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InP nanopore arrays for photoelectrochemical hydrogen generation

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Received 22 September 2015, revised 14 December 2015 Accepted for publication 15 December 2015 Published 18 January 2016

Abstract

We report a facile and large-scale fabrication of highly ordered one-dimensional (1D) indium phosphide (InP) nanopore arrays (NPs) and their application as photoelectrodes for photoelectrochemical (PEC) hydrogen production. These InP NPs exhibit superior PEC performance due to their excellent light-trapping characteristics, high-quality 1D conducting channels and large surface areas. The photocurrent density of optimized InP NPs is 8.9 times higher than that of planar counterpart at an applied potential of +0.3 V versus RHE under AM 1.5G illumination (100 mW cm⁻²). In addition, the onset potential of InP NPs exhibits 105 mV of cathodic shift relative to planar control. The superior performance of the nanoporous samples is further explained by Mott-Schottky and electrochemical impedance spectroscopy analysis.

Keywords: InP nanopore arrays, photoelectrochemical, hydrogen production

(Some figures may appear in colour only in the online journal)

1. Introduction

Photoelectrochemical (PEC) splitting of water to hydrogen and oxygen is one of the most promising forms of energy production, which is a very attractive and desirable way to solve the energy challenge with the associated detrimental environmental problem, as both water and sunlight are abundant on the Earth. Since Fujishima and Honda first demonstrated a PEC approach to realize water splitting using TiO₂ electrodes in 1972 [1], numerous photoactive materials have been investigated and optimized to improve PEC properties based on these considerations: small bandgap to utilize a significant portion of visible light, a proper conduction/valence band position to satisfy water oxidization and reduction potentials, fast carrier separation and transportation, and so on [2, 3]. Among various photoactive materials, indium phosphide (InP) is considered a highly promising photoactive material for solar-fuel conversion. As the first efficient photocathode for hydrogen evolution [4], InP has a number of attractive attributes: (1) its direct band gap of 1.34 eV can absorb light over a broad range of solar spectrum wavelengths, which makes it widely used in the field of solar cells. Recently, high-efficiency InP-based photovoltaic solar cells have been reported [5, 6]. (2) The conduction-band edge position of InP is more negative than the standard water reduction potential [7], hence electron transfer is more favorable in the PEC system. (3) The high optical absorption coefficients (typically $10^4 - 10^5 \text{ cm}^{-1}$) and low carrier recombination rates of InP can maximize short-circuit current density [8], which are the decisive factors in the selection of these materials for the construction of thin-laver conversion devices. For these reasons, over the past three decades, InP has been widely studied [4, 9–12] as a photoactive material for PEC water splitting since 1970s. However,





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the realization of p-type InP devices for overall water splitting without external bias is still challenging, due to its relatively high valance band position. To investigate n-type InP as photoanodes for water oxidation and/or other related oxidation reactions may provide more details of PEC performances of n-type InP and is also useful for future construction of InP based heterojunctions to ultimately achieve overall water splitting without external electric bias. Recently, InP photoanodes stabilized by effective protective coatings, have shown excellent photoanodic performances during long-term operation under water oxidation conditions in 1.0 M KOH solution [13, 14]. However, to the best of our knowledge, most work on n-InP mainly focused on planar InP.

One problem with planar InP is that a large amount of incident photons are reflected away from the InP surface, and these cannot produce electron-hole pairs. To maximize the solar-to-hydrogen efficiency, a low reflectance InP surface is required. In this regard, one-dimensional (1D) nanostructures such as nanowires, nanopore arrays (NPs) have been recognized for their potential as high performance photoelectrodes in PEC cells because they provide several advantages over their planar counterparts. First, 1D nanostructures arrays allow the incident light to scatter within their open interiors (i.e., light-trapping effect) [15, 16]. The scattering enhances the capability of light absorption by diminishing the reflection of incident light and increasing the photon path length. Second, 1D nanostructures arrays can decouple the directions of light absorption and charge-carrier collection and provide a unidirectional conducting channel for rapid electron-hole separation and charge transport, yielding a low recombination of electron-hole pairs [17-19]. In addition, highly ordered 1D nanostructure have extremely high surface areas for fast interfacial charge transfer and more active sites for fast electrochemical reactions [20], which would decrease the overpotential needed at the photoelectrodes and improve the chemical stability against corrosion [21]. The local current density needed to generate PEC products at a given rate per unit of semiconductor area for nanostructures are reduced, and the reduced current density through the local surface would further improve the PEC stability against corrosion [22].

For these reasons, in the last decade, 1D nanostucture arrays such as ZnO nanowires [23, 24], TiO₂ nanowires [25, 26], and Si nanoporous [22] have been extensively investigated as photoelectrodes materials and demonstrated to be efficient in improving conversion of solar energy to H₂ fuel due to their specific geometry. Recently, InP nanowires [27] and nanopillar [8] photoelectrodes have been studied for efficient solar-driven hydrogen production and exhibited excellent PEC performances in terms of energy conversion efficiency and stability. In this work, we present the synthesis and characterizations of InP NPs, and their applications as photoelectrodes for PEC hydrogen generation. Especially, the surface recombination in InP NPs is investigated in detail by measuring PEC properties. These nanopores are prepared by the electrochemical anodization method, the main advantages of this method for these self-organization InP NPs are facile and scale-up synthesis process. This InP NPs have unique features such as large surface area and low optical reflectance. Especially, InP NPs with pores diameter of sub-50 nm and wall thickness of ~40 nm were successfully synthesized. The nanopores with pore diameters smaller than the wavelength of incident photons are beneficial to enhance light harvesting [22], and nanopores with walls thickness close to the width of space–charge region are expected to perform better than thicker ones [28]. Our results reveal that this InP NPs possess excellent PEC performances in comparison to their planar control.

2. Experimental details

Wafers were monocrystalline, Sn-doped, n-type indium phosphide (n-InP) supplied by GRINM. They had a surface orientation of (100) and a carrier concentration in the range $1-4 \times 10^{18} \, \text{cm}^{-3}$. They were first mechanically mirror polished on one side with emery paper and diamond suspension. To fabricate working electrodes, wafers were cleaved into coupons along the natural {011} cleavage planes. Then the coupons were degreased by successively sonicating in acetone and ethanol for 5 min each step to remove contaminants followed by rinsing in deionized water and then dried in nitrogen. Ohmic contact was made by alloying indium to the back of the coupons by using direct current magnetron sputtering; they were then annealed at 350 °C for 1 min in N₂ atmosphere. The high purity silver paint was smeared on the In films in order to establish an electric contact with a copper plate. The copper plate except the coupon was painted with inert epoxy to ensure only the coupon contact with the electrolyte. Then the copper plate with the coupon was pressed in an O-ring of an electrochemical cell leaving the coupon exposed to the electrolyte. The electrode area was typically 0.48 cm². A conventional two-electrode cell configuration was used. The coupon electrode was used as the anode and graphite electrode was used as the cathode. A power supply was connected between the anode and cathode with the electrodes separated by a distance of 6 cm. Before etching, the coupons were etched with the mixture of HF (49%) and H_2O (1:10) for 1 min to remove the native oxides from them surface. Electrochemical etching of planar InP to form the porous structures was first carried out in an aqueous solution of 2.1 M HCl (aq) under a constant anodizing voltage of 7 V in darkness at room temperature. Next, the coupons etched were then immersed in a mixture solution of pure HCl and pure H₃PO₄ (1:3 HCl/H₃PO₄ by volume) at room temperature for 1 min to remove the disordered irregular top layer. After ultrasonic washing in deionized water for 1 min, followed by drying under a stream of N2 (g), the black InP NPs samples were obtained. To study the photoanodic activity dependence on the length of InP nanopores, four different lengths of InP NPs were prepared by controlling the etching time between 15 and 90 s.

The crystal structure and phase of the samples before and after etching were determined by x-ray diffraction (XRD: D8 ADVANCE x-ray diffractometer, Bruker, Germany) with Cu Ka radiation (1.54 Å). Scanning electron microscopy (SEM)

data were obtained by using an FEI Sirion 200 scanning electron microscope (SEM). Porous samples were scored on the back and cracked along the (110) directions to obtain cross sectional images, and the resulting pieces were mounted to the SEM stub using carbon tape. The room-temperature photoluminescence (PL) spectra of the as-grown porous InP and planar samples were recorded by using an excitation wavelength of 514 nm. The reflectance spectrum of porous InP was measured by using a Lambda 750S spectrometer (Perkin-Elmer) consisting of a deuterium and tungsten-halogen lamp, photomultiplier, and integrating sphere with 60 mm. The samples were placed at the end of the sphere at normal incidence.

PEC measurements were performed in a three-electrode PEC cell with the InP materials as the working electrode, Ag/ AgCl as the reference electrode, and a Pt wire mesh as the counter electrode. An electrochemical workstation (PAR-STAT 4000) instrument was used to measure PEC properties of electrodes. Unless otherwise stated, all PEC measurements were conducted under 1 sun AM 1.5 simulated sunlight with an SOLARDGE 700 solar simulator integrating a 300 W xenon arc lamp and an AM 1.5G filter. The intensity of the Xe lamp was measured by Solar Simulator Spectroradiometer (LS-100, EKO Instruments Co., Ltd, Japan), and the incident illumination was adjusted to 100 mW cm⁻² by changing the position of the lamp relative to that of the electrochemical cell. All samples were front-illuminated through a quartz glass, because front-illumination resulted in a much higher photocurrent generation. The illuminated area was 0.48 cm^2 for all experiments, and the photocurrent density was calculated based on the projected area of the electrode, as opposed to the actual surface area. All PEC measurements were conducted in an aqueous solution containing 0.35 M Na₂S and 0.5 M Na₂SO₃ (pH 13.6), unless otherwise stated. Prior to the measurement, the electrolyte was degassed and purged with N₂. The PEC current density-voltage (I-V) curves were measured sweeping the potential to the positive direction with a scan rate of 50 mV s^{-1} . Cyclic voltammetric data were recorded also at this scan rate. Potentials are reported as measured versus Ag/AgCl and as calculated versus RHE using the Nernstian relation $E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059$ pH + $E_{Ag/AgCl}^{0}$ [26], where E_{RHE} is the converted potential versus RHE, $E_{Ag/AgCl}$ is the experimental potential measured against the Ag/ÅgCl reference electrode, and $E^{0}_{Ag/AgCl}$ is the standard potential of Ag/AgCl at 25 °C (0.1976 V). The applied bias photon-to-current efficiency (ABPE) was calculated using the following equation [29]:

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

where *I* is the photocurrent density, V_{bias} is the applied bias between working electrode and RHE, and P_{light} is the incident illumination power density (AM 1.5G, 100 mW cm⁻²). ΔG_{rev}^0 is the Gibbs free energy per coulomb of electrons for the redox reactions on electrodes. Because the current study uses polysulfide as hole scavengers, ΔG_{rev}^0 is 0.5 V [30].



Figure 1. X-ray diffraction pattern for planar InP and as-grown porous InP.

Electrochemical impedance spectroscopy (EIS) was carried out to understand the charge transfer process between photoelectrodes/electrolyte interfaces. All the measurements were performed on the same workstation under the opencircuit condition with the frequency ranging from 0.1 Hz to 100 kHz and ac small signal amplitude of 10 mV. Mott –Schottky plots were measured in the dark at an AC frequency of 1.0 kHz.

3. Results and discussion

XRD patterns (figure 1) obtained from the InP material before and after etching matched that of cubic InP (JCPDS Card 01-070-2513). The position of each peak is the same for all samples, indicating no change of lattice constant for the InP before and after etching. Figure 2(a) is a typical low magnification SEM image of the as-grown porous InP film, which reveals a regularly arranged pore structure of the film. Closer observation (figure 2(b)) reveals that these nearly square pores have an average pore diameter (r_{p}) of approximately 50 nm and wall thickness of around 40 nm. The pores density $(N_{\rm p})$ is roughly $1.1 \times 10^{10} \,{\rm cm}^{-2}$. Shown in figure 2(c) is a cross-sectional view of the films showing that the films are composed of well-aligned nanopores of about 24.5 μ m in length, which grow vertically from an InP substrate, and that the wall thickness of the InP crystallite seen in the inset of figure 2(c) is in the range of 20–60 nm. We observed that the size distribution of the pores is almost independent of time. The average lengths of the nanoporous arrays were measured to be 4.3 μ m, 9.2 μ m, 16.9 μ m, and 24.5 μ m for etching times of 15 s, 30 s, 60 s, and 90 s, respectively. The length of the nanoporous films (L_p) linearly increased with etching time (T)(figure 2(d)) at a mean growth rate (k) of 0.25 μ m s⁻¹.

The room-temperature PL spectra of the planar and asgrown porous InP, which are often used to study the surface processes involving electron-hole recombination of semiconductors [31], were measured *ex situ* by using an excitation



Figure 2. Morphologies of InP nanopore array film: a typical top view SEM images at (a) low and (b) high magnifications, (c) cross section, inset shows the magnified images corresponding to part of (c). (d) Nanopore lengths were plotted versus time, showing that the growth rate is linear.



Figure 3. Room-temperature photoluminescence spectra of planar InP and as-grown InP NPs with different lengths under excitation wavelength of 514 nm.

wavelength of 514 nm. The PL spectrum recorded from the planar InP in figure 3 shows a strong near-band-edge emission at about 915 nm, which is consistent with the results reported previously [32, 33]. As soon as the porous film forms, the peak intensity of PL spectra drops drastically relative to planar InP, and the peak intensity continue to drop with the length increase. The progressive decrease of the peak intensity can be attributed to several effects such as the surface nonradiative recombination induced by surface defects



Figure 4. Total reflectance spectra of planar InP and InP NPs with different lengths as a function of wavelength. Inset showing optical photographs of InP NPs (black) and planar InP (gray).

[34]. It should be noted that the length of the NPs is long enough to ensure that most of the PL signal arises from the NPs rather than the bulk substrate. The total reflectance spectra of the ordered nanoporous InP and planar InP in the wavelength range of 250–1000 nm are shown in figure 4. As expected, the reflectance of InP NPs structures is significantly reduced in comparison with the planar InP structure across the whole measured spectrum. The greatly reduced reflectance of NPs is also evident in the optical photographs of the samples,



Figure 5. Photoelectrochemical open-circuit dark and photo potentials of nanoporous InP (a) and planar InP (b). The illumination was turned on and off with a period of 60 s.

with the nanoporous sample appearing black and planar sample gray (figure 4). Therefore, compared to planar counterpart, InP NPs can absorb more light, and higher photocurrent is expected. Another noticeable feature in figure 4 is that the reflectance of NPs is enhanced along with the length of the nanopores increase, which is consistent with 1D silicon nanostructures [35, 36].

PEC measurements were systematically performed to assess the PEC properties of photoelectrodes fabricated from the nanoporous InP and planar InP. A mixture of 0.35 M Na₂S and 0.5 M Na₂SO₃ aqueous solution was used as electrolyte and sacrificial reagent to maintain the stability of InP. This mixed electrolyte (S²⁻ + SO₃²⁻) was found to be better than either sulfite alone or sulfide alone for PEC H₂ production because sulfides are regenerated through the reaction of disulfide and sulfite as follows [37, 38]:

$$2S^{2-} + 2h^+ \to S^{2-}_2, \tag{1}$$

$$S_2^{2-} + SO_3^{2-} \to S_2O_3^{2-} + S^{2-},$$
 (2)

$$S^{2-} + SO_3^{2-} + 2h^+ \to S_2O_3^{2-},$$
 (3)

$$SO_3^{2-} + 2OH^- + 2h^+ \rightarrow SO_4^{2-} + H_2O,$$
 (4)

$$2SO_3^{2-} + 2h^+ \to S_2O_6^{2-}.$$
 (5)

And hydrogen gas is produced on the counter electrode by photogenerated electrons during illumination of photoelectrodes given by reaction:

$$2\mathrm{H}^+ + 2e^- \to \mathrm{H}_2. \tag{6}$$

Figure 5 shows the open circuit potentials (OCP) of the nanoporous InP and planar InP under chopped AM 1.5G illumination. Under light illumination, the OCPs are more negative of -1.21 V and -1.11 V versus Ag/AgCl for nanoporous InP and planar InP, respectively. When light is off, the OPCs shift to more positive values. This can be ascribed to the increased energy band upward bending in dark compared to that in light [39].

All phenomena associated with PEC systems are based on the formation of a semiconductor-electrolyte junction when a semiconductor photoelectrode is immersed in an appropriate electrolyte. The junction is also known as the space-charge layer where photogenerated electrons and holes are separated. As shown in inset of figure 6(a), the InP Fermi level equilibrates with the electrochemical potential of the redox pair by transfer of electrons from the semiconductor to the electrolyte. This produces a positive space-charge layer in the semiconductor, leading to conduction and valence band edges bending. As a result, a potential barrier is formed against further electron transfer into the electrolyte. In contrast, it drives holes toward the solution to oxidize S^{2-} and SO_3^{2-} . Holes, however, are the minority charge carrier in n-type InP, their density is extremely low. As a result, overall current is little in the absence of light. Indeed, both the InP cells showed negligible current under dark, until at more negative or more positive voltages, thus no leakage current was observed for the setup. Under light illumination, the holes density increases drastically due to light excitation. A great deal of holes photogenerated are subsequently collected and then transferred to the electrolyte. As a result, obvious photocurrents are observed. As shown in figure 6(a), under light illumination, significant photocurrents are observed for both InP cells. The photocurrents increased with increasing applied potential. The photocurrent density of InP NPs reached a maximum value of 26.5 mA cm^{-2} at 0.6 V versus RHE, which is ~3.6 times higher than that of planar InP $(7.4 \text{ mA cm}^{-2} \text{ at } 0.6 \text{ V} \text{ versus RHE})$. In addition, the onset potential (I = 0) of InP NPs electrode (-0.216 V versus)RHE) shifted negatively around 105 mV, relative to that of planar InP electrode (-0.111 V versus RHE). This can be attributed to the enhanced light absorption and the improved hole transfer to the electrolyte due to the large surface area of the nanopores structure, which result in a negative shift in the quasi-Fermi level and thus in the onset potential [40].

The significantly improved PEC performance for the InP NPs can be ascribed to the following reasons. First, the ordered NPs have lower reflectance than planar InP. Second,



Figure 6. Photocurrent density versus applied potential curves of (a) porous InP and planar InP (b) planar InP and InP NPs with different lengths measured in an aqueous solution containing Na₂S and Na₂SO₃ electrolyte under both dark and AM 1.5G illumination. The corresponding energy diagram of an n-type photoelectrodes is shown in the inset; E_{cb} is the conduction band edge, E_{vb} the valence band edge, and E_F the Fermi level, respectively.



Figure 7. Comparison of light absorption and photogenerated charge carrier separation and transport at planar and nanoporous arrays photoanodes.

the NPs structures drastically increase the surface area, leading to the greatly increase in the interface area between electrode and the electrolyte. Moreover, NPs decouple the light absorption and charge charge-carrier collection, hence photogenerated holes can be effectively collected over a short distance, at maximum, the radius of nanoporous walls, and photogenerated electrons rapidly transport to counter electrodes via the unidirectional conducting channel. In general, the improved PEC performance for the NPs electrodes can be attributed to the cooperative effects of: enhanced light harvesting, higher surface area, effective separation of electron-hole pairs from their specific geometry construction. These results precisely correspond to figure 7.

Our next study focused on the effect of the length of InP NPs on the PEC performance and observing how the changes affect the PEC performance. Figure 6(b) shows a set of linear sweep voltammagrams recorded from a planar InP electrode and nanoporous InP electrodes with various length under both dark and AM 1.5G light illumination. It can be observed that the photocurrent density of the InP NPs first increased with

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Table 1. Dependence of $V_{\rm oc}$ on NP length.							
L (μ)	4.3	9.2	16.9	24.5			
$V_{\rm oc}$ (mV versus RHE)	207	218	216	211			

the length and reached a maximum value at the length of 16.9 μ m; and then decreased with the further increases in NPs length. This can be ascribed to the trade-off between the surface area and recombination loss. On the one hand, longer NPs lead to enhancement of the light absorption and the increases in total surface area. On the other hand, the charge scattering and recombination will also increase with the length and this would reduce photocurrent. So the optimal length for maximum photocurrents in this case is around 16.9 μ m long. This phenomenon observed is consistent with silicon nanowire arrays photananodes, and coincidentally, the optimal length is very close to that of silicon [28]. A consistent trend was also observed for the $V_{\rm oc}$ value. In analogy to a solid-state p/n junction solar cell, the potential at I = 0 is defined as $V_{\rm oc}$, which represent the open-circuit voltage. Similar to photocurrent, V_{oc} is sensitive to optical power and surface states. The $V_{\rm oc}$ values were relatively stable and exhibited a slightly trend to decrease with the length (table 1). This is in line with the Mott-Schottky analyses. The decrease can be attributed to the increase in surface states per unit illumination area.

To investigate the photoresponse of the NPs and planar samples, the transient photocurrents of the samples were carried out during repeated on/off illumination cycles at 0.3 V versus RHE (figure 8(a)). Upon illumination with light, a large initial spike due to the transient effect in power excitation observed in photocurrent appears for all electrodes, followed by a fast decrease to steady state photocurrent, and the photocurrent quickly return to zero once the light is switched off, indicating the fabricated photo electrodes display fast light response and excellent switching performance. Moreover, a similar tendency on the relationship between the NPs length and photocurrent density is also observed. As shown in figure 8(a), the steady state photocurrent density of nanopores with length of 16.9 μ m is ~3 mA cm⁻², which is 1.21, 1.67, 2.1, and 8.9 times higher than that of 24.5 μ m, 9.2 μ m, 4.3 μ m and planar, respectively. It further confirmed superior performance for the nanoporous InP electrode over that of planar InP electrode and nanopores with length of 16.9 μ m have the highest photocurrent. However, significant photocurrent decaying in the initial seconds of illumination before steady-state photocurrents reached can be seen in the InP nanoporous electrodes during repeated on-off cycles of illumination. The significant photocurrent decay observed during the initial excitation period can be ascribed to one of two reasons: (1) the inability of the redox pair to fast scavenge photogenerated holes or (2) dominant charge recombination/ scattering at the InP nanoporous electrodes/electrolyte interface [41].

If the scavenging of holes is a limiting factor, this effect can be overcome by increasing the concentration of the redox pair. To evaluate this possibility, typical curves of chopped transient photocurrent density versus time were measured in Na₂S electrolyte with different concentration between 0.1 and 1 M (figure 8(b)). As expected, upon illumination, the photocurrent increased with the concentration of Na₂S increase. However, the trend of the pronounced photocurrent decaying in the initial seconds of illumination still exists at higher concentrations of Na₂S. The fact that we continue to observe the decay of the photocurrent at higher Na2S concentrations rules out the above possibility that inefficient holes scavenging is the origin of the observed effect. Therefore, this trend observed indicates the presence of surface recombination caused by surface defects within nanopores. In addition, the cyclic voltammetry of nanoporous InP photoelectrodes in 0.35 M Na₂S and 0.5 M Na₂SO₃ aqueous solution under AM 1.5G illumination also show small hysteresis induced by surface states (figure 9). Surface states can be passivated by using a surface coating [42], which is expected to improve incident photon to current conversion efficiencies of InP NPs and is the subject of ongoing research in our laboratories.

The stability of the nanoporous electrode was investigated at +0.35 V versus RHE under continuous AM 1.5G illumination for longer time period (figure 10). Upon illumination, we observed a spike in photoresponse due to the transient effect, and the photocurrent then quickly returned to a steady state. Significantly, we only observed a small decay of photocurrent density in a continuous running, and 92% of the initial photocurrent was sustained after 4000 s, indicating that the InP NPs as photoanodes are well stable in this PEC system. The long term stability of InP NPs could be achieved by atomic layer deposition a thin protective shell on the InP core. We then carried out systematic amperometric I-t studies on InP NPs under AM 1.5G as a function of applied potential. As the photocurrent is not stable at applied potential more than +0.6 V versus RHE, and it is relative small at applied potential less than +0.25 V versus RHE, thus *I*-t behavior was investigated at potential range between +0.25 V and +0.6 V versus RHE (figure 11(a)). The steady photocurrent density determined from the I-t curve was used to calculate ABPE of nanoporous InP photoanode. Figure 11(b) shows that the maximum ABPE value is 0.67% at 0.35 V versus RHE.

To study the intrinsic electronic properties of the planar and nanoporous InP in electrolyte solution, electrochemical impedance measurements were performed on the samples in the dark to determine the capacitance of electrodes. Motte– Schottky curves obtained for all the samples have been presented in figure 12. All the samples exhibited positive slopes, indicating the semiconductor thin films to be of n-type. The carrier density (N_d) and flat band potential (V_{fb}) at semiconductor/electrolyte interface can be calculated using the Mott–Schottky equation given below:

$$\frac{1}{C^2} = \left(\frac{2}{e_0 \varepsilon \varepsilon_0 N_{\rm d} A^2}\right) \left(V - V_{\rm fb} - \frac{k_{\rm B} T}{e_0}\right)$$

where *C* is the space–charge capacitance, e_0 is the electron charge, ε and ε_0 are the dielectric constant of semiconductor electrode and permittivity of the vacuum respectively, N_d is



Figure 8. Amperometric *I*–*t* curves of (a) the planar InP and InP NPs with different lengths measured in an aqueous solution containing Na_2S and Na_2SO_3 electrolyte and (b) InP NPs measured in an aqueous solution containing different Na_2S concentration between 0.1 and 1 M at an applied voltage of +0.3 V versus RHE at 100 mW cm⁻² with 60 s light on/off cycles.



Figure 9. Cyclic voltammetry of nanoporous InP photoelectrodes in $0.35 \text{ M} \text{ Na}_2\text{S}$ and $0.5 \text{ M} \text{ Na}_2\text{SO}_3$ aqueous solution under AM 1.5G illumination (100 mW cm⁻²).

the carrier density, A is the area, V is the electrode applied potential, $V_{\rm fb}$ is the flat band potential, $k_{\rm B}$ is the Boltzmann constant, and T is the absolute temperature. So, by extrapolating the lineal region in these plots the flat band potential can be determined. The flat band potential ($V_{\rm fb}$) of planar InP determined from a Mott–Schottky measurement is at about -0.5 V versus RHE at pH = 13.6 (figure 12(a)). The dopant density of planar InP calculated from the slope of the Mott–Schottky plot using the equation below is 3.3×10^{18} cm⁻³, which is in the range given by the wafer supplier

$$N_{\rm d} = (2/e_0\varepsilon\varepsilon_0)[\mathrm{d}(1/C^2)/\mathrm{d}V]^{-1}$$

In contrast to planar InP, InP NPs exhibited a nonlinear behavior. The flat band potential $V_{\rm fb}$ of the NPs with different



Figure 10. Stability test of InP NPs at +0.35 V (versus RHE) under AM 1.5G illumination.

length was similar, which is consistent with [34], and measured (figure 12(b)) to be ~ -0.375 V versus RHE. Another noticeable feature in Mott–Schottky plots was that the slope gradually decreased with the length of the nanopores increase, which indicates slightly increased carrier densities induced by the surface defects.

For a square-shaped n-type semiconductor, the majority carrier-depleted zones, the space-charge layers, should be generated at both sides of the porous walls. Therefore, the width of the space-charge layer (W) at the electrode/electrolyte interface can also be derived from the Mott-Schottky plot relationship and is described by

$$W = [2\varepsilon\varepsilon_0(V - V_{\rm fb})/e_0N_{\rm d}]^{1/2}.$$

According to equation above, the thickness of spacecharge layer during anodic polarization of the InP NPs at



Figure 11. (a) Amperometric *I*-*t* curves of the InP NPs as a function of applied potential from +0.25 V (bottom) to +0.6 V (top) (versus RHE) at a step of 0.05 V. (b) Applied bias photon-to-current efficiency of InP NPs photoanode as a function of applied potential.



Figure 12. Mott-Schottky plots for (a) planar InP and (b) InP NPs with different length measured at 1 kHz.

0.6 V versus RHE has been calculated to be about 18.7 nm. Assuming the space–charge layers generated at both sides of the nanoporous walls, then the obtained total values of space–charge layer width was 37.4 nm, which is smaller than the thickness of some of InP nanoporous walls (20–60 nm), indicating that the nanoporous is not fully depleted yet. When the space–charge thickness is smaller than the walls thickness, then an increase of photocurrent as a function of electrode applied potential should be observed, which is consistent with the *I–V* curves shown in figure 6.

EIS is a powerful tool for studying two-phase interfacial properties between electrodes and solutions [43]. To understand the charge transport behavior, EIS was performed on the different InP films under both dark and light illumination covering the frequency range of 10^5 –0.1 Hz using an amplitude of 10 mV at the OCP of the system. The EIS response of the planar (figure 13(a)) and nanoporous InP films with length of 16.9 μ m (figure 13(b)) are plotted as nyquist diagrams in figure 13. Equivalent circuit modeling was made based on the impedance experimental data, which is plotted as real

admittance versus imaginary admittance. The data configuration in figure 13 all fall into the first quadrant, thus implying that no inductance is needed in the model. Therefore, a model for the equivalent circuit is proposed as shown in figure 13(a), whereas other models have also been used to describe the PEC behavior [44]. In our model, R_s represents the bulk resistive loss predominantly at the interface of the material surface and the electrolyte, $R_{\rm H}$ and $\rm CPE_{\rm H}$ correspond to the resistance and the Helmholtz layer capacitance in the electrolyte side, respectively; while R_{sc} and CPE_{sc} are associated with the internal electron-hole recombination resistance and space-charge layer capacitance in the depletion layer. It should be pointed out that, two constant phase elements (CPE) can be visualized as a non-ideal capacitor. Using the model, the solid lines represent results of fitting and the symbols represent experimental data. As can be seen, this model fitted well for both InP films under both dark and light illumination.

The fitted data for these elements are summarized in table 2. It can be observed that the value of bulk resistance R_s

Figure 13. Nyquist plots of (a) planar InP and (b) InP NPs under dark and light illumination conditions. The scatter points in the plots represent the original experimental data, whereas the solid lines are the fitted curves using the equivalent circuit model in figure 13(a).

Table 2. Electrochemical parameters determined from EIS analysis.

	$R_{\rm S}\left(\Omega ight)$	$R_{\rm H}\left(\Omega\right)$	CPE _H (µF)	$R_{\rm SC}\left(\Omega\right)$	$\begin{array}{c} \text{CPE}_{\text{SC}} \\ (\mu\text{F}) \end{array}$
In dark					
Planar InP	4.89	8105	60.5	164 960	4.195
InP NPs In light	5.01	1926	164.81	20 238	71.66
Planar InP InP NPs	4.82 5.06	2455 392	11.947 313.46	85 065 5892	8.028 254.68

is nearly constant under both dark and light illumination. However, the values of charge transfer resistance $R_{\rm H}$ and recombination resistance $R_{\rm sc}$ under light illumination is much smaller than the ones under dark for both InP films, which indicates that the Helmholtz layer and depletion layer were greatly modified by photogenerated carriers. This is in good agreement with previous investigations [45]. It should be noted that the values of $R_{\rm H}$ and $R_{\rm sc}$ for planar InP, are greater than the ones of InP NPs under both dark and light illumination, thus explaining the origin of higher PEC capability of InP NPs.

As expected, the considerable Helmholtz-layer capacitance of InP NPs should be ascribed to the larger surface area of nanostructure as compared to planar structure [46]. Under illumination, the electron Fermi level in the InP shifts upward and approaches its flat band potential, leading to a small depletion layer thickness, hence higher chemical capacitance $(CPE_{SC}^{Light} > CPE_{SC}^{Dark})$ [47].

4. Conclusions

In summary, we have successfully developed a simple twostep anodization method for the rational synthesis of 1D InP NPs as efficient photoelectrodes for PEC hydrogen generation. The InP NPs with length of 16.9 μ m generated a photocurrent density of 3 mA cm⁻² at an applied potential of +0.3 V versus RHE under simulated AM 1.5G illumination (100 mW cm⁻²), which is 8.9 times higher than that of planar control. The greatly enhanced PEC performance can be attributed to the cooperative effect: enhanced light absorption, high-quality 1D conducting channels as well as enlarged contact area with the electrolyte due to the specific geometry of NPs. PL spectra and PEC properties indicate that there is nonradiative recombination caused by surface defects within nanopores. Further improvements via passivating surface states are expected to maximize the photoconversion efficiency.

Acknowledgments

This work was supported by National 863 Program 2011AA050518, the Natural Science Foundation of China (Grant nos. 11174197, 11574203, and 61234005).

References

- [1] Fujishima A and Honda K 1972 Nature 238 37
- [2] Chen X B, Shen S H, Guo L J and Mao S S 2010 Chem. Rev. 110 6503
- [3] Walter M G, Warren E L, McKone J R, Boettcher S W, Mi Q X, Santori E A and Lewis N S 2010 Chem. Rev. 110 6446
- [4] Heller A 1984 Science 223 1141
- [5] Wallentin J et al 2013 Science 339 1057
- [6] Cui Y et al 2013 Nano Lett. 13 4113
- [7] Zaban A, Micic O I, Gregg B A and Nozik A J 1998 Langmuir 14 3153
- [8] Lee M H et al 2012 Angew. Chem., Int. Ed. Engl. 51 10760
- [9] Ellis A B, Bolts J M and Wrighton M S 1977 J. Electrochem. Soc. 124 5
- [10] Heller A and Vadimsky R 1981 Phys. Rev. Lett. 46 1153
- [11] Ang P G P and Sammells A F 1984 J. Electrochem. Soc. 131 1462

- [12] Ohmori T, Mametsuka H and Suzuki E 2000 Int. J. Hydrog. Energy 25 953
- [13] Chen L et al 2015 J. Am. Chem. Soc. 137 9595
- [14] Sun K, Kuang Y, Verlage E, Brunschwig B S, Tu C W and Lewis N S 2015 Adv. Energy Mater. 5 1402276
- [15] Lee Y J, Ruby D S, Peters D W, McKenzie B B and Hsu J W P 2008 Nano Lett. 8 1501
- [16] Cao X, Chen P and Guo Y 2008 J. Phys. Chem. C. 112 20560
- Boettcher S W, Spurgeon J M, Putnam M C, Warren E L, Turner-Evans D B, Kelzenberg M D, Maiolo J R, Atwater H A and Lewis N S 2010 Science 327 185
- [18] Liu N, Schneider C, Freitag D, Hartmann M, Venkatesan U, Müller J, Spiecker E and Schmuki P 2014 Nano Lett. 14 3309
- [19] Pu Y-C, Ling Y, Chang K-D, Liu C-M, Zhang J Z, Hsu Y-J and Li Y 2014 J. Phys. Chem. C. 118 15086
- [20] Shi J, Hara Y, Sun C, Anderson M A and Wang X 2011 Nano Lett. 11 3413
- [21] Seabold J A, Shankar K, Wilke R H T, Paulose M, Varghese O K, Grimes C A and Choi K-S 2008 Chem. Mater. 20 5266
- [22] Oh J, Deutsch T G, Yuan H-C and Branz H M 2011 Energy Environ. Sci. 4 1690
- [23] Brillet J, Yum J-H, Cornuz M, Hisatomi T, Solarska R, Augustynski J, Graetzel M and Sivula K 2012 Nat. Photonics 6 824
- [24] Seol M, Jang J-W, Cho S, Lee J S and Yong K 2013 Chem. Mater. 25 184
- [25] Hoang S, Berglund S P, Hahn N T, Bard A J and Mullins C B 2012 J. Am. Chem. Soc. 134 3659
- [26] Hoang S, Guo S, Hahn N T, Bard A J and Mullins C B 2012 Nano Lett. 12 26
- [27] Gao L, Cui Y, Wang J, Cavalli A, Standing A, Vu T T, Verheijen M A, Haverkort J E, Bakkers E P and Notten P H 2014 Nano Lett. 14 3715

- [28] Yuan G, Zhao H, Liu X, Hasanali Z S, Zou Y, Levine A and Wang D 2009 Angew. Chem., Int. Ed. Engl. 48 9680
- [29] Bolton J R 1996 Sol. Energy 57 37
- [30] Kim H and Yong K 2013 Appl. Phys. Lett. 103 223903
- [31] Kang Q, Lu Q Z, Liu S H, Yang L X, Wen L F, Luo S L and Cai Q Y 2010 Biomaterials 31 3317
- [32] Liu A 2001 Nanotechnology 12 L1
- [33] Takizawa T, Arai S and Nakahara M 1994 Japan. J. Appl. Phys. 33 L643
- [34] Santinacci L, Gonçalves A-M, Simon N and Etcheberry A 2010 Electrochim. Acta 56 878
- [35] Huang S F et al 2014 ACS Appl. Mater. Interfaces 6 12111
- [36] Huang Z P, Fang H and Zhu J 2007 Adv. Mater. 19 744
- [37] Park H, Choi W and Hoffmann M R 2008 J. Mater. Chem. 18 2379
- [38] Banerjee S, Mohapatra S K, Das P P and Misra M 2008 Chem. Mater. 20 6784
- [39] Zhong M et al 2015 J. Am. Chem. Soc. 137 5053
- [40] Kim W, Seol M, Kim H, Miller J B, Gellman A J and Yong K 2013 J. Mater.Chem. 1 9587
- [41] Robel I, Subramanian V, Kuno M and Kamat P V 2006 J. Am. Chem. Soc. 128 2385
- [42] Formal F L, Tétreault N, Cornuz M, Moehl T, Grätzel M and Sivula K 2011 Chem. Sci. 2 737
- [43] Li H, Zhou Y, Chen L, Luo W, Xu Q, Wang X, Xiao M and Zou Z 2013 Nanoscale 5 11933
- [44] Qi H, Wolfe J, Wang D P, Fan J H, Fichou D and Chen Z 2014 Nanoscale 6 13457
- [45] Leever B J, Bailey C A, Marks T J, Hersam M C and Durstock M F 2012 Adv. Energy Mater. 2 120
- [46] Wu X, Ling Y, Liu L and Huang Z 2009 J. Electrochem. Soc. 156 K65
- [47] Lopes T, Andrade L, Ribeiro H A and Mendes 2010 Int. J. Hydrog. Energy 35 11601