Chapter

Recent Progress in Gallium Nitride for Photoelectrochemical Water Splitting

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Abstract

With the constant consumption of traditional energy sources, it is urgent to explore and develop new energy sources. Photoelectrochemical (PEC) water splitting is a method of preparing energy that can continuously generate hydrogen fuel without pollution to the environment. As an important part of the PEC water splitting system, the choice of semiconductor photoelectrode is crucial. Among these materials, gallium nitride (GaN) has attracted considerable attention due to its tunable band gap, favorable band edge positions, wide band gap, and good stability. In the past years, many reports have been obtained in GaN for PEC water splitting. This review summarizes the GaN as photoelectrodes for PEC water splitting, and methods to improve the efficiency of GaN for PEC water splitting also will be summarized from change morphology, doping, surface modification, and composition of solid solution or multiple-metal incorporation. Eventually, the future research directions and challenges of GaN for PEC water splitting are also discussed.

Keywords: photoelectrochemical water splitting, GaN, semiconductor

1. Introduction

Rising energy demand due to population growth has led to the rapid consumption of fossil fuels and serious environmental problems [1]. Currently, most of the world's energy comes from fossil fuels, which will eventually lead to its predictable depletion. The decline of fossil energy reserves and the urgency to reduce greenhouse gas emissions to alleviate climate warming is forcing us to seek a cleaner, more renewable, and sustainable alternative energy source [2, 3]. Hydrogen is considered as a future ideal energy carrier to replace fossil fuels due to its high gravimetric energy density and zero carbon emissions [4–6]. But the achievement of this clean energy scheme largely depends on economically efficient hydrogen production technologies. At present, the industrial production of hydrogen is mainly realized by the reforming of hydrocarbon steam in fossil energy or coal through reaction to fossil fuels under the control of steam, which is not only expensive but also causes large emissions [7, 8]. Therefore, the use of renewable energy to produce hydrogen is considered, despite challenges stand in the way [7, 9].

In recent years, solar energy has attracted much attention as the largest renewable energy source on the planet. If solar energy can be effectively used, it will

provide a continuous supply of energy for future energy [10, 11]. However, the vision of solar power to provide a significant portion of the global infrastructure is far from being realized. The main challenge comes from not having a cost-effective way to store solar energy. Solar water splitting is a prospective, environmentally friendly, and sustainable method to achieve this beautiful vision [10, 12, 13]. There are three types of solar water decomposition systems, photovoltaic electrolysis (PV-E), photochemical (PC) systems, and photoelectrochemical (PEC) cells, as shown in **Figure 1**. PV-E is achieved by connecting the photovoltaic cell and water electrolyzer. The advantage of this strategy is its solar-hydrogen conversion efficiency of more than 10%, but it is still too expensive compared to traditional hydrogen production methods [14–18]. The maturity of PV-E technology also determines that it is difficult to improve efficiency, so it is particularly important to find economical and suitable solar-hydrogen conversion methods. PC is a simple and cost-effective solar-hydrogen conversion method, but its conversion efficiency is less than 1%. In addition, the potentially explosive hydrogen-oxygen mixture produced requires expensive equipment for separation to avoid reaction, which greatly increases production costs [19]. In this case, PEC provides considerable conversion efficiency at an affordable cost [20, 21]. PEC integrates the light absorption and electrochemical processes of PV-E into a single unit. Two gases generated separately at the anode and cathode avoid further separation, which is helpful for reducing costs. If the conversion efficiency can reach 10% and the life span reaches 5 years, PEC is expected to be a replacement for traditional hydrogen production methods [22–24].

Basically, solar energy is converted into chemical energy stored in the form of hydrogen molecules by PEC devices [25, 26]. And a PEC device usually includes a metal electrode and a semiconductor photoelectrode. Ideally, semiconductors need to have a proper band gap and band structure to provide sufficient reaction potential and cover the solar spectrum as much as possible. In addition, excellent carrier transport performance and good physicochemical stability are also essential. Although a large number of semiconductor materials such as ZnO [27, 28], TiO_2 [29, 30], WO_3 [31, 32], and $BiVO_4$ [33, 34] have been studied for photohydrolysis experiments, no dependent material meets all the critical conditions described above. Usually, overall water splitting consists of two half-reactions: oxidation of water and reduction of protons.

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 \; E_{ox} = +1.23\ V \quad (1)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \quad E_{red} = 0\ V \quad (2)$$

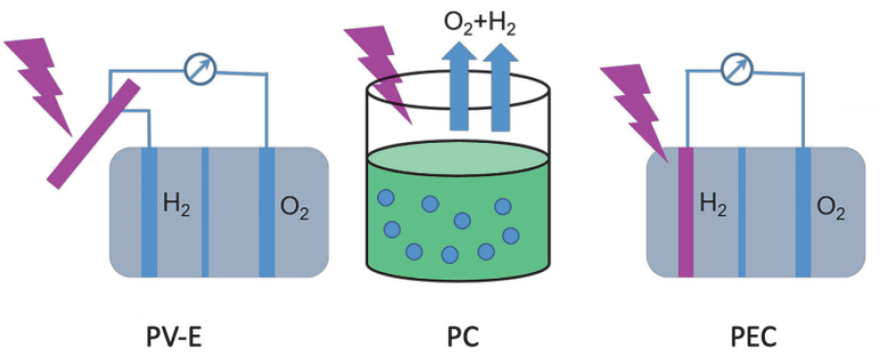

Figure 1.
Schematic of three types of solar water splitting system: PV-E, PC system, and PEC cell.

It can be seen from the equation that the minimum voltage for water splitting is 1.23 V, which requires that the energy absorbed by exciting an electron is not less than 1.23 eV. In order to meet this requirement, the photon energy absorbed by the photoelectrode must also be at least 1.23 eV. But in fact, the energy required due to the energy loss caused by the failure to reach the ideal structure is far more than 1.23 eV [35, 36].

In general, PEC water splitting includes the following processes:

1. Under light irradiation, carriers are generated in the semiconductor with a suitable band gap.

2. Photogenerated carriers separate and migrate to the surface of the semiconductor.

3. Redox reactions are induced by photogenerated carriers on semiconductor surfaces (**Figure 2**) [37, 38].

The number of photogenerated carriers is determined by the absorption efficiency of the semiconductor, which also reflects the utilization of sunlight. The separation and migration processes of carriers are related to how many can reach the semiconductor surface. Unfortunately, some carriers are lost resulting from recombining on their way to the surface. And the carriers that reach the surface of the semiconductor want to trigger an efficient water splitting reaction, which must meet the following requirements. First, the conduction band edge potential of the semiconductor material should be lower than H_2 evolution potential, while the valence band edge potential should be higher than O_2 evolution potential [39]. This means that the band gap of the semiconductor should be greater than 1.23 eV. Semiconductor materials need to have stronger absorption in the solar spectrum to generate more photogenerated carriers. Although wide band gap semiconductor materials are likely to meet matching at the band edge positions, the absorption of sunlight is very limited [7, 9, 40]. Second, carriers need to be separated and transmitted quickly to reduce recombination, thereby improving the utilization efficiency of photogenerated carriers for PEC water splitting. Finally, materials used for PEC water splitting should be cost-effective and have good stability in the catalytic process [41].

Among semiconductor materials commonly used in PEC water splitting, gallium nitride (GaN) has been regarded as a promising candidate [42, 43]. GaN is likely to

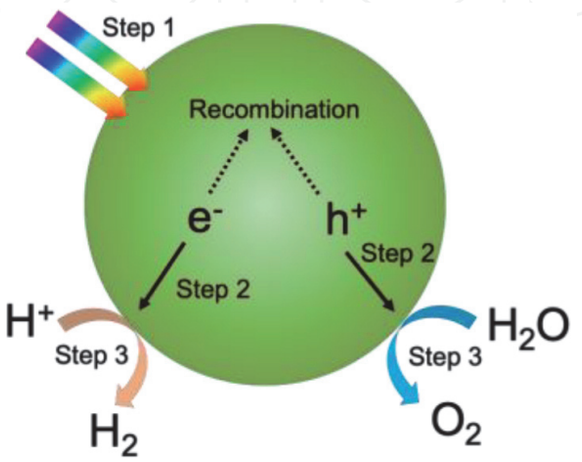

Figure 2.
Schematic illustration of typical PEC water splitting.

achieve self-driven overall water splitting because its band gap has good energy alignment with the water redox potential [43, 44]. In addition, GaN is inherently chemically inert even in a harsh environment, which guarantees the stability of the device [45, 46]. Furthermore, the band gap of GaN and its alloys can be tuned by alloying with Indium (In) to span nearly the entire solar spectrum [47, 48]. However, to achieve practical hydrogen production, GaN is still facing many challenges as an excellent photoelectrode material, including how to get a larger reaction area, how to enhance the absorption of light, and how to separate and transport photogenerated carriers more quickly and effectively [49, 50]. Correspondingly, many strategies have been proposed to address the mentioned drawbacks of GaN photoelectrode. Compared with thin-film and bulk counterpart, nanostructures have a smaller size and a larger surface area, which is helpful for shortening the transmission distance and promotes the separation of carriers. Thus the efficiency of carrier collection and utilization will be higher [51–53]. Doping is also one of the commonly used approaches to effectively improve the electrical and optical properties of GaN, which can directly tune the energy band structure and carrier transmission [54, 55]. Moreover, PEC water splitting kinetics can be promoted through the surface decoration of co-catalysts, which can enhance the transmission of carriers for water redox reaction [56, 57].

In this review, we summarize the recent progress of using GaN as photoelectrode for PEC water splitting and enumerate some commonly used strategies to improve the performance of photoelectrode. In the end, we also have a brief outlook of GaN for PEC water splitting.

2. Basic principles of solar water splitting

2.1 PEC cell configurations

In the introduction section, we briefly introduced the three types of solar water splitting. In this section, we will focus on the different structures of the PEC cell, which can be achieved by an n-type semiconductor as photoanode (or p-type semiconductor as photocathode) or connecting two different semiconductors.

For a semiconductor PEC cell with a half-reaction to occur on working electrode, a counter electrode is required to complete the other half-reaction circuit. Generally, a reference electrode is connected to the working electrode to characterize an externally applied voltage. If necessary, there are two compartments or ion exchange membranes between the working and counter electrodes to avoid product crossover. To overcome the thermodynamic obstacles of water splitting and the potential losses caused by the recombination process, the band gap of the working electrode is at least 1.6 eV [58–60]. However, the visible light absorption efficiency will be attenuated if the band gap is too wide. To solve this problem, that is, potential loss mechanisms that include reverse contact and overpotential caused by poor catalytic activity, the semiconductor material should be deposited on a highly conductive substrate to form a good ohmic contact, which allows most carriers to be quickly injected from the working electrode into the counter electrode [61, 62].

Obtaining enough photovoltage from a single photoelectrode to achieve solar water splitting is a challenge. It will be more favorable that combinates with dual semiconductors, because the second photoelectrode can replace the opposite electrode where the other half-reaction occurs and compensate for the lack of photovoltage [7]. To increase the light utilization, lighting should be irradiated from a larger band gap photoelectrode (transparent substrate) to a smaller band gap photoelectrode. In addition, these two semiconductors can form wireless

back-to-back ohmic contacts, sharing a transparent conductive substrate [63]. By doing so, the potential loss in the electrolyte and the pH gradient between the two photoelectrodes can be reduced. Similarly, lighting should pass from a larger band gap material to a smaller band gap material. This series of battery structure is a relatively effective device [64].

2.2 Calculation of efficiencies

Comparing onset potentials and photocurrent density (normalized to the projected surface area of the photoelectrode) at 1.23 V versus RHE (photoanode) and 0 V versus RHE (photocathode) is a well-known method to evaluate the performance of water splitting. Since the product of water splitting is hydrogen, solar-to-hydrogen (STH) is the most critical parameter of merit to evaluate the performance and the efficiency of PEC water splitting on the device. It is defined as the following equation: [65].

$$\eta_{STH} = \left[\frac{\Phi_{H_2}(mols^{-1}m^{-2}) \times G^0_{f,H_2}(kJmol^{-1})}{P_{light}(Wm^{-2})}\right]_{AM\ 1.5G} \tag{3}$$

where Φ_{H2} is the hydrogen gas production rate, G^0_{f,H_2} is the Gibbs free energy of hydrogen gas (237 kJ mol^{-1} at 25°C), and P_{light} is the total solar irradiation input. The light source should match the solar spectrum of air mass 1.5 global (AM1.5 G). Since the redox reaction needs to consider the current loss, the Faraday efficiency needs to be considered. So, the STH formula is expressed as:

$$\eta_{STH} = \left[\frac{J_{SC}(mAcm^{-2}) \times 1.23\ V \times \eta_F}{P_{light}(mWm^{-2})}\right]_{AM\ 1.5G} \tag{4}$$

In general, J_{SC} can use current density instead of under zero bias and stable-state conditions. Applied bias photon to current conversion efficiency (ABPE) is also an important parameter for PEC water splitting systems, which is often used to evaluate the performance of a single photoelectrode independently. It can be written as: [65].

$$\text{ABPE} = \left[\frac{J_{SC}(mAcm^{-2})(\times 1.23\ V - V_{app}) \times \eta_F}{P_{light}(mWm^{-2})}\right]_{AM\ 1.5G} \tag{5}$$

where V_{app} is the applied potential between photoelectrode and the counter electrode.

It is important to understand the efficiency of photons to convert electrons/holes at certain wavelengths of PEC water splitting. Therefore, the incident photon-to-current conversion efficiency (IPCE) or external quantum efficiency (EQE) is proposed and expressed as: [65].

$$\text{IPCE}(\lambda) = \text{EQE}(\lambda) = \frac{electronflux\ (mols^{-1})}{photonflux\ (mols^{-1})} = \frac{|j_{ph}(mAcm^{-2})| \times hc\ (Vm)}{P_\lambda(mWcm^{-2}) \times \lambda(nm)} \tag{6}$$

where λ is the wavelength, P_λ is the incident light power, h is Planck's constant, c is the speed of light, and j_{ph} is the photocurrent density. Besides, integrating the IPCE value with the standard AM1.5G solar spectrum can estimate the total photocurrent density under solar light illumination. Its formula is defined as: [65].

$$J_{AM\ 1.5} = \int (IPCE_{\lambda} \times \Phi_{\lambda} \times e) d\lambda \quad (7)$$

where e is the elementary electron and Φ_{λ} is photon flux of irradiation.

3. Approaches to increase GaN-based PEC water splitting efficiency

3.1 Surface decoration

Up to now, considerable efforts have been investigated on surface decoration to enhance PEC water splitting performance [66]. In this regard, various co-catalysts were studied by depositing on the surface of GaN to improve the efficiency of PEC water splitting. For instance, the quantum efficiency of the solid solution of GaN and ZnO for overall water splitting in the visible light region achieves the highest value of 2–3% after modified with a mixed oxide of Rh and Cr nanoparticles [67]. A Co-Pi catalyst photoelectron deposited on GaN thin-film photoelectrodes eliminated the anomalous two-plateau behavior and current spikes, which revealed that the Co-Pi catalyst is helpful for suppressing surface recombination and increases the photocurrent [47]. A similar but deeper achievement was carried out by Tricoli et al. for hybridizing highly transparent Co_3O_4 nano-island catalysts on GaN nanowire to enhance the water oxidation activity. The result shows that the per-metal turnover frequencies in 1 M NaOH aqueous solution are 0.34–0.65 s^{-1} at an overpotential of 400 mV, which is the best result of Co-based electrocatalysts until this report. This was attributed to Co_3O_4 that can play a role as hole scavenger, collecting photogenerated holes rapidly and suppressing carrier recombination [68]. Additionally, a size-controlled effect of poly-protected Rh nanoparticles on the photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ was studied by Teranishi et al. for the first time. Their results show that the activity of smaller Rh cores is higher than the larger ones, which benefits from its increased surface area and improves charge separation efficiency [69]. This study was inconsistent with the previous report by Kamat et al. The greater the shift in the Fermi level observed in smaller gold nanoparticles, which is reflected in the higher photocatalytic reduction efficiency, the stronger the photocurrent [70].

Apart from nanoparticles, core-shell heterostructure is another important approach for surface decoration. GaN-InGaN core-shell rod arrays as photoanode for visible light-driven water splitting were studied by Waag et al. The core-shell structure extends the use of sunlight to the visible light region, thereby greatly improving the efficiency of water splitting. The photocurrent density of (0.3 mA/cm^2 at 1.35 V) GaN-InGaN was 10-fold higher than that of GaN (0.03 mA/cm^2 at 1.35 V), as shown in **Figure 3** [71]. Mi et al. employed GaN-InGaN core-shell nanowire for PEC water splitting, and the high incident photon-to-current conversion efficiency of up to ~27% is obtained [72]. It is expected to achieve higher PEC activity by surface treatment of GaN. And as far as the current development is concerned, it is foreseeable that surface modification is still a good strategy to achieve efficient water splitting.

3.2 GaN material having different morphologies

As an important part of the PEC water splitting system, the morphology of semiconductor materials is very important. Different morphologies have a great influence on the efficiency of PEC water splitting. Many different morphologies of GaN for PEC water splitting have been proposed. Xi and co-workers used

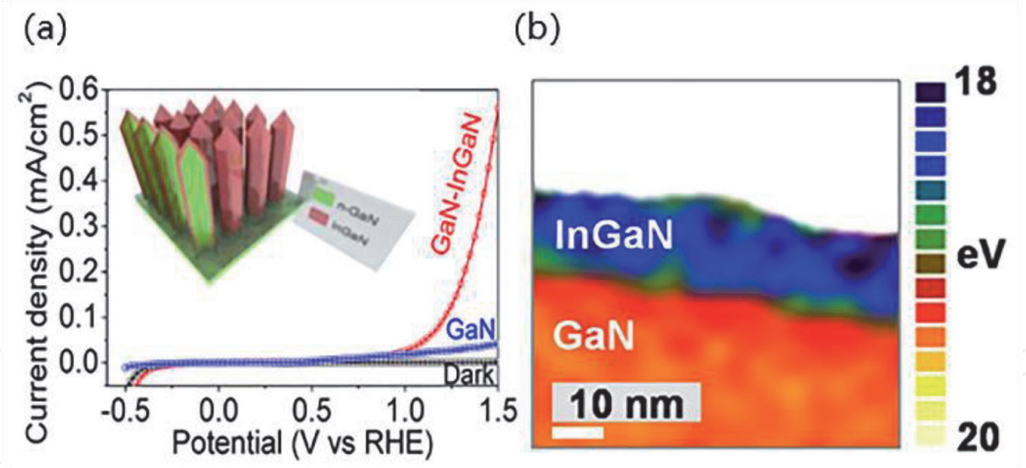

Figure 3.
(a) Current density of 3D GaN-InGaN core-shell rod array (red) and 3D GaN rod array (blue) in 0.01 M H_2SO_4 solution under 100 mW/cm² illumination using AM 1.5 filter [71]. (b) Plasmon energy map in the highlighted region showing the indium incorporation in the InGaN shell [71]. (a and b) Reproduced from Ref. [71] with permission from the American Chemical Society.

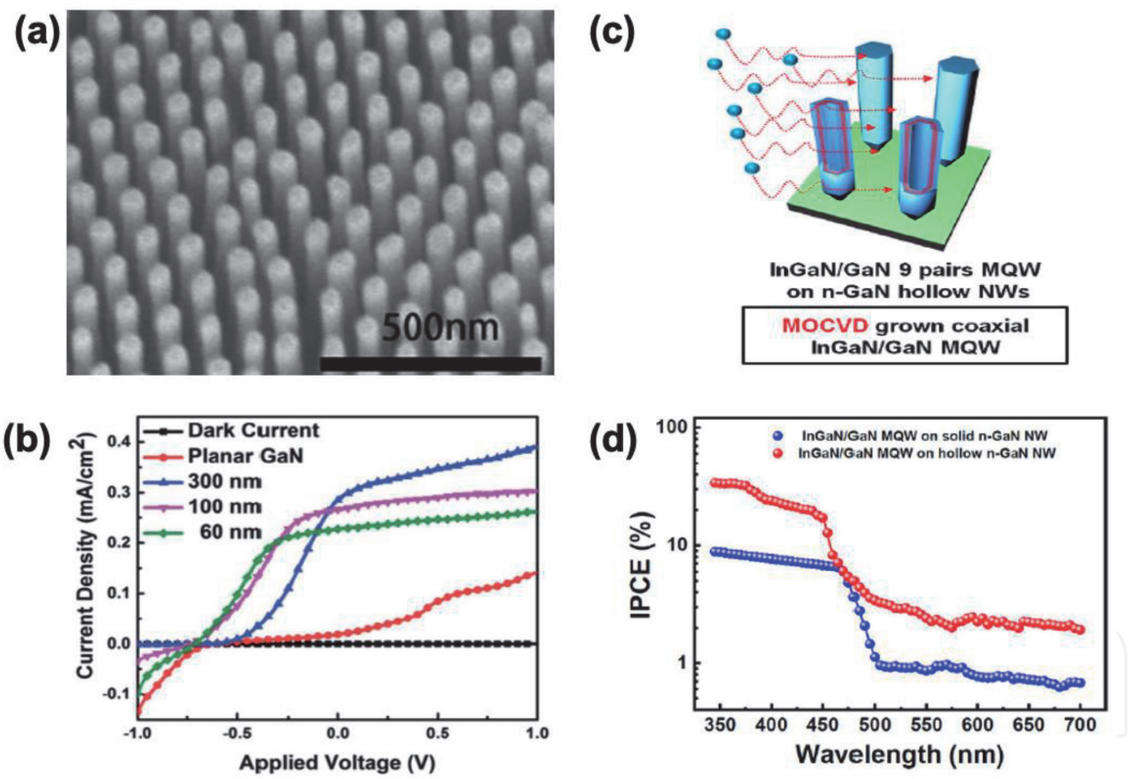

Figure 4.
(a) SEM images of GaN nanowires, (b) linear sweep voltammetry of GaN nanowires with diameters of 60, 100, and 300 nm and planar GaN [73]. (c) Structure schematic of InGaN/GaN MQW on n-GaN hollow NWs, (d) comparison of IPCE values for InGaN/GaN MQWs grown on solid and hollow n-GaN nanowires [74]. (a and b) Reproduced from Ref. [73] with permission from The Royal Society of Chemistry. (c and d) Reproduced from Ref. [74] with permission from Springer Nature.

metal–organic chemical vapor deposition (MOCVD) to fabricate GaN nanowires, and it has obtained high photocurrent density value at an applied bias voltage from −1 to 1 V [73]. Its morphology was shown in **Figure 4a**. It can be found from **Figure 4b** that compared to the planar structure and other diameters, 300 nm has a stronger current density due to a larger body-to-surface ratio, thereby increasing the efficiency of PEC water splitting. GaN microwires still have problems such as low crystal quality and light absorption. To further improve the efficiency of PEC

water splitting, Park et al. used the plasma-assisted molecular beam epitaxy (PAMBE) technique to grow InGaN/GaN multiple quantum wells (MQWs) grown on hollow n-GaN nanowires (**Figure 4c**) [74]. The hollow and InGaN/GaN multiple quantum well structures of the nanowires allow the incident light to be refracted multiple times, increasing the absorption of light. **Figure 4d** shows the incident photon-to-current conversion efficiency value of the device, which can be found that the highest IPCE value of the device is as high as 33.3% and 415 μmol of hydrogen gas was generated within 1 hour.

Nanopores, nanocones, and honeycombs are other nanostructures of GaN. **Figure 5a** shows the GaN nanopore structure [43], nanopore structure used electrochemical lateral etching and ICP etching to prepare laterally porous, vertically holes well-ordered GaN. This structure reduces the UV reflectivity. The ordered vertical holes not only help open the embedded channels to the electrolyte on both sides and reduce the migration distance of bubbles in the water splitting reaction but also help to modulate the light field. Incident light can be modulated and captured into the nanopore to enhance the absorption of light, so the saturation photocurrent was 4.5 times that of the planar structure, as shown in **Figure 5d**. Moreover, GaN with aligned nanopore structure had been fabricated by combining MOCVD using a lateral anodic etching, as shown in **Figure 5b** [75]. Laterally porous 3D hierarchical nanostructures not only provided a large contact area between the electrode and the electrolyte but also increased the absorption of light and provided a channel for the transmission of light and electrons. The device also achieved high values of photocurrent of 0.32 mA/cm^2 by using etching voltages at 10 V (**Figure 5e**). Kim et al. had prepared GaN truncated nanocones [76], which was shown in **Figure 5c**. GaN truncated nanocones have concentrated incident light inside the nanostructure and enhanced the light trapping with reduced light losses from surface reflection. The relationship between current density and potential was shown in **Figure 5f**, which indicated that the photocurrent of GaN truncated nanocones was three times higher than the planar structure.

The above structures are expected, and GaN can also have nanorods [77], nanocolumns [78], nano-pyramids [79], and so on. It can be known from the above results that changing the morphology of GaN influences the efficiency of PEC water

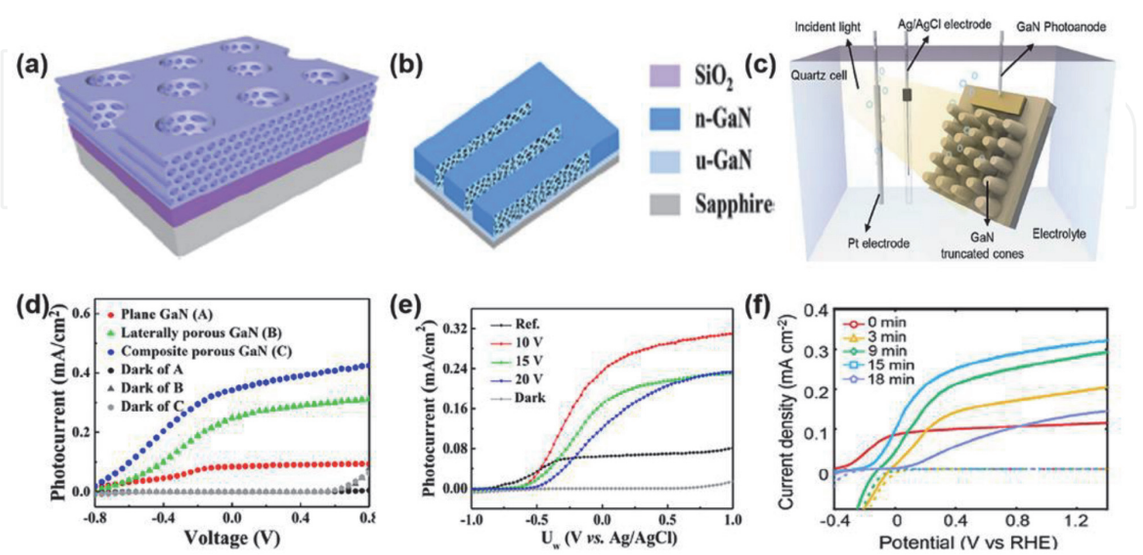

Figure 5.
(a) [43], (b) [75], and (c) [76] are the structure schematics of the composite porous GaN, laterally porous GaN, and photoelectrochemical cell, respectively. (d) Relation curves between photocurrent density and voltage of the above three GaN photoelectrodes [43]. (e) The photocurrent and applied current curves under different GaN etching voltages [75]. (f) Dark (segment) and illumination (straight) conditions for photocurrent density in linear scanning voltammetry [76]. (a and d), (b and e), and (c and f) reproduced from Ref. [43, 75, 76], respectively, with permission from the American Chemical Society.

splitting, which mainly affects the light absorption efficiency of GaN and reduces light reflection and loss. Therefore, it is very important to choose the appropriate semiconductor morphology for PEC water splitting system.

3.3 GaN material having different doping

Doping is a commonly used and effective method to improve the performance of materials. It mainly adjusts the energy band of the material, so that the photogenerated electrons and holes are better transported and high efficiency of PEC water splitting is obtained. Zhou and co-workers doped ZnO-GaN (GZNO) solid solution with La, as shown in **Figure 6a** [80]. La-dopant incorporation is optimized to adjust the bending of the band gap, which increases the thickness of the space charge region, thereby improving the separation of photogenerated carriers. **Figure 6c** shows the photocatalytic performance of GZNO and 3% La GZNO. It can be clearly seen that the photocatalyst doped with La produces more hydrogen and oxygen under the same conditions, which indicates that the performance of the photocatalyst is significantly improved after doping. **Figure 6b** shows the schematic of Ni-doped AlN and two-dimensional GaN monolayers [81]. By controlling the doping content of Ni, it can adjust the band bending of GaN. **Figure 6d** displays the binding strength of GaN and AlN composites with different transition metals doped. It can be found that Ni doping is the best for OER because they have small OER overpotentials.

GaN doped with Mn [82], Mg [83], or CrO are also reported [84]. Doping is also a good method to improve the efficiency of PEC water splitting. It mainly adjusts the energy band of GaN through doping, thereby promoting the separation of photogenerated electrons and holes and effectively preventing the recombination of

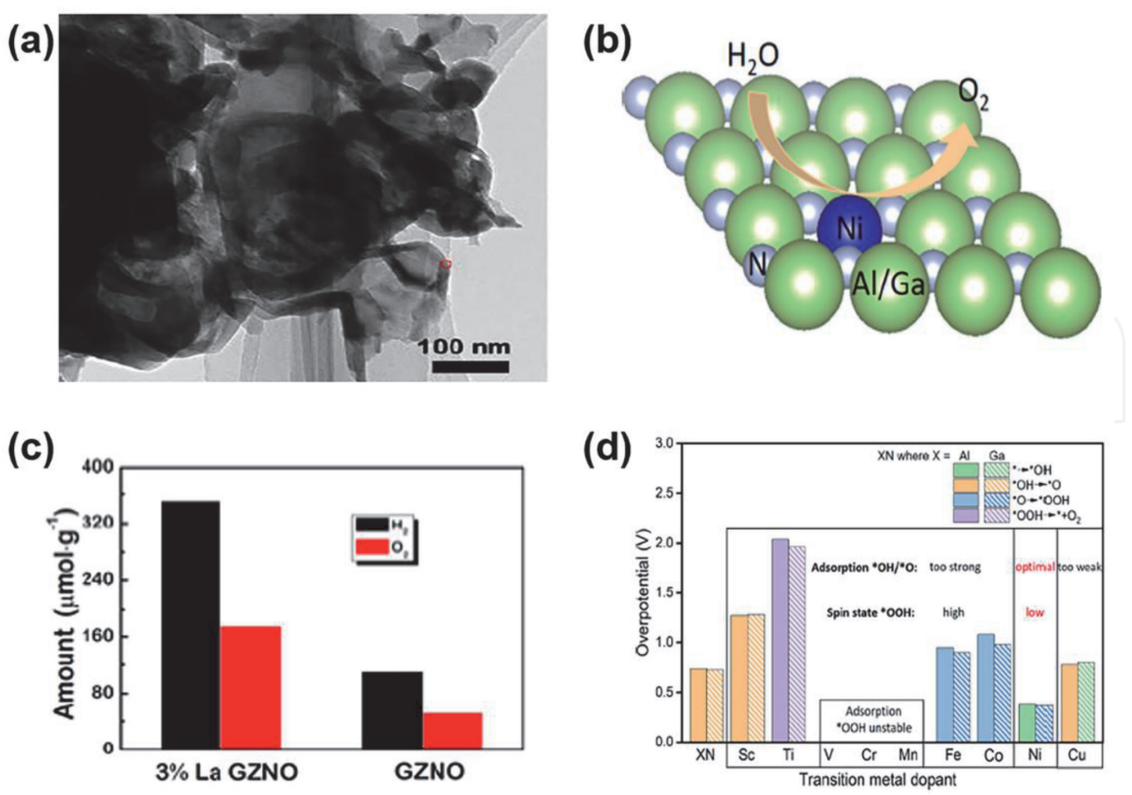

Figure 6.
(a) TEM images of 3% La GZNO [80]. (b) Schematic diagram of Ni-doped structure [81]. (c) The amount of H_2 and O_2 produced by overall water splitting after 8 hours of GZNO and 3% La GZNO [80]. (d) Binding strength of OH or O of different transition metal-doped GaN and AlN composites [81]. (a and c) Reproduced from Ref. [73] with permission from The Royal Society of Chemistry. (b and d) Reproduced from Ref. [74] with permission from the American Chemical Society.

carriers. However, excessive doping will deteriorate the crystal quality of the material. So, it is important to choose the doping material and control dopant incorporation.

3.4 Composition of solid solution

The solid solution is a wurtzite structure composite material composed of GaN and ZnO mixed in a certain proportion. It adjusts the doping content of ZnO to change the band gap of the solid solution and realizes PEC of water splitting under the visible light. This concept was first proposed by Maeda and co-workers [85]. And then, Ohno et al. used $Rh_{2-y}Cr_yO_3$ nanoparticles to modify the solid solution, and the device shows outstanding stability; it has been working continuously for half a year under light irradiation, as shown in **Figure 7a** [86]. The co-catalyst is beneficial to suppress the oxidative decomposition of the solid solution, thereby making the device more stable. NiCoFeP and flux-assisted method can also be used to modify the solid solution to improve the efficiency of PEC water splitting [87, 88]. The conversion efficiency of solar energy using NiCoFeP-modified solid solution exceeds 1% at 1.23 V vs. RHE. To further improve the efficiency of PEC water splitting, solid solution nanosheets modified with Rh nanoparticles have been proposed, as shown in **Figure 7d** [89]. This shows 0.7 μmol h^{-1} g^{-1} of hydrogen production in an aqueous H_2SO_4 solution. The nitridation process was used to change the morphology from hexagonal 2D $ZnGa_2O_4$ nanosheets to 2D $(GaN)_{1-x}(ZnO)_x$ nanosheets, reducing the path of carrier transportation and decreasing the recombination of electrons and holes. So, the composition of a solid solution or multiple-metal incorporation can expand the light absorption range of the device, improving the absorption of light and increasing the efficiency of PEC water splitting.

3.5 The multiple-metal incorporation

The method of forming multiple-metal incorporation is similar to that of a solid solution. Different In content incorporation can change the band gap of GaN to widen the absorption spectrum range. Many different multiple-metal incorporations have been proposed [90–94]. AlOtaibi et al. grown InGaN/GaN core-shell

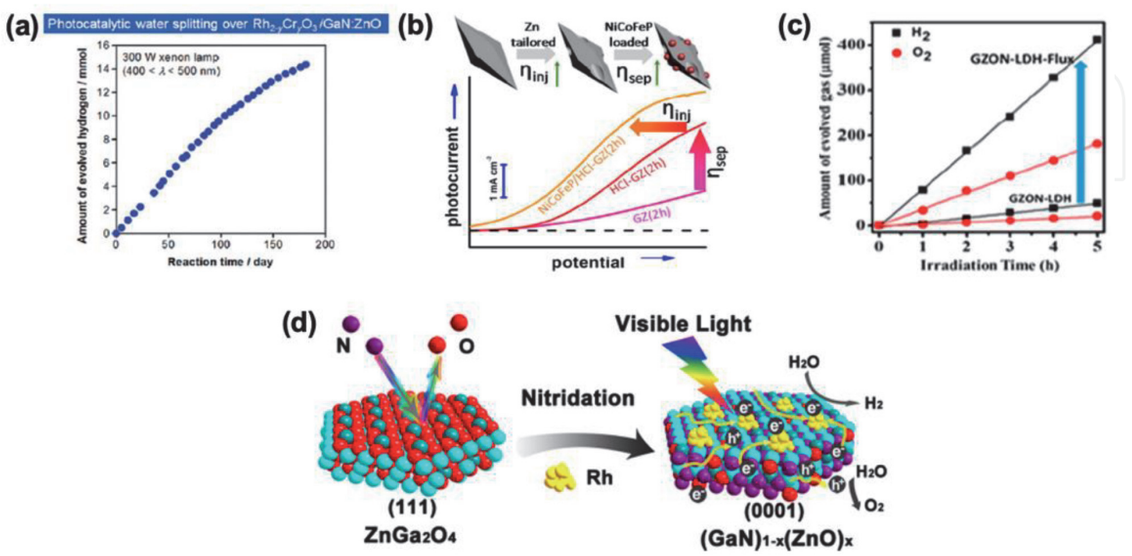

Figure 7.
(a) Curve of total hydrogen production over time [86]. (b) The relationship between photocurrent and voltage for GaN-ZnO in different ways of treatment [87]. (c) Variation curve of the amount of hydrogen and oxygen produced with time of $(GaN)_{1-x}(ZnO)_x$ solid solutions from Zn_2Ga-LDH modified with $Rh_{2-y}CryO_3$ nanoparticles [88]. (d) Structure conversion flowchart from 2D $ZnGa_2O_4$ to 2D $(GaN)_{1-x}(ZnO)_x$ [89]. (a–d) Reproduced from Ref. 86–89 with permission from the American Chemical Society.

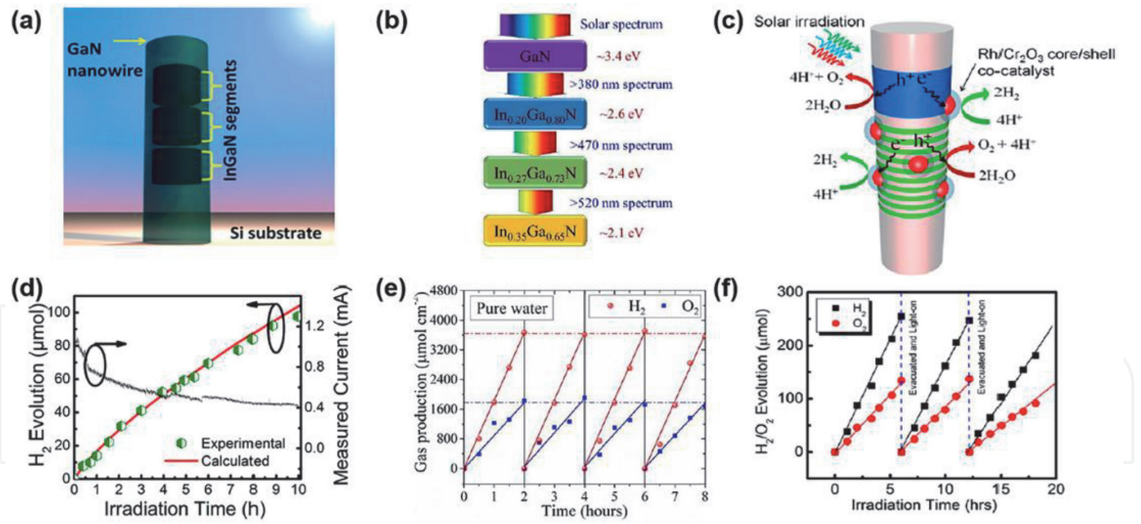

Figure 8.
(a) Schematic of the InGaN/GaN core-shell structure [72]. (b) Schematic diagram of ideal light absorption structure of a multiband InGaN stack with different indium compositions [95]. (c) Schematic diagram of photocatalytic overall water splitting reaction mechanism [48]. (d) Hydrogen production in 1 mol/L HBr at 0.2 V vs. the counter electrode [72]. (e) Hydrogen and oxygen produced as a function of time under multiple experiment cycles [95]. (f) Hydrogen and oxygen evolution as a function of irradiation time under full arc (>300 nm) 300 W xenon lamp irradiation [48]. (a and d) and (c and e) Reproduced from Ref. [48, 72] with permission from the American Chemical Society. (b and f) Reproduced from Ref. [95] with permission from The Royal Society of Chemistry.

nanowire arrays on Si substrate by catalyst-free MBE, as shown in **Figure 8a** [72]. It has a photoelectric conversion efficiency of up to 27% under ultraviolet and visible light irradiation. The photoelectrode continued to work for 10 hours, and the hydrogen production was consistent with the theoretical value (**Figure 8d**), which indicates that the photoelectrode has good stability and hydrogen production ability. And the quadruple-band InGaN nanowire arrays were integrated on a nonpolar substrate, which includes $In_{0.35}Ga_{0.65}N$, $In_{0.27}Ga_{0.73}N$, $In_{0.20}Ga_{0.80}N$, and GaN and exhibits a solar-to-hydrogen efficiency of ~5.2% in a relatively stable state (**Figure 8b**) [95]. Multiband nanowire arrays enhance light absorption to improve the performance of PEC water splitting. Moreover, the multiband nanowire array photoelectrode has good stability and high photocatalyst efficiency for overall water splitting, as shown in **Figure 8e**. To improve the efficiency of the photolysis of water, InGaN heterostructures have been proposed. Kibria and co-workers have fabricated InGaN/GaN nanowire heterostructures, in which the internal quantum efficiency is about 13% [48]. The nanowire heterostructure is shown in **Figure 8c**. The combination of GaN and InGaN expands the light absorption range of GaN from ultraviolet light to visible light, which greatly improves the light absorption range and improves the efficiency of photolysis. The InGaN/GaN nanowire heterostructure photoelectrode also exhibits extremely high stability and high hydrogen production capabilities, as shown in **Figure 8f**. Moreover, nanowire arrays [96], tunnel junction nanowire [97], have also been reported.

In summary, the multiple-metal incorporation can greatly improve the efficiency of PEC water splitting of GaN. The structures and In content will greatly affect the efficiency of PEC water splitting. So, it is important to choose a suitable structure and the In content while preparing the GaN-based photoelectrode.

4. Conclusion

This review mainly introduces the application of GaN in the PEC water splitting system and summarizes the methods to improve the efficiency of PEC water

splitting. The methods to enhance efficiency are mainly carried out in the following four aspects, such as morphology, doping, surface modification, and composition of solid solution or multiple-metal incorporation. Up to now, GaN has made great progress in the application of PEC water splitting; the solar-to-hydrogen efficiency of 12.6% has already been obtained without any external bias [98], better than CoP catalyst electrodes (6.7%) reported recently [99], but it still not as excellent as TiO_2 (18.5%) [100]. And its properties need to be further optimized to improve the absorption efficiency of visible light, increase the carrier migration speed, and facilitate carrier transport. The follow-up works are suggested from the following aspects:

1. At present, most water splitting processes are carried out in alkaline or acidic solutions. It should be considered how to ensure the stability and catalytic activity of metal nitrides for a long time.

2. Although the theory of water splitting is simple, the reaction process is still not clear, and in-depth study of the mechanism is helpful for the design of the catalyst.

3. Reasonable design of the composition and structure of the catalyst to adjust its electronic structure, band gap, band edge potential, and microstructure help to improve the catalytic performance. We believe that with the deepening of research, the efficiency of GaN for water splitting can be further promoted.

Conflict of interest

The authors declare no conflict of interest.

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