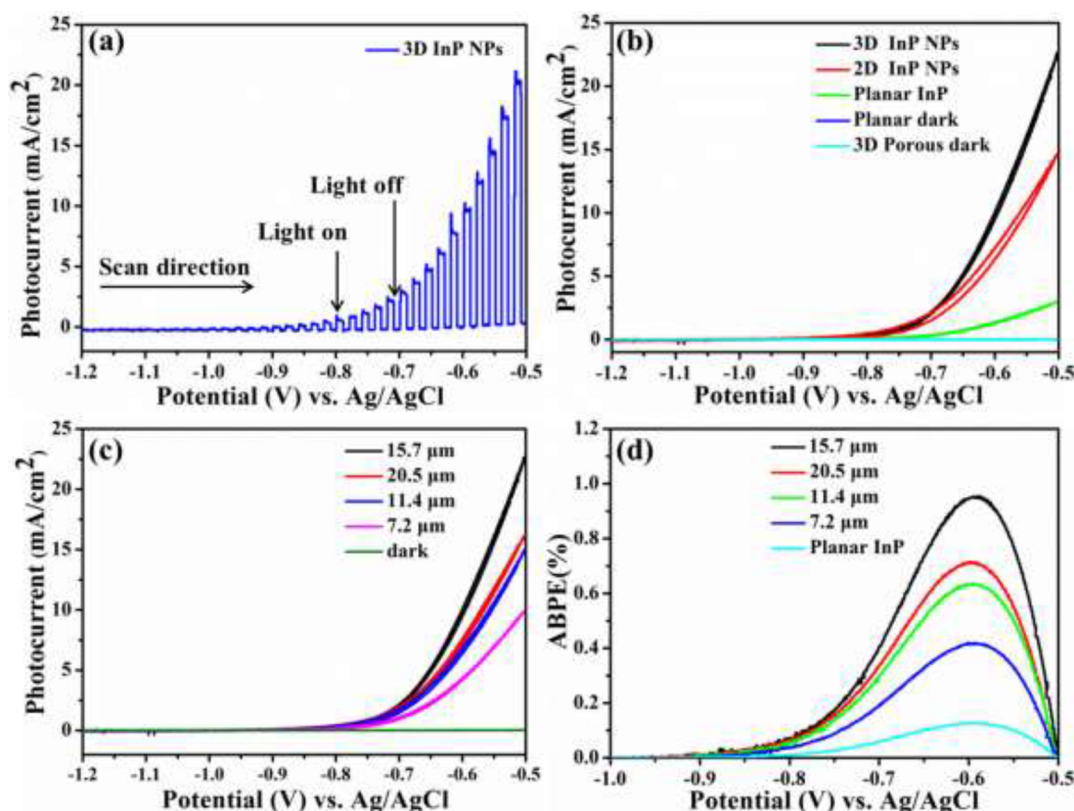
Since  $d_p$  is linearly dependent on  $t$ , eq 1 can be rewritten as following:

$$A_p = 4\sqrt{2}r_p \times N_p \times k \times t \quad (2)$$

According to eq 2, the specific area is directly proportional to the anodic time.  $A_p$  can thus be deduced from  $k$  and  $t$ . The calculated area increases strongly during the porous etching. Considering an initial surface exhibiting a nominal area of  $1 \text{ cm}^2$ ,  $A_p$  rises to  $80\text{--}200 \text{ cm}^2$  after  $100 \text{ s}$ . The significant increased specific area provides large surfaces for PEC reactions. The aligned 3D NPs further favor the interfacial



**Figure 2.** (a) Cross-sectional SEM image of the porous InP after anodic etching. The different areas are marked as the I and II areas. The inset presents a higher magnified view of the top part of the porous layer. (b) Amplification of the bottom layer in panel a. (c) Top-view SEM image before wet chemical etching. (d) Top-view SEM image after wet chemical etching.



**Figure 3.** PEC measurements of the photoelectrodes in 0.35 M Na<sub>2</sub>S and 0.5 M Na<sub>2</sub>SO<sub>3</sub> aqueous solution (pH = 13.6). (a) Current density–voltage behavior of 3D InP NPs with 15.7 μm length under interrupted illumination. (b) Cyclic voltammetry for direct comparison of three types of InP films. (c) Cyclic voltammetry of 3D porous InP films with various lengths. (d) Calculated photoconversion efficiencies.

charge transfer across the InP/electrolyte interface for enhanced PEC performances.

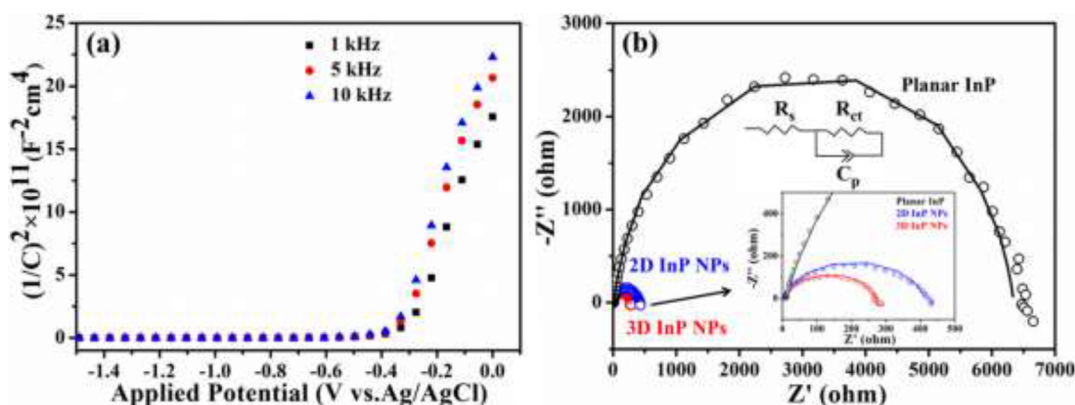
The XRD pattern (Supporting Information, Figure S2) obtained from the as-prepared 3D InP NPs matched well with the cubic InP (JCPDS Card No. 01-070-2513). A typical Raman spectrum of the 3D InP NPs is shown (Supporting Information, Figure S3). The peak located at 297 cm<sup>-1</sup> is attributed to a TO phonon mode, and the peak at 337 cm<sup>-1</sup> corresponds to the LO phonon mode.<sup>40</sup>

Three-dimensional NP structure improves light absorption compared to its planar counterpart due to its specific geometry. We can clearly see that the 3D InP NP sample has a black appearance instead of the mirror-like silver-colored planar InP wafer. UV–vis diffuse reflection spectra (Supporting Information, Figure S4) were used to quantify the light absorption property. The light reflection was significantly reduced for 3D NP samples compared to the planar one in the whole measured wavelength. In addition, we found that the superior antireflection properties of the 3D NPs are ascribed to the parallel nanopores that enable strong light trapping and scattering inside nanopores, which leads to the enhanced optical absorption.

Figure 3a shows a typical current density–potential (*J*–*V*) curve of the 3D InP NP photoanode obtained under chopped simulated solar light illumination (100 mW cm<sup>-2</sup>). The dark current density remained at a very low level in the scanned potential range, indicating almost no chemical reactions in the dark. Typical anodic current spikes were observed when light was turned on. These spikes represented the accumulation of photoexcited holes at the electrode/electrolyte interface without injection to electrolyte.<sup>41</sup> caused by either carrier

oxidized trap states in semiconductors<sup>42</sup> or a slow oxidation reaction at the interface.<sup>43</sup> Such spikes can be suppressed when holes oxidized the electrolyte under improved interface charge transport kinetics. From the plot, the photocurrent density was very small at low bias. This is consistent with the n-InP/KCl(aq)–Fe(CN)<sub>6</sub><sup>3-/4-</sup> junction.<sup>44</sup> Compared to the data on n-InP/CH<sub>3</sub>OH–Me<sub>2</sub>Fc<sup>+/0</sup> contacts studied previously,<sup>30</sup> the low current density indicates that the hole transfer was very slow at the n-InP/Na<sub>2</sub>S–Na<sub>2</sub>SO<sub>3</sub> interface. This may be due to a small potential barrier formed at the *n*-InP/polysulfide electrolyte interface.

The CV characteristics in Figure 3b explained a superior performance of the 3D InP NP photoanode over 2D InP NPs and planar InP photoanodes. The dark current of 3D NPs and planar electrodes was always near zero in the tested potential region. Upon illumination, the photocurrent density of 3D NP photoanode reached 22.5 mA cm<sup>-2</sup> at -0.5 V vs Ag/AgCl, while that of 2D NPs and planar InP photoanodes was 15 and 3 mA cm<sup>-2</sup>, respectively. In addition, the onset potential (defined as the potential at which *J*<sub>p</sub> = 1 mA cm<sup>-2</sup>) of 3D NP electrode shifted negatively around 100 mV, relative to that of planar InP electrode. This negative shift can be ascribed to the improved holes transfer to the electrolyte due to the large surface area of the porous three-dimensional structure. Remarkably, there was almost no hysteresis observed for 3D NPs; whereas hysteresis was observed for 2D NPs. The hysteresis behavior of porous InP prepared in HCl electrolytes has been observed in a previous report.<sup>35</sup> The hysteresis between the forward and reverse scan directions can be ascribed to an altered occupation density of surface states, which would result in a shift of the band bending between forward and reverse scans.<sup>45</sup> The



**Figure 4.** (a) Mott–Schottky plots of a 3D InP nanopore in the dark at frequencies of 1 (black line), 5 (red line), and 10 kHz (blue line) and an AC current of 10 mV with a three-electrode system. (b) Nyquist plots of various types of InP films under simulated solar light illumination. The inset depicts the equivalent circuit model used for fitting and shows an expanded region around the low impedance.

decreased hysteresis behavior clearly implies that 3D NPs have an effectively passivated surface compared to the 2D one.

The photocurrent density of 3D InP NPs is determined by the porous films thickness. Figure 3c shows the performance of 3D NPs with different film thicknesses. The photocurrent onset potential was relatively stable, independent of film thickness. However, the photocurrent density at more positive potentials increased with the films thickness which is likely related to improved light absorption and increased surface areas in 3D InP NPs, and then it decreased which is likely caused by the increased charge transport distance for long 3D NPs. Three-dimensional InP NPs with the film thickness of 15.7  $\mu\text{m}$  exhibited the best performance.

In the present system, the generated photocurrent is related to hydrogen gas generation at Pt cathodes. The hydrogen generation rate can be estimated using the applied bias photon-to-current efficiency (ABPE)<sup>36</sup>

$$\text{ABPE}/\% = \left[ \frac{I(\Delta G_{\text{rev}}^0 - V_{\text{bias}})}{P_{\text{light}}} \right] \times 100 \quad (3)$$

Figure 3d shows the photoconversion efficiency of 3D NP films at different thicknesses and the planar samples. The photoanode with a 15.7  $\mu\text{m}$  thick NP film exhibited the maximum efficiency of 0.95% at  $\sim -0.6$  V vs Ag/AgCl, which is about 7.3 times higher than that of planar counterparts. More importantly, the maximum efficiency of the 3D NPs is  $\sim 40\%$  greater than the value for 2D NPs (0.67%) with a similar thickness.<sup>36</sup> These results clearly demonstrate advantages of the porous three-dimensional structures for higher PEC efficiency.

The stability of 3D NP photoanode was investigated by measuring  $J_{\text{ph}}$  at  $-0.7$  V (vs Ag/AgCl) under continuous simulated solar light illumination (Supporting Information, Figure S5). The photocurrent ( $\sim 0.32$  mA  $\text{cm}^{-2}$ ) for the planar InP electrode decreased to about 84% of the initial current within 2000 s. The decrease of photocurrent is due to the poor anticorrosive ability of bulk InP in electrolyte under illumination. The photogenerated holes were not efficiently transported to oxidize polysulfide in electrolyte but self-oxidize InP. In contrast, the 3D NPs showed improved photostability and maintained the initial photocurrent ( $\sim 2.1$  mA  $\text{cm}^{-2}$ ) after 2000 s. The improved stability can be ascribed to the specific geometry of 3D NPs, resulting in more efficient holes consumption at the nanopores/electrolyte junction, which in return relieves the charge recombination and photocorrosion of

InP. Although 3D NPs show improved stability compared to a planar one, the development of an efficient PEC cell without sacrificial reductants is eventually required and urgent for PEC hydrogen production.<sup>46</sup>

To understand the electronic properties of the 3D nanopores in electrolyte solution, we have conducted the Mott–Schottky (M-S) experiments in the dark to determine carrier density and flatband potential. The flatband potential ( $V_{\text{fb}}$ ) and carrier density ( $N_{\text{d}}$ ) can be quantified by the M-S eq 4. As expected, the planar InP exhibits an ideal linear M-S curve vs the applied potential (Supporting Information, Figure S6). The  $V_{\text{fb}}$  of planar InP is found to be  $-1.5$  V vs Ag/AgCl. The  $N_{\text{d}}$  is estimated to be  $3.3 \times 10^{18}$   $\text{cm}^{-3}$ , which agrees well with the carrier density value given by the InP wafer vendor.

$$\frac{1}{C^2} = \left( \frac{2}{e_0 \epsilon_0 N_{\text{d}} A^2} \right) \left( V - V_{\text{fb}} - \frac{k_{\text{B}} T}{e_0} \right) \quad (4)$$

In contrast to flat samples, the M-S plots (Figure 4a) collected from 3D NPs exhibit a nonlinear behavior due to the pore geometry at low applied potential region. This is in good agreement with the previous work. An inflection point around  $-0.35$  V is observed on the M-S plot; positive to this voltage, the  $1/C^2$  increases significantly. According to eq 5 and analysis of Santinacci et al.,<sup>47</sup> the width of the space charge layer depends on the applied bias. At low potential region ( $< -0.35$  V), the space charge layer is thin ( $W < 40$  nm); the depletion layer therefore follows the surface topography, and the  $1/C^2$  decrease indicates the increased specific area.

$$W = \left[ \left( V - V_{\text{fb}} - \frac{k_{\text{B}} T}{e_0} \right) \frac{2 \epsilon_0}{e_0 N_{\text{d}}} \right]^{1/2} \quad (5)$$

The width of the depleted region increases with the band bending. Once the entire porous layer is fully depleted, at  $-0.35$  V, it no longer contributes to the capacitance; consequently a linear evolution of  $1/C^2$  is again obtained with a slope similar to that of planar InP. At a potential of  $-0.35$  V,  $W$  has been calculated to be 40 nm; it corresponds to half of the pore wall thickness.

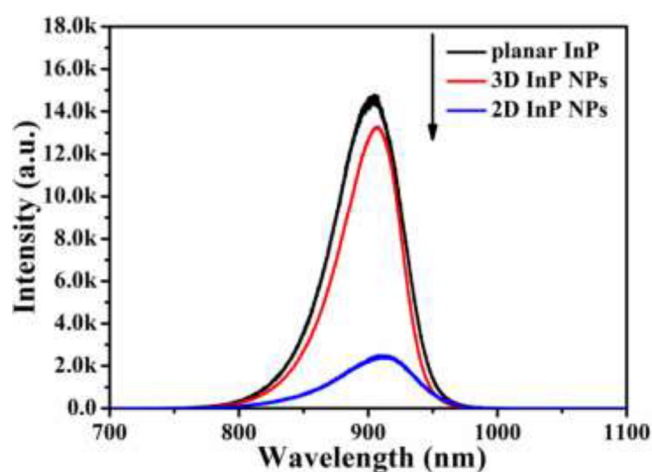
$$N_{\text{d}} = (2/e_0 \epsilon_0) [d(1/C^2)/dV]^{-1} \quad (6)$$

The carrier density of 3D InP NPs can be determined from eq 6 under circumstances of not fully depleted. The calculated

carrier density is  $3.9 \times 10^{18} \text{ cm}^{-3}$  at frequency of 10 kHz (Supporting Information, Figure S5).

To gain more insight into the principle of the enhancement of PEC performance, electrochemical impedance spectroscopy (EIS) was performed on various InP photoanodes under illumination. In the Nyquist plot, the radius of each arc is associated with the charge-transfer process at the corresponding electrode/electrolyte interface. A smaller arc radius implies a faster interfacial charge transfer and a more efficient charge separation.<sup>48</sup> As evident in Figure 4b, the impedance arcs of both porous InPs were much smaller than that of planar InP, indicating that porous array structures can significantly facilitate the charge separation and transport due to the increased contact surface area. In addition, the smallest arch for 3D NPs was observed, suggesting that an effective separation of photogenerated electron–hole pairs and faster interfacial charge transfer occurred on the 3D InP NPs. This result is consistent with the PEC measurements, which show the highest conversion efficiency for the 3D NPs.

Photoluminescence (PL) spectroscopy was carried out on all InP films to understand the extent of radiative charge carrier recombination. In most of the semiconductors, a weaker PL signal mean a lower electron–hole recombination rate, and hence a longer lifetime of photogenerated carriers.<sup>49</sup> In porous InP, however, a lower PL intensity indicates a higher charge recombination rate because PL quenching has been attributed to the creation of surface states that act as nonradiative recombination centers.<sup>50–52</sup> As shown in Figure 5, the etched



**Figure 5.** Room-temperature photoluminescence spectra of various types of InP films.

and unetched InPs are with the essentially same peak position, whereas the PL intensity decreases in the order of planar InP, 3D InP NPs, and 2D InP NPs. The PL intensity of 3D NPs increases significantly relative to the 2D one, which indicates that the recombination of the photogenerated charge carriers is greatly reduced in 3D NPs. We suspect that such a huge difference is associated with the difference in electrolytes. It has been suggested that anodization of InP in NaCl electrolytes results in effective passivation of the porous surface states as compared to anodization in HCl electrolytes.<sup>53</sup>

In order to explore the passivation mechanism of NaCl electrolytes, XPS experiments were carried out on both 3D InP NPs and 2D InP NPs. XPS analysis revealed the presence of indium, phosphorus, oxygen, and chlorine (Supporting

Information, Figure S7). The In 3d<sub>5/2</sub> (444.3 eV) and P 2p (129.3 eV for P 2p<sub>1/2</sub> and 128.5 eV for P 2p<sub>3/2</sub>) core levels for both samples exhibit the typical features for bulk InP<sup>54</sup> except for an additional component in the P 2p region at ca. 133.3 eV. This could be ascribed to In(PO<sub>x</sub>)<sub>y</sub>, and the O 1s (531.3 eV) response confirmed the presence of P–O–P or P–O bindings.<sup>55</sup> The native oxide was presumably formed during the sample transfer from the electrochemical cell to the XPS chamber. The presence of a Cl element on the porous InP surface confirmed the creation of surface states.<sup>47</sup> We also found that the percentage of chlorine atoms is 1.6% and 0.9% for 2D InP NPs and 3D InP NPs, respectively; thus the decreased chlorine content could be one of the reasons that surface state density is reduced in the 3D InP NPs.

A schematic diagram (Supporting Information, Figure S8) is shown to understand the mechanism of PEC hydrogen generation from water with the 3D InP NP photoelectrode. Upon illumination, electron–hole pairs are produced on the semiconductor of InP, the photogenerated holes can be more easily scavenged by the sacrificial agents (S<sup>2–</sup> and SO<sub>3</sub><sup>2–</sup>) as the short hole diffusion length and large specific area owing to the 3D NPs morphology. Simultaneously, the photogenerated electrons should be efficiently delivered to the cathode to react with water to produce hydrogen via unidirectional conduction pathway.

## 4. CONCLUSIONS

In summary, 3D InP NPs with unique NP architectures were fabricated via a facile two-step etching procedure. The fabricated 3D InP NPs drastically improve the PEC hydrogen production efficiency of ~40% compared to 2D InP NPs. Such large improvement is ascribed to the improved photogenerated charge separation efficiency and the decreased charge-transfer resistance at 3D NP electrode/electrolyte interface as evidenced in PEC, electrochemical impedance, and PL analyses. We suggest that the 3D InP NPs with high PEC properties and an easy fabrication process may find other applications in energy storage, energy conversion, and sensor devices.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06200.

Additional electrochemical data, XRD and Raman patterns, SEM images, XPS analysis, and other complementary information (PDF)

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### Notes

The authors declare no competing financial interest.

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