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A one-step method to fabricate novel threedimensional GaP nanopore arrays for enhanced photoelectrochemical hydrogen production[†]

Gallium phosphide nanopore arrays with unique three-dimensional interior architectures (3D GaP NPs) are fabricated by electrochemical etching in a neutral solution. As the photoanodes for photoelectrochemical (PEC) hydrogen production, the 3D GaP NPs exhibited a larger photocurrent density (5.65 mA cm⁻² at 0 V vs. RHE, which is 58.3 and 2.3 times as large as that of the planar wafer and the NPs reported by our group in our previous work respectively) and a lower onset potential (-0.58 V vs. RHE, shifting negatively nearly 300 mV compared with its counterparts in the previous work). Besides the excellent light-trapping characteristics of the nanostructures, electrochemical impedance spectroscopy (EIS) further confirmed that the enhanced PEC performance was ascribed to the more efficient charge separation and transfer, and the increased surface area with the unique 3D NP arrays. Furthermore, the efficient charge separation may be attributed to the passivated surface states by the neutral solution.

Solar photoelectrochemical (PEC) hydrogen production is one of the promising technologies that could potentially provide a clear, cost-effective, and domestically produced energy carrier by taking advantage of ~120 000 TW of radiation that strikes the earth's surface.¹ The key factors to realize high efficiency are efficient utilization of solar light, effective collection of photogenerated charges, and fast water splitting reactions.^{2–6} Since Fujishima and Honda first reported the use of n-type TiO₂ for photoelectrochemical water splitting reactions,⁷ significant research efforts have been made to develop suitable semiconductors in photoelectrochemical cells (PECs) to convert sunlight into chemical fuel. Gallium phosphide (GaP) is a promising photoelectrode material for photochemical energy conversion with a mid-sized bandgap ($E_g = 2.26 \text{ eV}$) straddling the reduction and oxidation potential of water⁸ and an extremely negative conduction band, which can balance the driving force well for water splitting and the absorption of solar light.⁹

However, two major drawbacks limit the utilization of GaP in a PEC system. Firstly, its indirect bandgap results in weaker absorption at longer wavelengths.9 Secondly, the short carrier diffusion length $(L_{\rm D})$ in GaP leads to excessive minority carrier recombination.¹⁰ An effective approach to solving this problem is to use high aspect ratio nanostructures, such as nanopore arrays (NPs), to decouple light absorption and carrier collection direction. On the one hand, nanopore arrays allow incident light to scatter within their open interiors (*i.e.*, the light-trapping effect).¹¹ On the other hand, the short axial direction of the pore wall improves the carrier collection and yields low recombination by decreasing the distance the photogenerated charge carriers must travel before collection. In addition, highly ordered nanostructure arrays have extremely high surface areas for fast interfacial charge transfer and more active sites for fast electrochemical reactions,12 which would decrease the overpotential needed at the photoelectrodes.¹³

Although the preparation of porous GaP has been studied extensively,^{14–19} almost all employed hazardous acid solutions and reports on ordered GaP nanopore arrays are scarce.^{20–23} The surface of porous GaP is usually irregular nucleation layer, which is hard to remove, upon the ordered pore arrays.¹⁹ Our group has obtained ordered GaP NPs by a two-step method, which involves immersing the GaP samples into *aqua regia* to dissolve the irregular layer after electrochemical etching in the acid solution.^{24,25} However, the two-step method is a little complicated, and the employed hydrobromic acid (HBr) and highly corrosive *aqua regia* may be dangerous for production on a large scale.

Herein, we report a facile one-step electrochemical etching by substituting a neutral sodium bromide (NaBr) solution for the hydrobromic acid solution with no requirement of *aqua regia*



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Fig. 1 Schematic illustration of (a) a single-crystal GaP wafer before etching, (b) electrochemical etching set-up, (c) the etching voltage curve across the etching process (d) as-etched GaP nanopore arrays with 3D interior architectures and (e) the process of photoelectrochemical hydrogen production.

etching to fabricate well-ordered GaP NPs. As illustrated in Fig. 1, a two-electrode set-up was used for electrochemical etching, and a GaP sample and a graphite electrode were used as the working electrode and the counter electrode, respectively. Besides safety, the use of a neutral electrolyte instead of an acid electrolyte may passivate the surface states, leading to enhanced PEC performance.²⁶ The etching voltage was increased with a scan rate of 20 mV s^{-1} from 0 to 25 V, and was then held for different times (t_c) to obtain nanopores with different lengths (Fig. 1c). Furthermore, as illustrated in Fig. 1d and e, the interior of the nanopore in this work is a novel 3D architecture, which enlarges the surface area, improves light absorption, enables rapid charge separation and interfacial charge transfer, and hence enhances the performance of the PEC. Na₂S and Na₂SO₃ were used as sacrificial reagents to maintain the stability of InP. The mechanism of hydrogen generation is discussed in the ESI.[†]

A J-V curve of the electrochemical etching process is shown in Fig. 2d. The current oscillations observed in Fig. 2d inset may be related to the synchronized pore-diameter oscillations.²⁷ Fig. 2a shows a typical low magnification top-view SEM image of the as-grown 3D GaP NPs, which reveals well-ordered pore arrays within the large area. Fig. 2b further reveals that the nanopore is a triangle with a side length of approximately 90 nm. The size of the nanopore could be adjusted by changing the concentration of the etching solution (Fig. S4, ESI⁺) and the scan rate of the etching voltage (Fig. S5, ESI⁺). The triangular symmetry indicates that the side walls are the (110)-crystal planes, which are the most stable planes in zinc blende structures.²² As shown in the cross-sectional view of the nanopore arrays in Fig. 2c, the interior of the nanopore is a novel 3D architecture with an undulate pore wall, contributing to a larger specific area and enhanced light absorption. The thickness of the wall is about 100 nm or less, which matches with the minority carrier diffusion length



Fig. 2 (a) Low-magnification and (b) high-magnification top-view SEM image of the as-etched 3D GaP nanopore arrays. (c) Cross-sectional SEM image of the 3D GaP NPs. (d) Current density *vs.* voltage curve in the electrochemical etching process. (e) XRD patterns of GaP. (f) Reflectance spectra of a planar GaP wafer and 3D GaP NPs with different etching times.

of n-GaP,¹⁰ reducing the bulk recombination and improving carrier collection. The disappearance of the irregular nucleation layer could be attributed to the polarization etching voltage. A Detailed discussion is presented in the ESI.[†]

XRD patterns obtained from the GaP samples before and after etching (Fig. 2e) matched that of zinc blende GaP (JCPDS Card 32-0397). The peak position was the same for both samples, indicating no change in phase for the GaP after etching.

The total reflectance spectra of the ordered 3D GaP NPs and the GaP wafer in the wavelength range of 250-850 nm are shown in Fig. 2f. The as-etched samples were denoted as t_c , and the GaP wafer was denoted as planar. (The nanopore lengths of the samples are displayed in Fig. S1, ESI.[†]) The light reflectance of the 3D NP sample was significantly reduced compared with the planar wafer in the range below 500 nm, where the photon was mainly absorbed to excite the electron from the valence band to the conduction band. The superior antireflection properties of the 3D NPs can be ascribed to the nanopores that enable strong light trapping and scattering inside, which leads to enhanced optical absorption. As for sub-band gap light (above 500 nm), which made no contribution to the photogenerated charges, the reflectance of the NPs increased sharply and exceeded that of the planar wafer. This can be ascribed to the significant internal reflection in the NP samples.¹⁵

Fig. 3a shows a typical current density–potential (J–V) curve of the 3D GaP NP photoanodes obtained under simulated solar light illumination (100 mW cm⁻²) and under dark conditions. The photocurrent onset potential shifted negatively with an increase in the etching time, which can be attributed to the enhanced light



Fig. 3 PEC measurements of the GaP photoanodes in 0.25 M Na₂SO₃ and 0.35 M Na₂S (pH = 13.35) under illumination of 100 mW cm⁻². (a) Current density vs. potential curves of 3D GaP NPs with different etching times under illumination and dark conditions. Inset shows the curves of the planar GaP wafer and the 300 s sample. (b) Chronoamperometric curves (at 0 V vs. RHE) of the 3D GaP NPs with different etching times and GaP wafers. The illumination was turned on and off for a period of 60 s. Inset shows the planar wafer.

absorption⁹ and more active sites due to the increase of the pore length. The most negative onset potential can reach -0.58 V vs. RHE, shifting negatively, nearly 300 mV, relative to its counterparts in our previous work.²⁵ The dark current density remained at a very low level in the scanned potential range, indicating that almost no chemical reactions occurred in the dark. It can be observed that the photocurrent density of the 3D GaP NPs first increased with the etching time (i.e. pore length) and reached a maximum value at 100 s and then decreased with a further increase in the etching time (*i.e.* pore length). This can be ascribed to the trade-off between the surface area and recombination loss. On the one hand, longer NPs lead to enhanced light absorption and increase the total surface area. On the other hand, the surface states and defects, and hence recombination will also increase with the pore length, resulting in reduced photocurrent. So the optimal time for which the etching voltage is held after polarization is 100 s in this case. The maximum photocurrent is 5.65 mA cm⁻² at 0 V vs. RHE, which is 2.3 times as large as that reported in the previous work,²⁵ even though the illumination employed in the previous work (400 mW cm⁻²) is four times that used in this work. In addition, the maximum photocurrent is 58.3 times that of the planar wafer.

The applied bias photon-to-current efficiency (ABPE) of the 3D GaP NPs (100 s) is shown in Fig. S3 (ESI \dagger). The ABPE was calculated using the following equation.²⁸

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

The ΔG_{rev}^0 in the current study is 0.5 V.²⁹ The maximum ABPE value is 2.82% at about 0 V νs . RHE, which was about 3 times higher than that obtained in our former work.²⁶

To investigate the photoresponse of the 3D NPs, the transient photocurrent measurements of the samples were carried out during repeated on/off illumination cycles at 0 V *versus* RHE (Fig. 3b). The photocurrent attains the steady state quickly upon illumination with low spike, indicating that the fabricated photoanodes display fast light response, which can be attributed to the rapid charge transfer and low recombination at the 3D GaP NP electrodes/electrolyte interface.³⁰ The photocurrent quickly returns to zero once the illumination is switched off, indicating the excellent switching performance of the photoelectrodes. Moreover, the value of the steady state photocurrent is consistent with that shown in Fig. 3a.

Motte–Schottky curves of the wafer and 3D GaP NPs are presented in Fig. 4a and b respectively. Both the plots exhibit positive slopes, indicating that the GaP samples are n-type. The carrier density (N_d) and flat band potential (V_{fb}) can be quantified using the equation given below.

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

By linear fitting, the flat band potential can be determined. The flat band potential ($V_{\rm fb}$) of the planar GaP wafer obtained from the Motte–Schottky curve is about -0.65 V vs. RHE. The dopant density of the planar sample calculated from the slope of the plot is 5×10^{17} cm⁻³, which agrees with the value given by the wafer supplier. And the $V_{\rm fb}$ of the 3D GaP NPs with a maximum photocurrent is about -0.51 V vs. RHE. Actually, the flat band potentials of the GaP NPs with different etching times were similar, which is consistent with ref. 31. Different from ref. 32, the flat band potential and the onset potential of the GaP NPs shifted oppositely from the planar. The difference between $V_{\rm fb}$ and $V_{\rm onset}$ could be attributed to the kinetic overpotentials of the reaction. So the lower onset potentials of the NPs indicated that the nanostructures could decrease the overpotential more efficiently.¹³ More details are given in the ESI.[†]

To gain more insight into the principle of the enhancement of PEC performance, electrochemical impedance spectroscopy (EIS) was performed on GaP NPs etched in different solutions (NaBr or HBr) and planar wafers. As evident in Fig. 4c, the impedance arcs of both NPs were much smaller than that of planar GaP, indicating that porous arrays can significantly facilitate faster interfacial charge transfer and more efficient charge separation due to the increased surface area.³³ Furthermore, the smallest arc of NPs etched in the NaBr solution was observed, suggesting that more efficient separation of photogenerated electron–hole pairs and faster interfacial charge transfer occurred in these NPs compared to those etched in a HBr solution, which may be attributed to the fact that the neutral electrolyte passivates the



Fig. 4 (a) Mott–Schottky plot of the planar GaP wafer. The surface area is 0.25 cm². (b) The Mott–Schottky plot of 3D GaP NPs. (c) The Nyquist plots of the planar wafer and GaP NPs etched in NaBr and HBr solutions. Inset depicts the equivalent circuit model used for fitting and shows an expanded region around the low impedance. (d) Room-temperature photoluminescence spectra of planar GaP and NPs etched in the two different solutions.

surface states and reduces surface defects compared with the acid electrolyte employed in the previous work. This result is consistent with the enhanced PEC performance of the 3D GaP NPs.

Room temperature photoluminescence (PL) spectroscopy was carried out on GaP samples etched in different solutions. As shown in Fig. 4d, the peak positions were red shifted relative to the bandgap of GaP (2.26 eV), which may be ascribed to the levels in the band gap introduced by the surface states.^{34,35} The higher PL signal may indicate more photogenerated carrier recombination resulting from surface state defects. We suspect that etching GaP in a NaBr solution results in passivation of the porous surface states when compared with in a HBr solution.

In summary, we developed a facile one-step electrochemical etching method to fabricate ordered 3D GaP NPs with unique interior architectures. The as-etched 3D GaP NPs exhibited excellent performance for PEC hydrogen production. Owing to the improved surface area, passivated surface states, and hence facilitated photogenerated charge separation and transfer, an onset potential of -0.58 V *vs.* RHE was achieved. The maximum photocurrent reached 5.65 mA cm⁻² (0 V *vs.* RHE), which was 2.3 and 58.3 times as large as that shown in the previous work²⁵ and in the planar wafer, respectively. Further improvements *via* protecting GaP, such as use of TiO₂ overlayers,³⁶ against photocorrosion are expected to stabilize the photoanodes for overall water splitting.

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Conflicts of interest

There are no conflicts to declare.

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