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# One-dimensional III-nitrides: towards ultrahigh efficiency, ultrahigh stability artificial photosynthesis

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The depletion of carbon-based fuels and emerging environmental problems are more than ever driving the demand for green energy sources. Artificial photosynthesis demonstrated by catalytically active semiconductors can convert solar energy into storable energy sources such as hydrogen and carbon products by water splitting and carbon dioxide reduction reaction, respectively. Semiconductors with one-dimensional (1D) nanostructures have gained tremendous attention due to their large surface area and enhanced light absorption. However, semiconductor nanostructures suffer from degradation caused by oxidation, corrosion, and undesirable changes in morphology during reaction in aqueous electrolytes. In this review, 1D nanostructured III-nitrides are introduced to offer a comprehensive overview of their synthesis methods, unique structural, electronic, optical, surface, and catalytic properties, as well as their efficiency, and stability for artificial photosynthesis. Band gap engineering and tandem stacking of 1D III-nitrides for broadband light absorption are highlighted. Recent findings on the inherent catalytic activity and stability of 1D III-nitrides are presented. Furthermore, this paper summarizes the ability of cocatalysts integrated on 1D III-nitrides to overcome the performance bottlenecks of water splitting and CO<sub>2</sub> reduction reactions. Finally, the challenges of 1D III-nitrides for practical application of photo(electro)chemical reactions and prospective insights for future development are provided.

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## 1. Introduction

A massive amount of energy is consumed to maintain daily human life and most of the energy depends on fossil fuels such as petroleum, coal, and natural gas. However, the depletion of

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*thesis including water splitting, CO<sub>2</sub> conversion, NH<sub>3</sub> synthesis, and C–N coupling.*

fossil fuels propel the cost of energy and emerging environmental issues, which are driving the demand for green energy technology. In this regard, hydrogen ( $H_2$ ) fuel has attracted a lot of attention as an alternative future energy source because high-purity  $H_2$  gas can be produced from earth-abundant water resources with zero greenhouse gas emissions.<sup>1,2</sup> Along with alternative  $H_2$  fuels, carbon dioxide ( $CO_2$ ) recycling is being extensively studied as a future energy technology.<sup>3,4</sup>  $CO_2$ , the main cause of global warming, can be converted into value-added chemicals through catalytic reactions. Inspired by photosynthesis, which transforms  $CO_2$  and  $H_2O$  into hydrocarbons using solar energy in the natural carbon cycle, artificial photosynthetic devices have been developed to convert solar energy to  $H_2$  fuel or carbon-based chemicals using  $CO_2$  and  $H_2O$ .<sup>5-9</sup> Up to now, efficient artificial photosynthetic devices for  $H_2$  production and  $CO_2$  recycling have been demonstrated by the integration of semiconductors and cocatalysts. In this configuration, semiconductor materials absorb the light and excite photogenerated electrons and holes into conduction and valence bands, respectively. The photogenerated charge carriers then separate and migrate to the cocatalyst surface to participate in redox reactions. Therefore, artificial photosynthetic devices must overcome the technical challenges of limited light absorption, inefficient charge carrier separation/transfer, and low catalytic activity before they can be put to practical use.

Over past decades, the rapid development of nanotechnology has enabled the fabrication of nanostructured semiconductors in 1-dimensional (1D) morphology, including nanowires, nanorods, and nanofibers.<sup>10</sup> These 1D semiconductors have shown distinct physical and chemical characteristics different from their planar counterparts. The large surface-to-volume ratio of 1D nanostructures promotes surface chemical reactions by providing many catalytically active sites.<sup>11</sup> New crystal orientations, which are difficult to obtain in planar structures, have been exposed to the surface and boosted catalytic reactions.<sup>12</sup> Nanostructures have enhanced light absorption by suppressing Fresnel reflection and by scattering the incident light.<sup>13,14</sup> In addition, charge carrier separation and transfer have become much easier since the diffusion lengths of charge carriers have been shortened from the microscale to the nanoscale.<sup>15</sup> These advantages of 1D semiconductors have demonstrated much enhanced photoelectrochemical and photocatalytic performance compared to planar structures.<sup>16-18</sup> However, there are still many challenges remaining, such as inefficient light absorption, poor stability, and sluggish kinetics of surface chemical reactions. To mitigate these problems, 1D III-nitrides (*i.e.*, GaN, InN, and their alloys) have emerged as next-generation artificial photosynthetic semiconductors.

III-Nitrides have been designed and tailored for application in each particular photo(electro)chemical system. Ternary alloying (InGaN) of III-nitrides could allow fine-tuning of the band gap and lattice parameters to access ideal band edge positions and to realize epitaxial growth of high-quality crystals. The energy band gap of III-nitrides can be controlled across nearly the entire solar spectrum while straddling a broad range of redox potentials (Fig. 1a).<sup>19-21</sup> Hence, charge carrier transport at the III-nitride/electrolyte interface is energetically feasible for

water splitting and  $CO_2$  reduction reactions. III-Nitrides typically have a wurtzite crystal structure with a polar *c*-plane. Since the polarity of III-nitrides leads to the preferential growth of planar film along the *c*-axis, the catalytic activity of the polar *c*-plane has been commonly studied for artificial photosynthesis. However, 1D III-nitrides, having a small portion of polar top surface and abundant nonpolar side surfaces, have enabled crystal facet engineering to improve the performance of photoelectrodes and photocatalysts. Each crystal orientation of III-nitrides has different surface electronic structure, surface potential, and catalytic activity. Thus, various optoelectronic and catalytic characteristics can be demonstrated by fabricating III-nitride nanostructures. Moreover, the surface band bending and electrical conductivity of 1D III-nitrides can be manipulated by n- or p-type doping for each particular artificial photosynthetic application.<sup>19</sup> Optimized surface band bending has promoted charge carrier separation in semiconductors, which can suppress charge carrier recombination. Interestingly, their surfaces can be terminated with nitrogen atoms, or nitrogen-rich nanoclusters, to protect against photo-corrosion and oxidation, resulting in unprecedented long-term stability (Fig. 1b).<sup>22</sup> Hence, 1D III-nitrides show grand promise in promoting  $H_2$  production by solar water splitting and  $CO_2$  upgrading by a solar-driven  $CO_2$  reduction reaction.

In this review, the fabrication methods of 1D III-nitride nanostructures are first presented. Then, recent progress in band engineering, doping, and the heterostructures of 1D III-nitride semiconductors for artificial photosynthetic applications is described. Material design strategies for enhancing catalytic reactions are classified into four parts of photoelectrochemical water splitting, photocatalytic water splitting, photoelectrochemical  $CO_2$  reduction, and photocatalytic  $CO_2$  conversion. Finally, the critical challenges and prospects of 1D III-nitride materials for realizing practical artificial photosynthesis are discussed.

## 2. Fabrication of 1-dimensional III-nitrides

One-dimensional III-nitride nanostructures have been fabricated by bottom-up growth or top-down etching methods (Fig. 2). In more detail, the growth strategies of 1D III-nitrides can be classified into catalyst-assisted or catalyst-free growth. The top-down methods can also be divided into dry or wet etching processes. In addition, a chemical synthetic method has demonstrated the growth of GaN nanowires using a solution-based synthesis of gallium oxide nanowires followed by nitridation under an  $NH_3$  atmosphere.<sup>23-26</sup> However, GaN nanowires in powder form, obtained by chemical synthesis, have many crystal defects and charge carrier trapping sites within the band gap, so there is a limit to their application to photoelectrodes. Thus, in the following sections, bottom-up growth and top-down methods for the fabrication of high-crystal-quality 1D III-nitrides are mainly described.

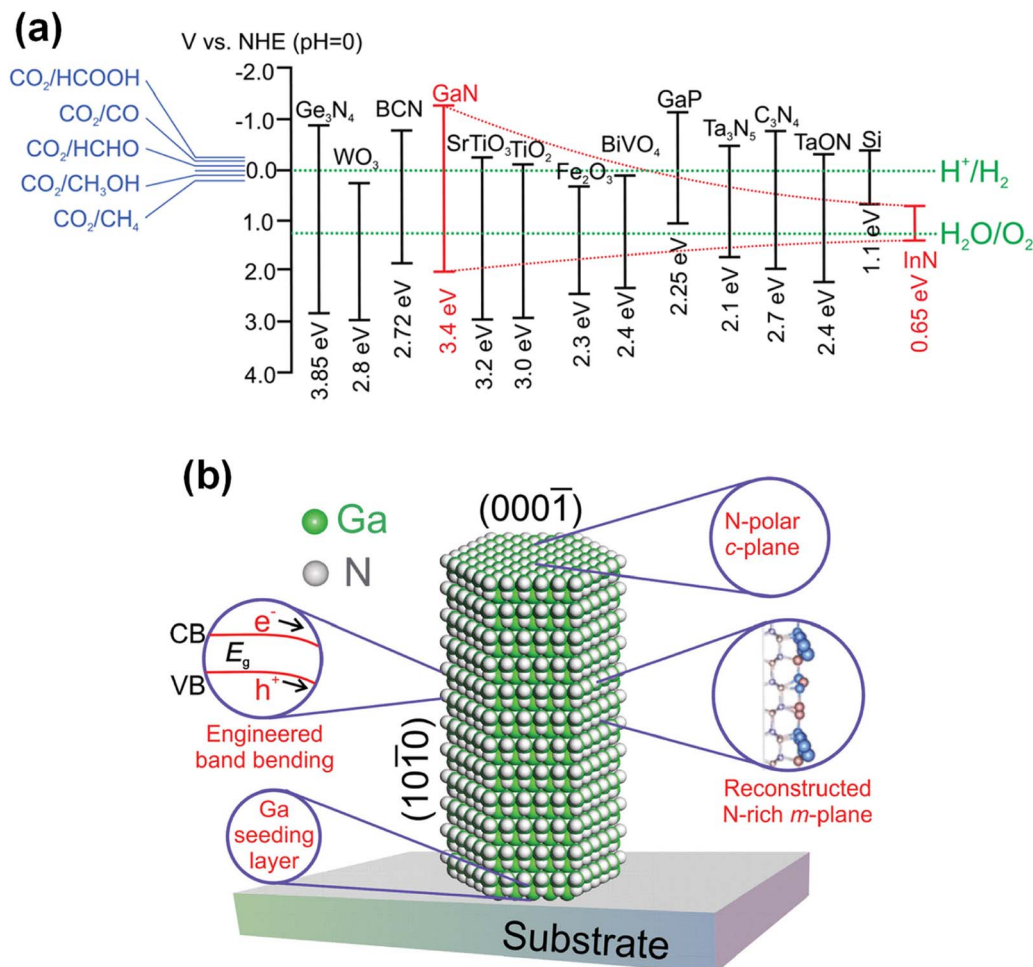


Fig. 1 (a) Schematic of the tunable  $\text{In}_x\text{Ga}_{1-x}\text{N}$  band structure compared to other semiconductors, including the redox potentials of water splitting and  $\text{CO}_2$  reduction. Reproduced with permission from ref. 19. Copyright (2016) Royal Society of Chemistry. (b) Schematic of the atomic and electronic structure of nitrogen-terminated GaN nanowire. Reproduced with permission from ref. 22. Copyright (2016) John Wiley and Sons.

## 2.1. Bottom-up growth

To date, most high-performing 1D III-nitride nanostructure photoelectrodes or photocatalysts have been fabricated based on the bottom-up method because this process offers high crystal quality with fewer defects. Moreover, tuning of morphology, incorporation of dopants, and constructing heterogeneous structures can be realized by varying the growth parameters, including the temperature, ratio of source materials, and growth duration. Previously, a vapor-liquid-solid growth mechanism was proposed for growing Si whiskers with Au catalysts.<sup>27</sup> At high temperature, sufficient to form Si:Au liquid droplets, the Si vapor preferentially incorporates into liquid metal catalysts and nucleates at the interface between Si crystals and liquid droplets, thereby resulting in high-quality Si crystal growth along the axial direction. Eventually, the Au catalyst droplets remain at the top of the Si whiskers. Because the liquid metal catalysts are preferential sites for the incorporation of vapor-phase Si, the morphology and composition of Si whiskers are determined, to a large extent, by the metal catalyst. This metal-catalyst-assisted vapor-liquid-solid growth

technique has been extended to the growth of 1D III-nitride semiconductors (Fig. 2a). III-Nitride nanowires, grown by the metal-organic chemical vapor deposition (MOCVD) method, have been successfully fabricated with various catalysts such as Au,<sup>28–30</sup> Ni,<sup>31–33</sup> AuNi alloy,<sup>34,35</sup> Fe,<sup>36</sup> and Cu<sup>37</sup> on different substrates, including sapphire, silicon, GaAs, and GaP.<sup>38</sup> Although the foreign metal catalysts promote the growth of 1D nanostructures, stacking faults and deep trapping states are unavoidable due to the difference in the crystal structure between the metals and III-nitrides. The defect states in photoelectrodes can degrade the photoelectrochemical performance by behaving as charge-trapping centers. In this regard, catalyst-free III-nitride nanowires have been extensively developed (Fig. 2b).<sup>38–40</sup> A molecular beam epitaxy (MBE) method under nitrogen-rich conditions can result in III-nitride nanowires through a diffusion-driven mechanism without any metal catalyst.<sup>41–44</sup> During growth, the supplied adatoms migrate along the lateral nonpolar planes of the nanowire and then primarily settle down on the top polar planes due to the lower chemical potential on the top surface, which consequently promotes the axial growth of the nanowires.<sup>45</sup> A distinctive

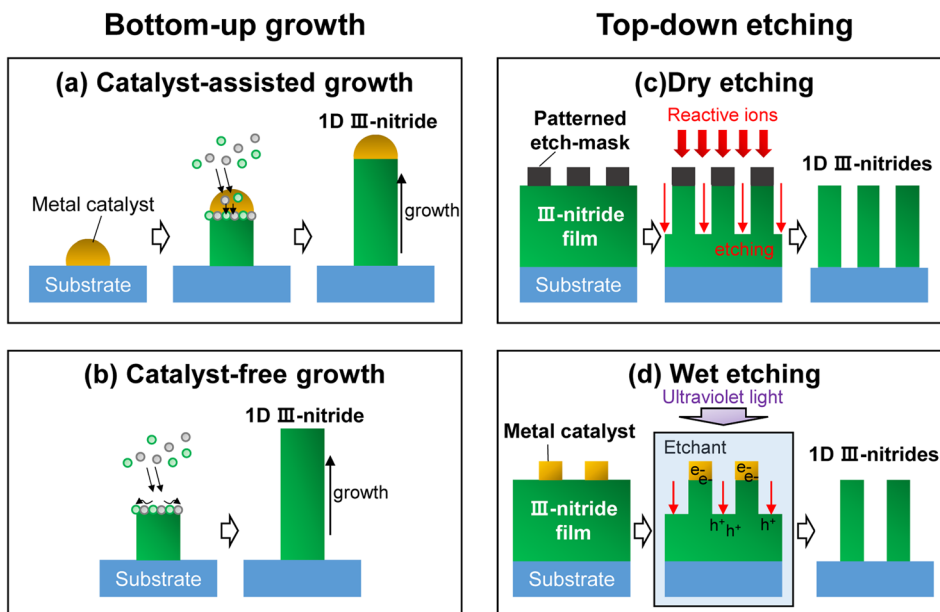


Fig. 2 Schematic illustrations of representative 1D III-nitride fabrication methods. Bottom-up growth can be classified into (a) catalyst-assisted growth and (b) catalyst-free growth. Top-down etching methods can be classified into (c) dry etching and (d) wet etching.

feature, that the diameter of the nanowires is inversely proportional to their length, indicates that there is competition between lateral expansion and vertical elongation of the nanowires on surfaces with different polarities.<sup>46,47</sup> Furthermore, it was found that the growth of nanowires proceeds through two steps of two-dimensional nuclei formation and transformation into nanowires.<sup>48</sup> This growth model suggests that III-nitride nanowires essentially do not have an epitaxial relationship with the underlying substrates and can be grown on any type of substrate.<sup>49–51</sup> In addition to the advantage of catalyst-free growth on arbitrary substrates, the MBE method for 1D III-nitride enables *in situ* growth of a heterostructure, effective n- or p-type doping, and tunable band gap energy. Therefore, 1D III-nitride semiconductors with appropriate band structure and surface atomic arrangement can be prepared for target catalytic reactions, including water splitting and CO<sub>2</sub> reduction reactions.

## 2.2. Top-down etching

Anisotropic etching of planar III-nitride film has demonstrated the fabrication of 1D nanostructures. Among top-down etching methods, dry etching (*i.e.*, reactive ion etching) of patterned GaN epilayers has been employed to fabricate photoelectrodes for solar water splitting (Fig. 2c).<sup>52–54</sup> The diameter, height, and aspect ratio of 1D nanostructures can be facilely controlled by tuning the pattern size and changing the reactive ion etching conditions. Because the etched 1D nanostructures have been patterned on high-quality III-nitride epilayers grown using mature planar film growth technology, material properties such as doping concentration, band gap, and multi-band structure can be precisely manipulated.<sup>55</sup> However, the patterning of the etch-masks (*i.e.*, photolithography, nanosphere lithography, nanoparticle coating, *etc.*) must be performed before the dry

etching process,<sup>56,57</sup> making fabrication difficult, complex, and costly. Moreover, the physical bombardment of highly reactive ions onto III-nitride epilayers inevitably results in surface defects, which act as recombination sites for photogenerated charge carriers and degrade the photoelectrochemical performance. These defects tend to be recovered, to some extent, by thermal annealing at high temperature for a long treatment time, but this process is also an obstacle to the formation of a heterojunction using semiconductor or catalyst materials that cannot withstand high temperatures. The limitations of top-down etching are also evidenced by the severe efficiency cliff of micro-light-emitting diodes.<sup>21,58</sup>

Anisotropic wet etching methods can fabricate III-nitride nanostructures. For instance, metal-assisted chemical etching, which has been studied for the fabrication of vertically aligned Si nanowires, can be applied to fabricate III-nitride nanostructures (Fig. 2d). Under light illumination, photogenerated electrons migrate to the pre-patterned metal catalyst, whereas photogenerated holes remain on the GaN surface.<sup>59</sup> Then, the photogenerated holes oxidize the exposed GaN epilayers, and the etchant rapidly removes the oxidized GaN, thereby resulting in a nanowire morphology. Choosing different metal catalysts on GaN films can switch the cathodic and anodic reaction sites and accordingly change the surface morphology.<sup>60</sup> Electrochemical wet etching can also fabricate nanoporous III-nitride photoelectrodes based on a combination of an oxidation process and a dissolution process in an acidic etchant under an anodic potential.<sup>61–63</sup> However, it is very difficult to control the morphology of nanostructures by the wet-etching process. The repeated oxidation and dissolution of III-nitride materials cause uncontrollable crystal facets and unavoidable amorphous oxide formation, which inhibit catalytic reactions. More importantly, the nanostructures can only be fabricated under specific



conditions. For example, electrochemical etching cannot operate on intrinsic or p-type GaN layers, limiting the application of artificial photosynthetic devices.

### 3. Photoelectrochemical water splitting

Photoelectrochemical water splitting can be classified into two half-reactions of H<sub>2</sub> evolution and O<sub>2</sub> evolution at photocathode and photoanode, respectively. The photoelectrochemical H<sub>2</sub> evolution reaction is driven by photogenerated electrons in semiconductors under an applied cathodic potential. Light with energy greater than the band gap of semiconductors excites photogenerated electrons in the conduction band, leaving photogenerated holes in the valence band. Then, photogenerated electrons in the conduction band migrate toward the surface (electrode/electrolyte interface) for the H<sub>2</sub> evolution reaction. Therefore, the conduction band edge position of the photocathode should be located above the reduction potential of water for an efficient H<sub>2</sub> evolution reaction. On the other hand, the photoelectrochemical O<sub>2</sub> evolution reaction occurs when the photogenerated holes in the valence band of semiconductors participate in the water oxidation reaction with the help of anodic potential. Hence, the valence band edge position of the photoanode should be positioned below the oxidation potential of water. Because III-nitride materials such as GaN or InGaN can satisfy both requirements of conduction and valence band edge positions for water reduction and oxidation, respectively, their photoelectrochemical water splitting properties have been extensively studied. In particular, GaN and InGaN nanostructures (*i.e.*, nanorods,<sup>64–66</sup> nanowires,<sup>67–76</sup> and nanowalls<sup>77</sup>) have attracted a lot of attention because they outperform planar structures in photoelectrochemical water splitting activity (Tables 1 and 2). Thus, recent strategies to enhance the photocurrent density and to reduce the overpotential of 1D nanostructured III-nitride photoelectrodes will be reviewed in the following sections.

#### 3.1. Doping and band engineering of 1D III-nitrides

Doping or alloying of III-nitrides can result in broadband light absorption, increased charge carrier concentration, and surface band bending. All these optoelectronic properties are closely related to photoelectrochemical water splitting performance.<sup>100</sup> Previously, the influence of Si doping on the photoelectrochemical performance of n-type InGaN nanowires photoanodes was investigated.<sup>78</sup> The Si dopant concentration was tuned by changing the Si effusion cell temperature ( $T_{\text{Si}}$ ) during the MBE growth of vertically aligned InGaN nanowires on an Si substrate (Fig. 3a). An Si-doped InGaN nanowire photoanode showed a maximum dopant concentration of  $2.1 \times 10^{18} \text{ cm}^{-3}$  at  $T_{\text{Si}} = 1120 \text{ }^\circ\text{C}$  (Fig. 3b). At this optimized n-type doping concentration, the conduction band edge and valence band edge still straddle the water redox potentials, thereby leading to  $\sim 9$  times higher photocurrent density compared to undoped InGaN nanowires (Fig. 3c). More recently, a Zn atom has been employed as a dopant to control the electronic structure and to modify the crystal structure of InGaN nanowires.<sup>79</sup> The amount of Zn dopant was changed by Zn cell temperature during the MBE growth of InGaN nanowires. Zn doping shifted the valence band edge more positively compared to the undoped InGaN nanowires, which can lead to enhanced water oxidation kinetics (Fig. 3d). In addition, Zn doping reduced In composition and prevented the formation of deep energy levels originating from In aggregation (Fig. 3e). The improved energy band structure and crystal quality of the Zn-doped InGaN photoanode greatly improved the photocurrent density by  $\sim 3$  times (Fig. 3f). The improved photoelectrochemical performance demonstrated by doping with transition metal opens up greater possibilities for the realization of III-nitrides as efficient water splitting photoelectrodes.

Alloying of In element to a GaN semiconductor can increase the charge carrier mobility and reduce the band gap energy to demonstrate broadband light absorption, thereby leading to an increase in photocurrent density for the photoelectrochemical

Table 1 Recent III-nitride photoanodes for photoelectrochemical water splitting

Photoanode	Cocatalyst	Potential	Electrolyte	Light intensity	Current density	Ref.
GaN nanorods/V-groove textured Si	—	1.14 V <sub>RHE</sub>	0.5 M NaOH	100 mW cm <sup>-2</sup> AM 1.5 S	801.62 μA cm <sup>-2</sup>	66
InGaN NWs	Ir NPs	0.61 V <sub>RHE</sub>	0.1 M PBS (pH $\sim$ 7)	500 mW cm <sup>-2</sup> AM 1.5G	$\sim$ 2 mA cm <sup>-2</sup>	67
GaN NWs	Au NPs	-0.4 V <sub>RHE</sub>	1 M NaOH	100 mW cm <sup>-2</sup>	$\sim$ 1 mA cm <sup>-2</sup>	68
GaN NWs	—	0.6 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	2.2 mA cm <sup>-2</sup>	72
ZnS/GaN NWs	Au NPs	0 V <sub>RHE</sub>	1 M NaOH	100 mW cm <sup>-2</sup>	1.15 mA cm <sup>-2</sup>	73
InGaN NWs on oblique pyramid-textured Si	NiOOH	1.0 V <sub>RHE</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	$\sim$ 0.4 mA cm <sup>-2</sup>	76
Si-doped InGaN NWs	—	1.597 V <sub>NHE</sub>	0.1 M PBS (pH = 7)	N/A	1.42 mA cm <sup>-2</sup>	78
Zn-doped InGaN nanorods	Au	1.23 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	1.65 mA cm <sup>-2</sup>	79
InGaN NWs	IrO <sub>2</sub>	0.6 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	5.2 mA cm <sup>-2</sup>	80
InGaN/GaN nanorods	—	1.35 V <sub>RHE</sub>	0.01 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5	0.3 mA cm <sup>-2</sup>	81
InGaN/GaN NWs	—	1.0 V <sub>Ag/AgCl</sub>	1 M HBr	100 mW cm <sup>-2</sup> AM 1.5	$\sim$ 23 mA cm <sup>-2</sup>	82
ZnS/GaN	—	0 V vs. Pt	1 M NaOH	500 mW cm <sup>-2</sup>	2.8 mA cm <sup>-2</sup>	83
C <sub>3</sub> N <sub>4</sub> /InGaN nanorods	—	1.23 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	13.9 mA cm <sup>-2</sup>	84
W <sub>x</sub> S <sub>1-x</sub> /GaN NWs	—	0.6 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	20.38 mA cm <sup>-2</sup>	85
InGaN nanorods/MXene	—	1.23 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	7.27 mA cm <sup>-2</sup>	86
n-InGaN/n <sup>+</sup> -GaN NWs/n <sup>+</sup> -p <sup>+</sup> -n Si	—	$\sim$ 0.6 V <sub>NHE</sub>	1 M HBr	100 mW cm <sup>-2</sup>	16.3 mA cm <sup>-2</sup>	87

Table 2 Recent III-nitride photocathodes for photoelectrochemical water splitting

Photocathode	Cocatalyst	Potential	Electrolyte	Light intensity	Current density	Ref.
p-GaN hexagonal microwell	2D-MoS <sub>2</sub>	0 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	2.15 mA cm <sup>-2</sup>	88
n <sup>+</sup> -GaN NWs/n <sup>+</sup> -p Si	MoS <sub>2</sub>	0 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	~40 mA cm <sup>-2</sup>	89
p-InGaN/TJ/n-GaN NWs/n <sup>+</sup> -p Si	Pt	0.26 V <sub>NHE</sub>	1 M HBr	130 mW cm <sup>-2</sup>	40.6 mA cm <sup>-2</sup>	90
p-InGaN/TJ/n-InGaN NWs/n-Si	Pt	0 V vs. Pt	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup>	2.8 mA cm <sup>-2</sup>	91
p-InGaN/TJ/n-GaN NWs/n-Si	Pt	0 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	12.3 mA cm <sup>-2</sup>	92
p-InGaN/TJ/n-InGaN NWs/n <sup>+</sup> -p Si	Pt	0.4 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	~9 mA cm <sup>-2</sup>	93
p-InGaN/TJ/n-InGaN NWs/n <sup>+</sup> -p Si	Pt	0 V vs. IrO <sub>x</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	~8.4 mA cm <sup>-2</sup>	94
GaN quasi-film/n <sup>+</sup> -p Si	Pt	0 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	~25 mA cm <sup>-2</sup>	95
Patterned GaN quasi-film/n <sup>+</sup> -p Si	Pt	0 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	~18 mA cm <sup>-2</sup>	96
n <sup>+</sup> -GaN NWs/n <sup>+</sup> -p Si	Pt	0 V <sub>RHE</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	~38 mA cm <sup>-2</sup>	97
GaN nanostructure/GaInP <sub>2</sub> /GaAs/Ge triple-junction	Pt	~1.2 V <sub>RHE</sub>	0.1 M H <sub>2</sub> SO <sub>4</sub>	100 mW cm <sup>-2</sup> AM 1.5G	~10.3 mA cm <sup>-2</sup>	98
n <sup>+</sup> -GaN NWs/n <sup>+</sup> -p Si	Pt	-0.6 V <sub>RHE</sub>	Seawater	900 mW cm <sup>-2</sup> AM 1.5G	~163 mA cm <sup>-2</sup>	99

water splitting reaction.<sup>101,102</sup> Previously, an In-rich InGaN nanowire photoanode with a small band gap of 1.7 eV was grown on an n-type Si substrate by the MBE method.<sup>80</sup> InGaN nanowires were vertically aligned on the Si substrate with an approximate diameter of ~200 nm and height of ~700 nm (Fig. 4a). To enhance the O<sub>2</sub> evolution reaction, IrO<sub>2</sub> nanoparticle cocatalysts were loaded on InGaN nanowires by a photodeposition process. The photoelectrochemical water oxidation performance of the InGaN nanowire photoanode was evaluated in an acidic electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>) under an air mass 1.5 global (AM 1.5G) simulated 1 sun illumination in a three-electrode configuration (Fig. 4b). The pristine InGaN

nanowires showed a low photocurrent density and a large overpotential due to the poor kinetics of the water oxidation reaction (Fig. 4c). However, after modification of InGaN with IrO<sub>2</sub> cocatalysts, the activity of the photoelectrode greatly improved. Due to the unique 1D nanowire structure, a low energy band gap of 1.7 eV, and appropriate band edge positions to straddle the redox potentials of water splitting, together with effective coupling with IrO<sub>x</sub> cocatalysts, the InGaN nanowires resulted in a low onset potential of 0.1 V<sub>RHE</sub>, a high photocurrent density of 5.2 mA cm<sup>-2</sup> at 0.6 V<sub>RHE</sub>, and a half-cell solar energy conversion efficiency up to 3.6%.

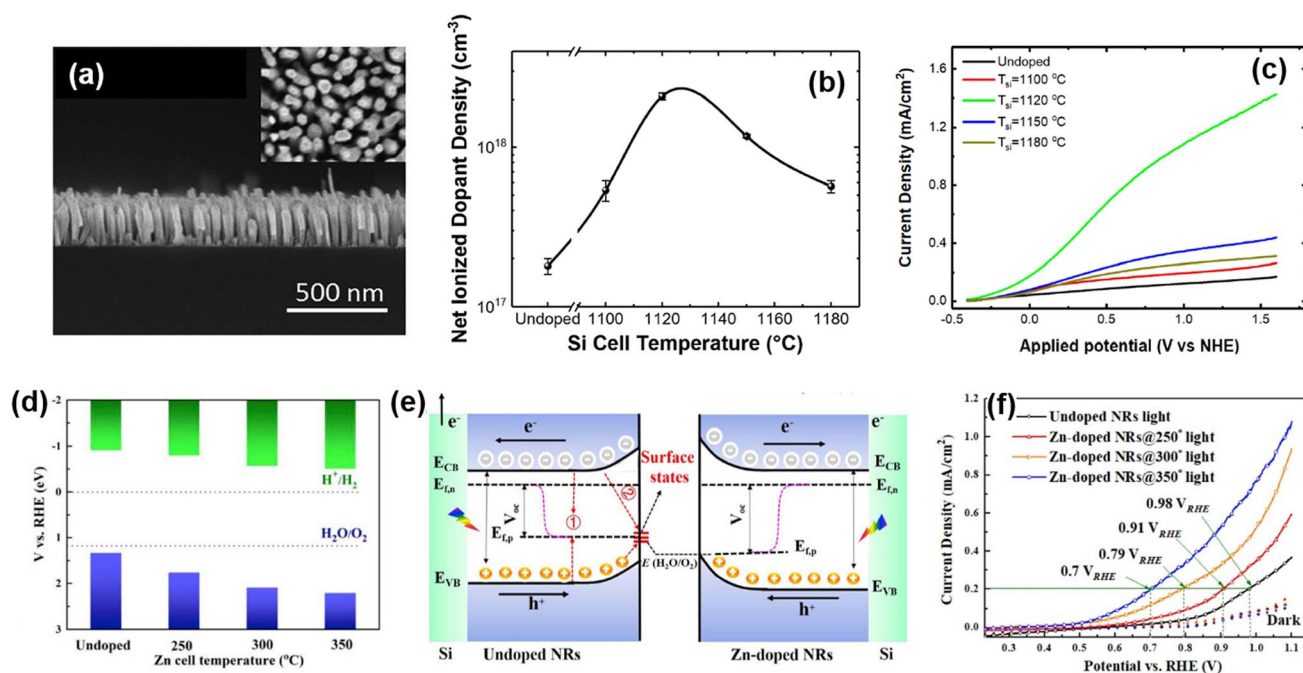


Fig. 3 (a) Cross-sectional view of the InGaN nanowire photoanode. (b) Net ionized dopant density of Si-doped InGaN nanowires with respect to Si cell temperature. (c) Linear sweep voltammetry (LSV) curves of Si-doped InGaN nanowire photoanodes. Reproduced from ref. 78. Copyright (2018) AIP Publishing. (d) Valence band and conduction band potentials of Zn-doped InGaN nanowires with respect to Zn cell temperature. (e) Band-bending diagram and charge carrier transport schematic of photoelectrochemical water oxidation for undoped and Zn-doped InGaN photoanodes. (f) LSV curves of Zn-doped InGaN nanowire photoanodes. Reproduced from ref. 79. Copyright (2020) Elsevier.

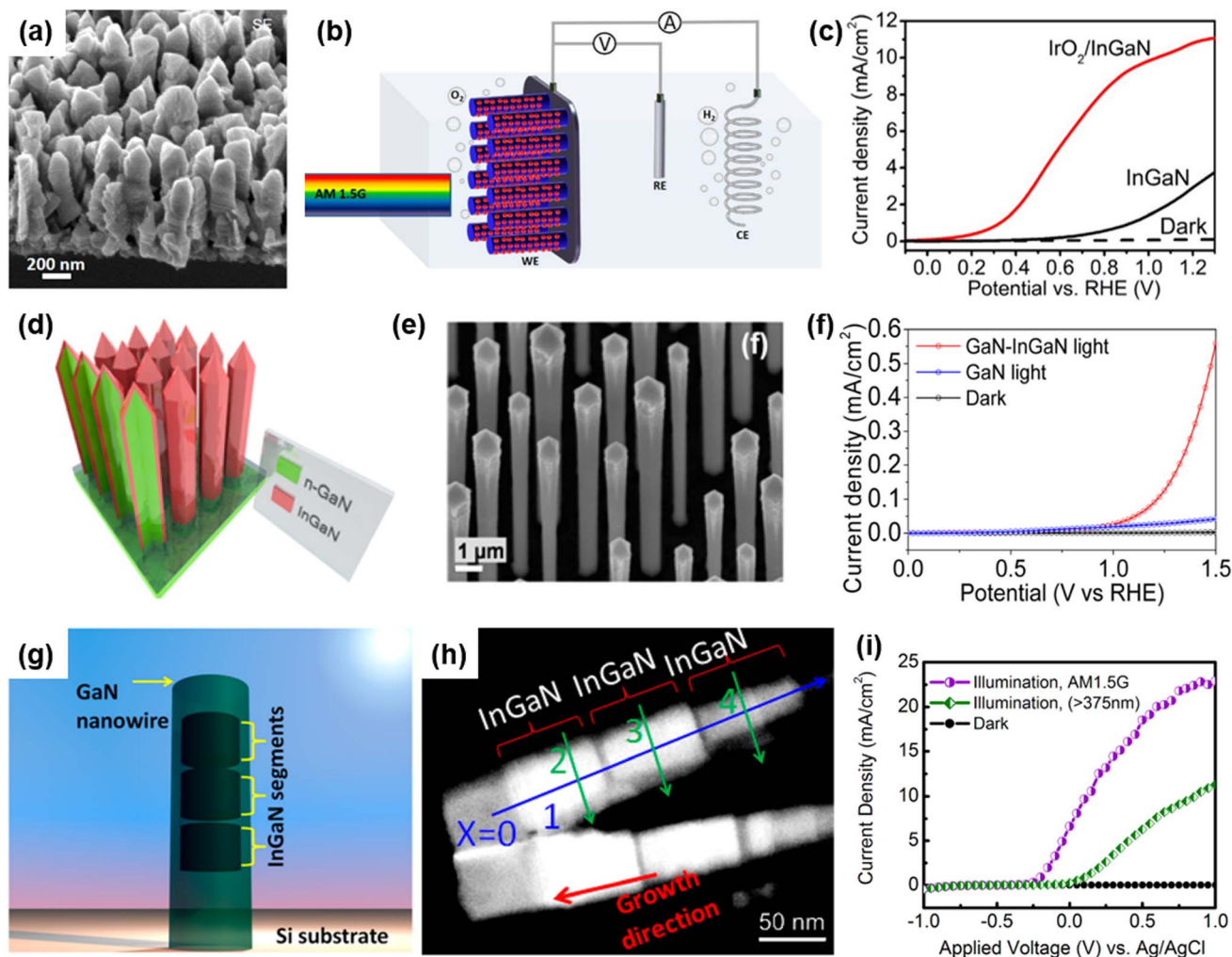


Fig. 4 (a) Scanning electron microscopy (SEM) image of the InGaN nanowire. (b) Schematic illustration of the three-electrode cell for photoelectrochemical water oxidation. InGaN nanowire photoanode, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. (c) LSV curves of InGaN and IrO<sub>x</sub>/InGaN photoanodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> under light illumination. Reproduced from ref. 80. Copyright (2018) American Chemical Society. (d) Schematic illustration and (e) SEM image of GaN/InGaN core/shell nanorod arrays. (f) Current density vs. potential plots of GaN/InGaN core/shell nanorods photoanode and GaN nanorods in 0.01 M H<sub>2</sub>SO<sub>4</sub> solution under 1 sun illumination using AM 1.5G filter. Reproduced from ref. 81. Copyright (2014) American Chemical Society. (g) Schematic illustration and (h) transmission electron microscopy (TEM) image of GaN nanowires with axially incorporated InGaN segments. (i) Anodic photocurrent density measured in 1 M HBr under simulated sunlight illumination with filters. Reproduced with permission from ref. 82. Copyright (2013) American Chemical Society.

In addition to the reduced band gap of InGaN nanowires, dual-band GaN/InGaN core/shell nanowires have been developed as visible-light-responsive photoelectrodes.<sup>103–106</sup> For instance, GaN/InGaN core/shell nanowire arrays were fabricated by sequential growth of n-type GaN nanorods followed by an n-type InGaN coating using the MOCVD method (Fig. 4d).<sup>81</sup> It is observed that GaN nanowires, with an average diameter of 900 nm and height of 14 μm, are covered by a 20 nm-thick InGaN layer (Fig. 4e). Compared to GaN nanowires, the GaN/InGaN nanowire photoanode showed 10-fold higher photocurrent density at an anodic potential of 1.35 V<sub>RHE</sub> (Fig. 4f). The photocurrent density enhancement was mainly attributed to the extended light absorption of the narrow band gap InGaN shells, which can utilize visible light and increase the number of photogenerated charge carriers. The InGaN segments can also

be incorporated into 1D GaN nanowires along the axial direction by MBE growth (Fig. 4g).<sup>82</sup> The high angle annular dark field (HAADF) image of InGaN/GaN nanowires illustrates the atomic number contrast between GaN (darker) and InGaN (brighter) regions and the presence of 3 segments of ~70 nm long InGaN passivated by the GaN layer (Fig. 4h). This dual-band photoanode was first tested using a 375 nm long-pass filter, which prevents excitation of the GaN region. The photoanode revealed a photocurrent density of ~11 mA cm<sup>-2</sup> at 1 V<sub>Ag/AgCl</sub>, indicating the excitation of charge carriers by InGaN segments under visible light. Notably, when an AM 1.5G filter was used, the photocurrent density was greatly enhanced to ~23 mA cm<sup>-2</sup> at 1 V<sub>Ag/AgCl</sub> because of concurrent excitation of charge carriers in both InGaN and GaN regions. From these results, it was found that the strategy of integrating ultraviolet-light-



absorbing GaN and visible-light-responsive InGaN into 1D nanostructures can have a synergistic effect on photoelectrochemical water splitting.

### 3.2. Heterostructure

The design of a heterostructure by the combination of two or more semiconductor materials is a promising strategy for broadband light absorption, suppression of electron-hole recombination, and increased lifetime of photogenerated charge carriers. When two semiconductors with different work functions are in contact, the built-in electric field at the heterojunction interface can promote charge separation and increase the current density for photoelectrochemical water splitting. Thus, GaN and InGaN nanostructures combined with other semiconductors ( $\text{ZnS}$ ,<sup>83</sup>  $\text{MoS}_2$ ,<sup>88</sup>  $\text{C}_3\text{N}_4$ ,<sup>84</sup>  $\text{W}_x\text{S}_{1-x}$ ,<sup>85</sup> MXene<sup>86</sup>) have been exploited in photoelectrochemical water splitting. For example, photoanodes, consisting of GaN nanowires coated with tungsten sulfide ( $\text{W}_x\text{S}_{1-x}$ ), were fabricated by MBE growth of GaN and solvothermal synthesis of  $\text{W}_x\text{S}_{1-x}$  (Fig. 5a).<sup>85</sup> The vertically grown GaN nanowires on an Si wafer had an average length of  $\sim 443$  nm and an average diameter of  $\sim 35$  nm (Fig. 5b). The average thicknesses of the  $\text{W}_x\text{S}_{1-x}$  layer could be varied from 0.79 to 3.23 nm depending on the synthesis conditions (Fig. 5c). The photoelectrochemical water oxidation performance was measured in 0.5 M  $\text{H}_2\text{SO}_4$  under 1 sun illumination. The GaN- $\text{W}_x\text{S}_{1-x}$  photoanode showed superior performance compared to GaN without  $\text{W}_x\text{S}_{1-x}$ . The photocurrent density was as high as  $20.38$   $\text{mA cm}^{-2}$  at  $0.6$   $\text{V}_{\text{RHE}}$  and a maximum applied-bias photon-to-current efficiency (ABPE) of 13.76% was achieved (Fig. 5d). This greatly improved performance was attributed to the type-II band structure formed at the GaN/ $\text{W}_x\text{S}_{1-x}$  interface (Fig. 5e). In this photoanode configuration, the photogenerated holes efficiently transfer to the valence band of  $\text{W}_x\text{S}_{1-x}$  for the water oxidation reaction while the photogenerated electrons migrate to the conduction band of GaN

nanowires, thereby leading to accelerated charge carrier separation and suppression of charge carrier recombination. In comparison to the deposition of semiconductors on 1D nitrides, direct growth of InGaN nanowires on MXene can also construct a heterostructure for photoelectrochemical water splitting.<sup>86</sup> An MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) film with a thickness of  $\sim 50$  nm was spin-coated on an n-type Si substrate. Then, InGaN nanorods were vertically grown on it by MBE (Fig. 5f). An MXene/InGaN nanorod photoanode revealed a very low onset potential and high photocurrent density of  $7.27$   $\text{mA cm}^{-2}$  at  $1.23$   $\text{V}_{\text{RHE}}$ , which is over 10 times higher than that of an InGaN/Si photoanode ( $0.71$   $\text{mA cm}^{-2}$ ) (Fig. 5g). The low onset potential and high photocurrent density originate from the type-II band alignment at the InGaN/MXene interface where the photogenerated carriers can be efficiently separated, with electrons transferring from InGaN to MXene and holes transferring from MXene to InGaN for water oxidation (Fig. 5h). Overall, type-II heterostructures at the III-nitride and other semiconductor interfaces were found to enhance the photoelectrochemical water splitting performance by promoting the separation of photogenerated charge carriers.

### 3.3. Tunnel junction

Tunnel junction diodes, that connect a top cell with a large band gap and a bottom cell with a small band gap, have been extensively studied to address the current-matching issues for dual or triple absorber solar cells and photoelectrodes in III-V systems.<sup>107–110</sup> Inspired by this strategy, III-nitride nanowire top cells grown on Si bottom cells have been developed for both photoanode and photocathode applications.<sup>90–92,111</sup> A recent theoretical study on InGaN/Si double-junction photocathodes indicated that a high photocurrent density of up to  $\sim 18$   $\text{mA cm}^{-2}$  can be demonstrated when an  $\text{In}_{0.46}\text{Ga}_{0.54}\text{N}$  top cell with a band gap of  $\sim 1.8$  eV is integrated on an Si bottom cell with a band gap of  $\sim 1.1$  eV (Fig. 6a).<sup>93</sup> Hence, a p-type InGaN

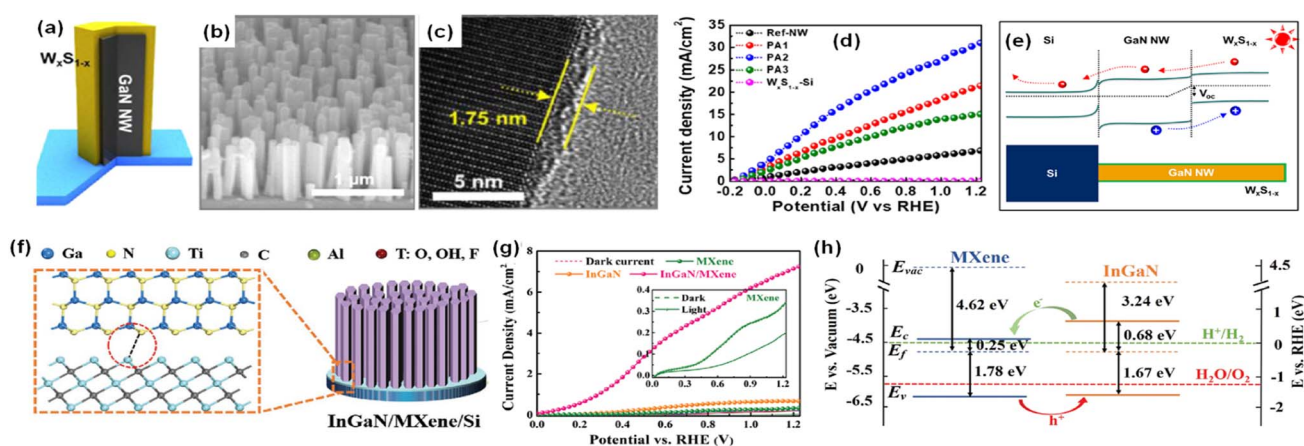


Fig. 5 (a) Schematic illustration, (b) SEM image, and (c) high-resolution TEM image of GaN nanowires covered with a  $\text{W}_x\text{S}_{1-x}$  layer. (d) Current density–potential curves of the GaN nanowires and GaN nanowires– $\text{W}_x\text{S}_{1-x}$  photoanodes in 0.5 M  $\text{H}_2\text{SO}_4$ . (e) Energy band diagram of photoanode under light illumination. Reproduced with permission from ref. 85. Copyright (2020) American Chemical Society. (f) Schematic illustration of InGaN/MXene nanorods. (g) LSV curves of InGaN, MXene, and InGaN/MXene photoanodes. (h) Proposed band diagram of the InGaN/MXene heterojunction. Reproduced with permission from ref. 86. Copyright (2020) John Wiley and Sons.



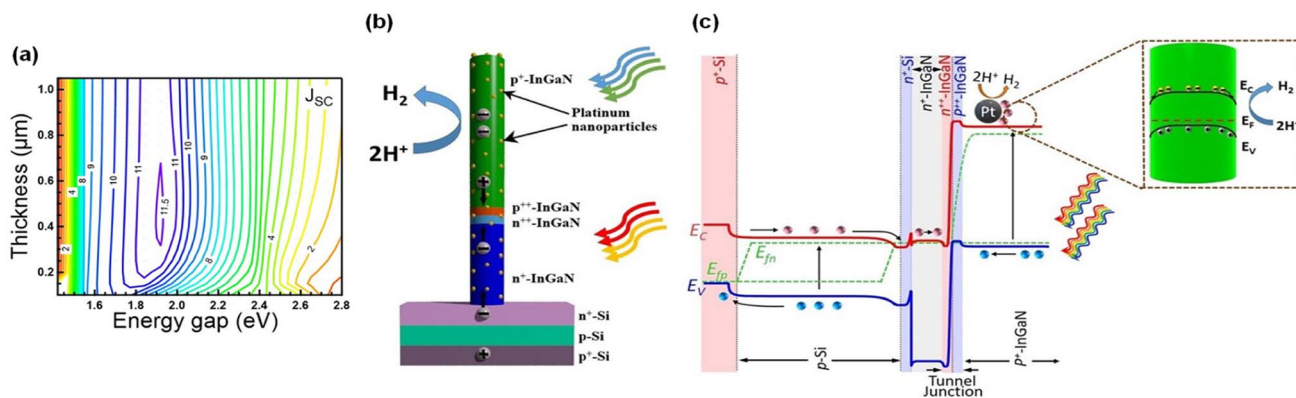


Fig. 6 (a) Theoretically calculated top  $p^+$ -InGaN thickness and energy gap dependence of the short circuit current density of an InGaN/Si double-junction photocathode. (b) Schematic of Pt-decorated  $p^+$ -InGaN/tunnel junction/ $n^+$ -InGaN nanowire on an  $n^+$ - $p$  Si wafer. (c) Energy band diagram under light illumination, showing charge carrier generation in bottom Si and top  $p^+$ -InGaN nanowire and electron migration to the lateral surface of  $p^+$ -InGaN for proton reduction reaction. Reproduced with permission from ref. 93. Copyright (2021) AIP Publishing.

nanowire top cell was fabricated on a planar  $n^+$ - $p$  Si bottom cell and the top and bottom light absorbers are electronically connected through a  $p^+$ -InGaN/ $n^+$ -InGaN NW tunnel junction (Fig. 6b). In this structure, photogenerated electrons in the conduction band of the Si bottom cell migrate to the  $n^+$ -InGaN segment, which then recombine with photogenerated holes in the valence band of the  $p^+$ -InGaN segment in the tunnel junction (Fig. 6c). Meanwhile, the photogenerated electrons in the conduction band of the top  $p$ -InGaN nanowires laterally diffuse to Pt nanoparticle cocatalysts due to downward surface band bending and finally participate in the  $H_2$  evolution reaction.

Even though the ideal band gap energy of an InGaN top cell on an Si bottom cell is  $\sim 1.8$  eV, it is extremely challenging to grow InGaN nanowires with high In composition ( $\sim 46\%$ ) because of unavoidable defect formation and phase separation. Therefore, an InGaN nanowire top cell with a band gap of 2.2 eV was integrated on an  $n^+$ - $p$  Si bottom cell through a nearly defect-free  $n^+$ -InGaN/ $p^+$ -InGaN NW tunnel junction for the photoelectrochemical  $H_2$  evolution reaction (Fig. 7a and b).<sup>94</sup> Unlike a previous tunnel junction formed in an Si bottom cell,<sup>87</sup> the tunnel junction was grown epitaxially in the InGaN nanowires (Fig. 7c–e). Since there is significantly reduced lattice mismatch, a high-crystal-quality tunnel junction can be formed with fewer defects and dislocations. Moreover, thin  $Al_2O_3$  layer

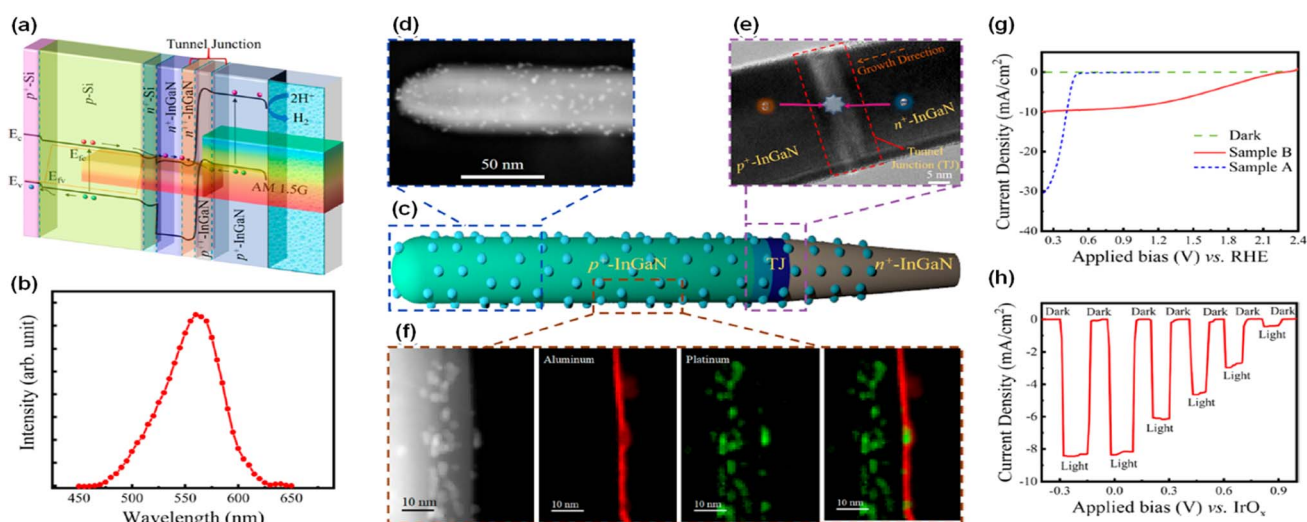


Fig. 7 (a) Band diagram of the  $p^+$ -InGaN/tunnel junction/ $n^+$ - $p$  Si photocathode.<sup>94</sup> (b) Photoluminescence spectrum of  $p^+$ -InGaN nanowires. (c) Schematic of a single nanowire with Pt cocatalysts and  $Al_2O_3$  layer. (d) High angle annular dark field (HAADF) image of top  $p^+$ -InGaN segment. (e) Bright-field image of tunnel junction region. The photogenerated holes from the  $p^+$ -InGaN top cell and electrons from the bottom  $n^+$ -InGaN recombine in the tunnel junction. (f) HAADF and elemental mapping showing Pt and  $Al_2O_3$  on the nanowire sidewall. (g) Three-electrode linear scan voltammetry curves of InGaN/Si single-junction (sample A) and double-junction (sample B) photocathodes. (h) Two-electrode chopped photocurrent density curve of InGaN/Si double-junction in 0.5 M  $H_2SO_4$  under AM 1.5G 1 sun illumination. Reproduced with permission from ref. 94. Copyright (2020) American Chemical Society.

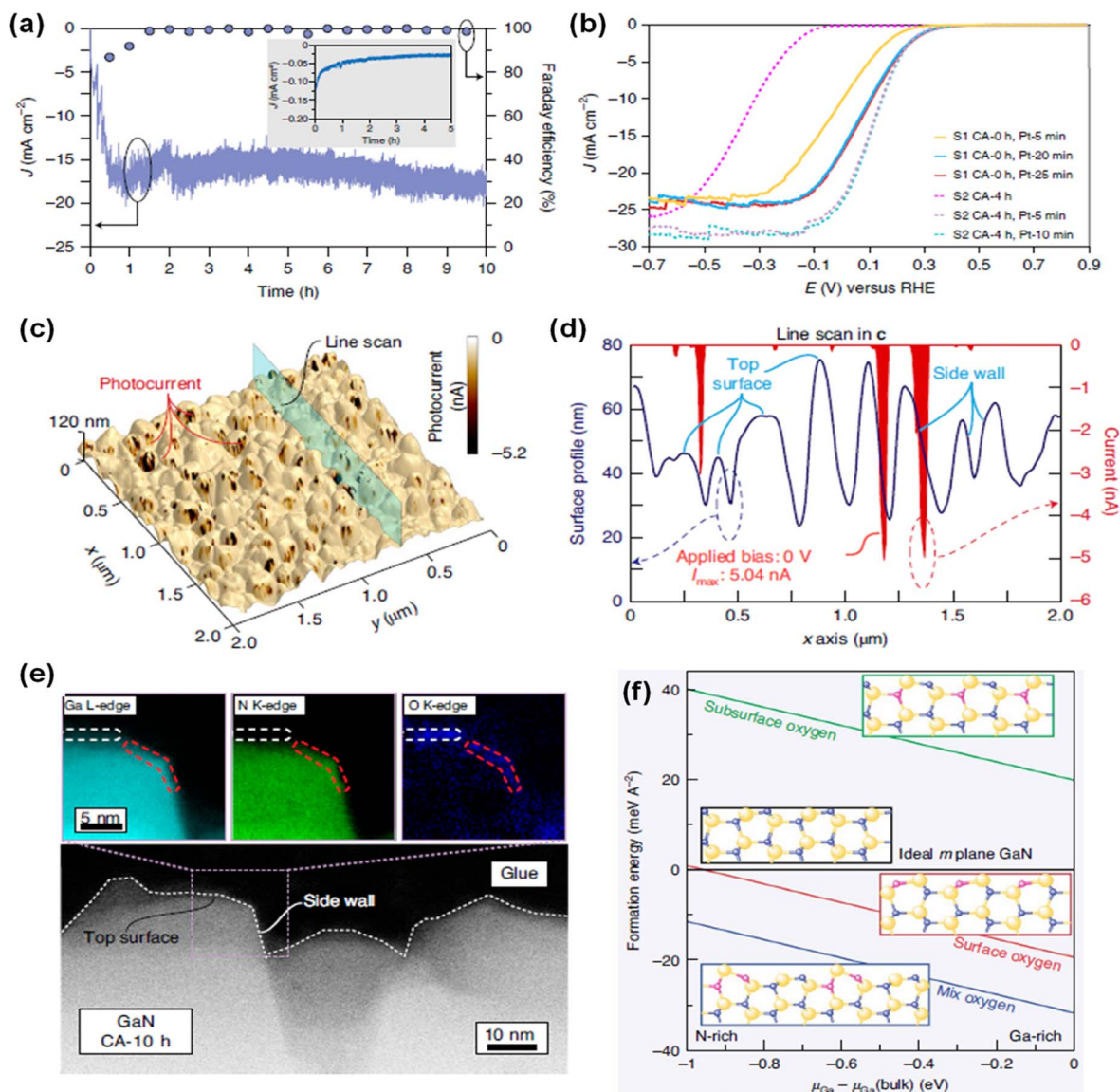
(1–2 nm) and Pt nanoparticle cocatalysts were deposited on the InGaN nanowires to passivate the surface defects and to prevent corrosion of the photocathodes, thereby leading to enhanced water splitting performance and stability (Fig. 7f). To elucidate the photoelectrochemical water splitting activity, an InGaN/Si double-junction photocathode (sample B) was compared with an  $n^+$ -InGaN/Si single-junction photocathode without the tunnel junction (sample A) (Fig. 7g). Single-junction InGaN/Si showed an onset potential of  $\sim 0.5 V_{\text{RHE}}$  whereas double-junction InGaN/Si remarkably increased the onset potential to  $\sim 2.3 V_{\text{RHE}}$ . The saturation photocurrent density for the double-junction cell was  $\sim 9 \text{ mA cm}^{-2}$  which is smaller than that of the single-junction cell ( $\sim 30 \text{ mA cm}^{-2}$ ) because the photocurrent density of the double-junction cell was limited by the top  $p^+$ -InGaN nanowires (with a band gap of  $\sim 2.2 \text{ eV}$ ) whereas the Si-based single-junction photocathode has a theoretical maximum photocurrent density of  $\sim 44 \text{ mA cm}^{-2}$ . In addition, the InGaN/Si double-junction photocathode exhibited an onset potential of  $\sim 0.7 \text{ V}$  vs. an  $\text{IrO}_x$  counter electrode in the 2-electrode configuration with a record-high solar-to-hydrogen (STH) efficiency of  $\sim 10.3\%$  under AM 1.5G 1 sun illumination (Fig. 7h). This double-junction photocathode provided sufficient built-in potential under solar light, leading to overall solar water splitting without additional electrical bias. Addressing the current-matching issues of top and bottom cells through a tunnel junction structure will further improve the photocurrent density while producing a built-in potential sufficient for overall water splitting.

### 3.4. Crystal orientation

Due to distinct atomic arrangements on the different crystal facets of semiconductor materials, anisotropic physical and chemical properties have been demonstrated. Electrical conductivity, surface adsorption of molecules, band edge position, and direction of charge carrier diffusion in the photoelectrodes are highly dependent on the crystal orientation. In addition, each crystal facet has a different intrinsic reactivity dependent on the pH and applied potential. Hence, understanding crystal facet effects on photoelectrochemical water splitting activity and stability is an essential issue. Previously, specific crystal facets have been exposed to the surface of various photoelectrodes of  $\text{TiO}_2$ ,<sup>112</sup>  $\text{Fe}_2\text{O}_3$ ,<sup>113,114</sup>  $\text{WO}_3$ ,<sup>115–117</sup>  $\text{BiVO}_4$ ,<sup>118,119</sup>  $\text{Cu}_2\text{O}$ ,<sup>120,121</sup>  $\text{Sb}_2\text{Se}_3$ ,<sup>122,123</sup> and  $\text{Ta}_3\text{N}_5$  (ref. 124 and 125) by selective nucleation, growth, or etching processes. Fine control over crystal orientation has exhibited an improvement in activity and stability for both photoelectrochemical  $\text{H}_2$  evolution and  $\text{O}_2$  evolution reactions. Although various studies have demonstrated efficient water splitting by optimization of the crystal structures of semiconductor materials, the effect of crystal facets of III-nitrides on water splitting performance has been largely unknown. Recently, GaN quasi-films grown on  $n^+$ -p Si photocathodes showed a gradual self-improvement in  $\text{H}_2$  evolution activity during the initial several hours of chronoamperometry (CA) measurement in  $0.5 \text{ M H}_2\text{SO}_4$  under 1 sun illumination at a cathodic bias of  $-0.6 V_{\text{RHE}}$  (Fig. 8a).<sup>95</sup> The linear sweep voltammetry (LSV) curves exhibited a positive shift

in onset potential from  $-0.46$  to  $-0.08 V_{\text{RHE}}$  after 10 h of CA testing. Owing to the self-improving characteristic of GaN quasi-film, the loading amount of noble metal Pt cocatalyst can be greatly reduced. On the pristine GaN/Si photocathode, 20 min of Pt deposition was required to achieve an onset potential of  $\sim 0.3 V_{\text{RHE}}$ ; meanwhile this onset potential can be demonstrated with 5 min of Pt deposition on a self-improved GaN/Si photoelectrode (Fig. 8b), indicating about a 4 times reduction in the amount of Pt cocatalysts. To elucidate the reason for the self-improvement, photoconductive atomic force microscopy measurements were carried out (Fig. 8c). Notably, pristine GaN and self-improved GaN showed similar surface morphology but a substantial difference in photocurrent profile. The photocurrent in self-improved GaN mainly flows through the side walls of the GaN grains, whereas the top surface barely contributes to the photocurrent (Fig. 8d). From the surface composition analysis of self-improved GaN through cross-sectional scanning transmission electron microscopy (STEM) measurement, a 1 nm-thin layer with Ga, N, and O was observed at the side wall and a relatively thick layer with Ga and O was formed on the top surface (Fig. 8e). Theoretical calculations suggested that partial substitution of nitrogen by oxygen during the reaction can stabilize the GaON phase on the outermost layer of the nonpolar side wall, whereas the GaO phase is more preferred on the polar top surface (Fig. 8f). These different atomic compositions, originating from the crystal facets and polarity of GaN, shifted the  $\text{H}_2$  evolution activity. The free energy of adsorption of hydrogen is smaller on GaON compared to the pristine GaN non-polar side wall, thereby resulting in the thermodynamically favorable production of  $\text{H}_2$ .

Inspired by the previous investigations, a detailed study on the effect of crystal facet and surface polarity of wurtzite III-nitride on photoelectrochemical activities was carried out. To identify the impact of crystal orientations with different polarities, GaN nanostructures were fabricated by both top-down and bottom-up methods, which allow the exposure of certain facets (polar top surface or nonpolar side wall) to the electrolyte (Fig. 9a).<sup>96</sup> First, the GaN quasi-film (sample A) was grown on the  $n^+$ -p Si wafer with preferential orientation along the  $c$ -plane direction (Fig. 9b). Then, patterning processes (photolithography and dry etching) were conducted to expose the nonpolar  $m$ -plane side walls (sample B). Even though a high photocurrent density ( $\sim 40 \text{ mA cm}^{-2}$ ) is expected from an Si-based photocathode under 1 sun illumination, sample A showed negligible photocurrent density (Fig. 9c). In stark contrast, sample B exhibited a much better onset potential of  $\sim 0.45 V_{\text{RHE}}$  and saturation photocurrent density of  $\sim 18 \text{ mA cm}^{-2}$ . Given that sample A and sample B are nearly identical except for the nonpolar surfaces exposed to the electrolyte, it is therefore found that the nonpolar surfaces of GaN are responsible for the  $\text{H}_2$  evolution reaction. Furthermore, GaN nanowire arrays were grown on the  $n^+$ -p Si wafer. Then, their surface exposure to the electrolyte was controlled by the deposition of an insulating parylene passivation layer, followed by an etch-back process to reveal the top portions of the GaN nanowires. The as-grown GaN nanowire/Si photocathode with Pt cocatalysts exhibited an onset potential of  $0.45 V_{\text{RHE}}$  and a maximum photocurrent



**Fig. 8** (a) Current density and faradaic efficiency (FE) measurement of GaN quasi-film/ $n^+ - p$  Si photocathodes for 10 h under 1 sun illumination at  $-0.6 V_{\text{RHE}}$ . Inset: Si control electrode. (b) LSV curves of pristine (CA-0 h) and 4 h tested (CA-4 h) GaN/Si photocathodes with different Pt deposition duration. (c) Topography of self-improved GaN quasi-film (CA-10 h) and (d) corresponding surface profile and photocurrent extracted from the line scan. (e) STEM image of CA-10 h surface with elemental mappings of Ga L-edge, N K-edge and O K-edge. (f) Calculated formation energy of nonpolar  $m$ -plane GaN surface with different oxygen configurations within the anion- and cation-rich limits. Reproduced with permission from ref. 95. Copyright (2021) Springer Nature Limited.

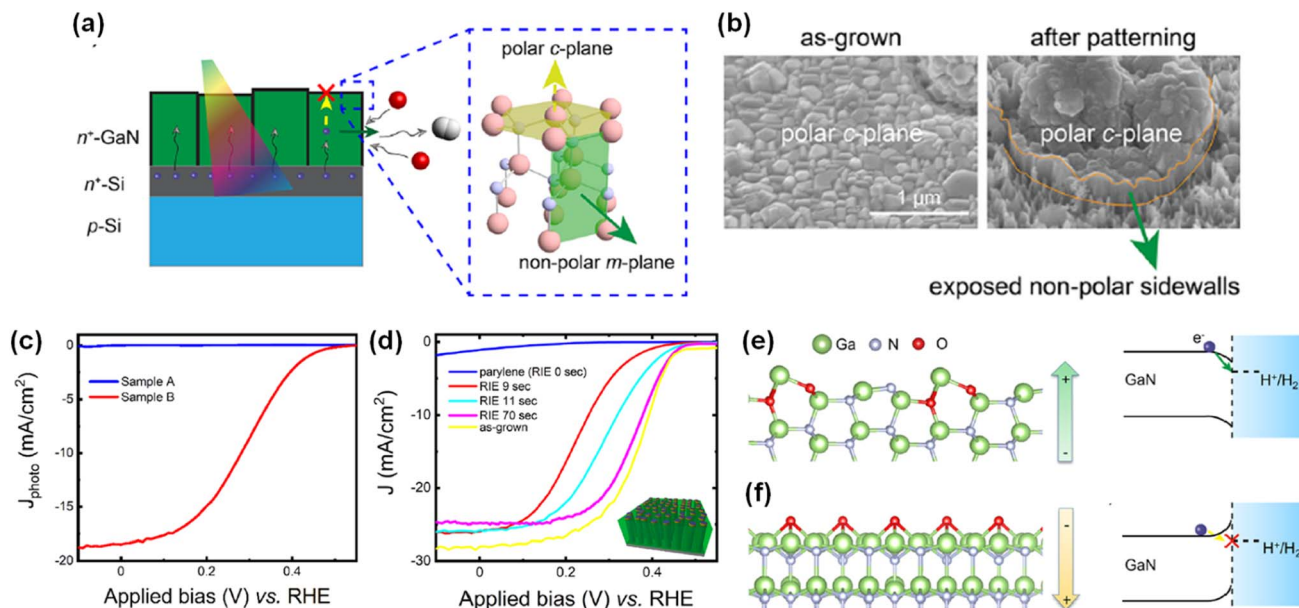
density of  $28 \text{ mA cm}^{-2}$  (Fig. 9d). Then, there was no photoresponse when the insulating passivation layer was deposited. However, after an initial etch-back process, the exposure of active nonpolar sidewalls of GaN nanowires greatly improved the performance. To understand the fundamental difference in the activity between polar and nonpolar planes, the role of oxygen was studied by density functional theory calculation. For the nonpolar surface, the most stable configuration was found to be gallium oxynitride formed by partial replacement of nitrogen by oxygen (Fig. 9e). On the other hand, for the polar surface, the most stable configuration was an oxygen-rich condition, which induces strong surface polarization and upward band bending at the surfaces (Fig. 9f). This observation

describes the reason for the facilitated electron transport at the nonpolar plane and limited transport at the polar one. It is therefore evident that selective exposure of desired crystal facets of a III-nitride nanostructure can enhance charge carrier transport and photoelectrochemical water splitting activity.

### 3.5. Protective 1D nitrides for long-term stability

Many semiconductor photoelectrodes have been studied and developed for photoelectrochemical water splitting with a suitable decoration with cocatalysts or modification of nanostructures.<sup>126–130</sup> However, most photoelectrodes with relatively high photocurrent density, such as Si and III-V





**Fig. 9** (a) Schematic illustration of the H<sub>2</sub> evolution reaction on the polar *c*-plane and nonpolar *m*-plane of wurtzite structure GaN. Photoexcited electrons preferentially migrate to the GaN nonpolar surfaces and reduce protons to H<sub>2</sub>. (b) SEM images of GaN quasi-film (sample A) and one that exposed the nonpolar sidewalls by a patterning process (sample B). (c) LSV curves of samples A and B in 0.5 M H<sub>2</sub>SO<sub>4</sub> under AM 1.5G 1 sun illumination. (d) H<sub>2</sub> evolution reaction of parylene-coated GaN nanowires. Longer durations of etch back exposed greater amounts of GaN nanowire nonpolar sidewalls. Schematic of configurations for surface polarization and surface energy band diagrams of (e) nonpolar *m*-plane with oxygen partial substitution and (f) polar *c*-plane with oxygen adsorption. Reproduced with permission from ref. 96. Copyright (2022) American Chemical Society.

semiconductors, suffer from a corrosion reaction in aqueous electrolytes because these materials have a very narrow window of stability based on their Pourbaix diagrams.<sup>131</sup> To prevent cathodic or anodic corrosion during the water splitting reaction, the photocathode should have the material's self-reduction potential above the energy level of H<sub>2</sub>O/H<sub>2</sub> and the photoanode should have the material's self-oxidation potential below the energy level of O<sub>2</sub>/H<sub>2</sub>O.<sup>132</sup> Several metal oxides such as TiO<sub>2</sub> (ref. 133) and Al<sub>2</sub>O<sub>3</sub> (ref. 134) satisfy these thermodynamic requirements and, thus, have been used as protective layers for photoelectrodes. However, the charge carriers in metal oxides are known to have poor mobilities and short diffusion lengths. Moreover, an unsuitable band alignment at the metal oxide/semiconductor interface is a major obstacle to realizing efficient photoelectrodes. To mitigate these limitations, N-terminated GaN nanowire arrays have been fabricated as multifunctional protection structures for the underlying n<sup>+</sup>-p Si photoelectrode (Fig. 10a and b).<sup>97</sup> GaN nanowires have several advantages of optical transparency, conduction band alignment between GaN and Si photocathode, and large surface area. GaN nanowires with a large band gap (~3.4 eV) are transparent for visible and infrared light and allow an Si photoelectrode to absorb broadband solar light. Also, the conduction band edges of n-type GaN nanowire and n<sup>+</sup>-Si are approximately aligned, so the photogenerated electrons can efficiently transfer from Si to GaN without significant electrical resistance (Fig. 10c). Moreover, the large surface area of GaN nanowires can be loaded with Pt cocatalysts and behave as active sites for the H<sub>2</sub> evolution reaction. As a result, Pt-decorated GaN/Si photocathodes

showed a high saturated photocurrent density of ~38 mA cm<sup>-2</sup> with a promising onset potential of ~0.5 V<sub>RHE</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> under 1 sun illumination (Fig. 10d). More notably, the Pt-decorated GaN/Si photocathodes showed excellent stability up to 3000 hours with relatively stable photocurrent densities of 37–38 mA cm<sup>-2</sup> at 0 V<sub>RHE</sub>.<sup>135</sup> Owing to the excellent physical and chemical stability of GaN nanowires,<sup>136</sup> GaN nanostructures have also been deposited on a III-V GaInP<sub>2</sub>/GaAs/Ge triple-junction photocathode as a protective scheme (Fig. 10e).<sup>98</sup> The GaN-protected triple-junction photocathode exhibited a saturated photocurrent density of 10.3 mA cm<sup>-2</sup>, an onset potential of 2.2 V<sub>RHE</sub>, and an ABPE of 12.6% (Fig. 10f). This photocathode can work continuously for 80 h without degradation (Fig. 10g), indicating the excellent stability, compatibility, and integrability of GaN nanostructures with high-performing semiconductors of Si and III-V photoelectrodes.

A green H<sub>2</sub> fuel can be produced by the photoelectrolysis of seawater, which is the most abundant water source on earth. However, due to the sluggish water dissociation reaction, unfavorable precipitation of insoluble salts (*e.g.*, Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>), and most importantly, the poor stability of semiconductors in harsh reaction conditions, the application of photoelectrodes for seawater splitting has been limited. However, GaN nanowires, grown on an n<sup>+</sup>-p Si photoelectrode, have enabled efficient and stable seawater H<sub>2</sub> evolution once Pt nanoclusters were decorated on the sidewalls of nanowires (Fig. 11a).<sup>99</sup> Compared to water dissociation on Pt, the heterolytic cleavage of the water molecule at a Pt-Ga site was facilitated due to the asymmetric atomic environment (Fig. 11b). The



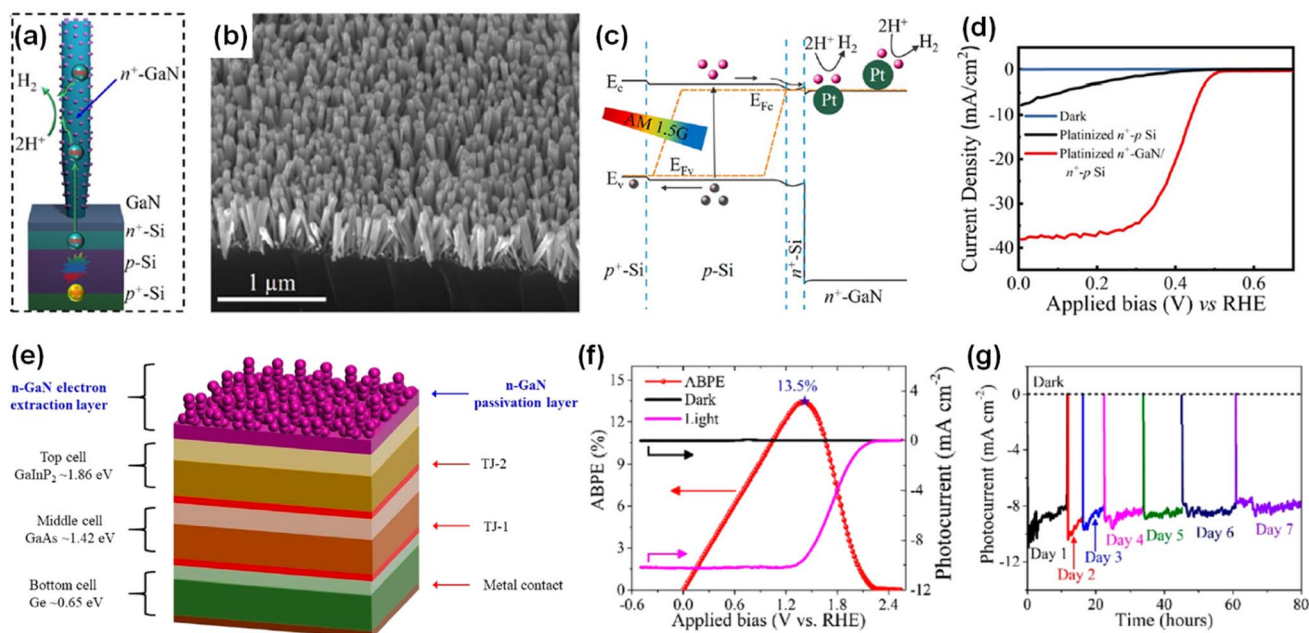


Fig. 10 (a) Schematic of GaN-nanowire-protected n<sup>+</sup>-p Si photocathode with Pt cocatalysts. (b) SEM image of GaN/Si photocathode. (c) Schematic of the energy band diagram of Pt-decorated GaN/Si photocathode under light illumination. (d) LSV curves measured under AM 1.5G 1 sun illumination in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Reproduced with permission from ref. 97. Copyright (2018) American Chemical Society. (e) Schematic illustration of the GaInP<sub>2</sub>/GaAs/Ge triple-junction photocathode protected by GaN nanostructures. (f) Photoelectrochemical H<sub>2</sub> evolution reaction performance and (g) long-term stability of GaN-protected triple-junction photoelectrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> under 1 sun illumination. Reproduced with permission from ref. 98. Copyright (2019) American Chemical Society.

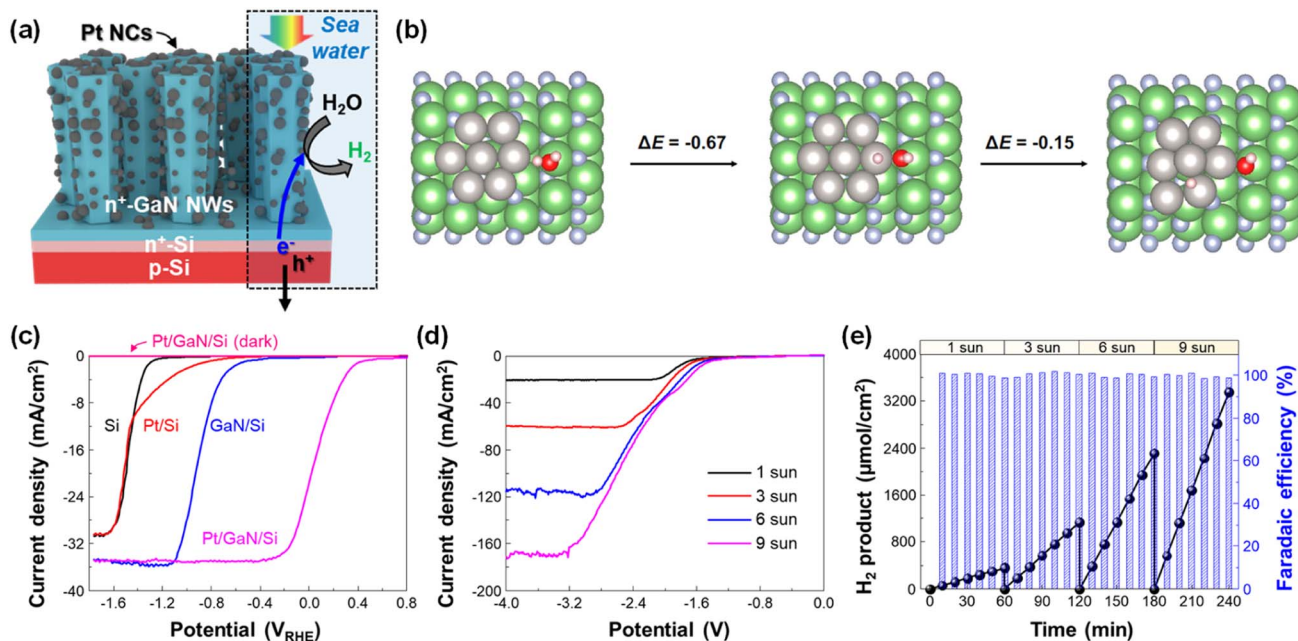


Fig. 11 (a) Schematic illustration of the Pt/GaN/Si photocathode for seawater H<sub>2</sub> evolution. (b) Optimized structures and calculated energy changes of water dissociation at the Pt-Ga site and subsequent H spillover to the Pt surface. All energy changes are in the units of eV. The white, red, blue, green, and grey spheres represent H, O, N, Ga, and Pt atoms, respectively. (c) LSV curves of Si, Pt/Si, GaN/Si, and Pt/GaN/Si measured with a 3-electrode configuration in 0.5 M NaCl solution under AM 1.5G 1 sun illumination or in the dark. (d) LSV curves of Pt/GaN/Si measured with 2-electrode configurations in 0.5 M NaCl under different light intensities. (e) Amount of H<sub>2</sub> product and faradaic efficiency measured under light intensities of 1, 3, 6, and 9 suns at -3 V. Reproduced with permission from ref. 99. Copyright (2023) Springer Nature Limited.

overall energy change of water splitting at the Pt/GaN interface is  $-0.81$  eV, indicating a spontaneous reaction without a thermodynamic energy barrier. Owing to the benefits from the synergistic interaction between GaN and Pt, an onset potential ( $0.16$  V<sub>RHE</sub>) and a saturated photocurrent density ( $\sim 35$  mA cm<sup>-2</sup>) of Pt/GaN/Si outperformed the other control devices (Fig. 11c). Moreover, the Pt/GaN/Si photocathode revealed a gradual increase in saturated photocurrent density, reaching  $\sim 165$  mA cm<sup>-2</sup> at  $-3.2$  V under concentrated solar light (9 sun) illumination in a 2-electrode configuration (Fig. 11d). Accordingly, the production rate of H<sub>2</sub> gradually increased from 359 (under 1 sun illumination) to 3351  $\mu\text{mol cm}^{-2} \text{h}^{-1}$  (under 9 sun illumination) while the faradaic efficiency was nearly 100% regardless of the light intensity (Fig. 11e). Therefore, a GaN-nanowire-protected Si photoelectrode is a promising platform for an efficient, stable, and energy-saving electrode for solar-assisted H<sub>2</sub> generation by seawater splitting.

## 4. Photocatalytic water splitting

In contrast to photoelectrochemical water splitting driven by solar light and electrical bias, photocatalytic water splitting, often referred to as type-I or type-II photoelectrochemical water splitting, is completely wireless and overall water splitting operates with only solar light as energy input. Moreover, in photocatalytic water splitting, pH-neutral pure water, or seawater can be readily utilized, in contrast to the strongly acidic or basic electrolytes commonly required for conventional photoelectrochemical water splitting. Therefore, photocatalytic water splitting is more amenable for the scaled-up production of solar hydrogen with reduced cost and enhanced stability. When the incident light illuminates the photocatalysts in water, the photocatalysts absorb photons with an energy larger than the band gap by exciting electrons in the conduction band and holes in the valence band. Then, the photoexcited electrons and

holes separate and are transported to the surface active sites for the catalytic reactions. Because both water oxidation ( $\text{H}_2\text{O} + 2\text{h}^+ \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+$ ) and reduction reactions ( $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$ ) occur at a photocatalyst, the semiconductor photocatalysts for overall water splitting should satisfy the requirements of band edge positions which must straddle the water reduction and oxidation potentials. Moreover, catalytic activity for stabilizing reaction intermediates is necessary to kinetically and thermodynamically enhance the productivity and selectivity for H<sub>2</sub> and O<sub>2</sub>. Therefore, it is highly desirable to develop a photocatalyst material with a suitable band gap, band edge position, and surface active site for overall water splitting. Up to now, some metal oxides (*i.e.*, TiO<sub>2</sub> and SrTiO<sub>3</sub>) have demonstrated overall solar water splitting since they satisfy the requirements of band edge positions.<sup>137,138</sup> However, those metal oxides possess relatively large band gaps due to the deeper-lying O 2p orbitals in the valence band edge. Consequently, they are photoresponsive only to ultraviolet light, which results in limited efficiency. In contrast, III-nitrides have a smaller band gap and less positive valence band edge positions, mainly consisting of N 2p orbitals. Therefore, 1D III-nitrides, such as InGaN nanowires, have shown great promise in photocatalytic water splitting (Table 3). Efficiency-enhancement strategies, such as band gap engineering, doping for surface band bending, and loading of cocatalysts, are introduced in the following sections.

### 4.1. Band gap engineering of 1D nitrides

Unlike conventional photocatalysts in powder form, GaN nanowires, vertically grown on an Si wafer, have a single-crystalline structure with a small number of defects, resulting in efficient charge carrier transport to the surface active sites for photocatalytic water splitting. Hence, GaN nanowires decorated with Rh/Cr<sub>2</sub>O<sub>3</sub> core/shell nanoparticles have been fabricated wherein the GaN is responsible for the O<sub>2</sub> evolution reaction,

Table 3 III-Nitride photocatalysts for photocatalytic overall water splitting

Photocatalyst	Cocatalyst	Solution	Light source	Performance	Ref.
p-InGaN/GaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub>	Artificial seawater	300 W Xe lamp	STH conversion efficiency = 1.9%	139
InGaN/GaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub> and Co <sub>3</sub> O <sub>4</sub>	H <sub>2</sub> O	300 W Xe lamp with AM 1.5G filter	STH conversion efficiency = 2.7%	140
InGaN/GaN core/shell NWs	Pt	220 ml H <sub>2</sub> O with 50 ml CH <sub>3</sub> OH	300 Xe lamp (1044 mW cm <sup>-2</sup> )	H <sub>2</sub> production rate = 253.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$	141
InGaN/GaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	300 W Xe lamp	H <sub>2</sub> production rate = $\sim 92$ mmol g <sup>-1</sup> h <sup>-1</sup>	142
Quadruple-band InGaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub> and Co <sub>3</sub> O <sub>4</sub>	H <sub>2</sub> O	300 W Xe lamp with AM 1.5G filter	STH conversion efficiency = $\sim 5.2\%$	143
Mg-doped GaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	300 W Xe lamp with $>375$ nm filter	H <sub>2</sub> + O <sub>2</sub> production rate = $\sim 570$ mmol g <sup>-1</sup> h <sup>-1</sup>	144
p-GaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	300 W Xe lamp	H <sub>2</sub> production rate = $\sim 4$ mol g <sup>-1</sup> h <sup>-1</sup>	145
p-GaN/InGaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	300 W Xe lamp with AM 1.5G filter	STH conversion efficiency = 1.8%	146
Mg-doped InGaN nanosheets	Rh/Cr <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	300 W Xe lamp with AM 1.5G filter	STH conversion efficiency = 3.3%	147
GaN nanorods	Rh and CoO <sub>x</sub>	H <sub>2</sub> O	300 W Xe lamp	Quantum efficiency = 6.9%	148
InGaN/GaN NWs	Rh/Cr <sub>2</sub> O <sub>3</sub> /Co <sub>3</sub> O <sub>4</sub>	H <sub>2</sub> O at 70 °C	300 W Xe lamp with AM 1.5G filter	STH conversion efficiency = 9.2%	149

the Rh core promotes the  $\text{H}_2$  evolution reaction, and the  $\text{Cr}_2\text{O}_3$  shell prevents the backward reaction (Fig. 12a).<sup>150</sup> From TEM characterization, it was found that GaN nanowires have a single crystalline structure and are uniformly coated by metallic Rh/ $\text{Cr}_2\text{O}_3$  core/shell nanoparticles (Fig. 12b). Photocatalytic water splitting has been successfully carried out on 1D GaN nanowires with Rh/ $\text{Cr}_2\text{O}_3$  cocatalysts in pure water under light irradiation. During  $\sim 18$  h of reaction, a stoichiometric ratio (2 : 1) of  $\text{H}_2$  and  $\text{O}_2$  gases was steadily generated (Fig. 12c).

Although wafer-level photocatalytic water splitting has been demonstrated by GaN nanowires, a very small portion of solar light (mostly ultraviolet light) can be absorbed due to the large band gap ( $\sim 3.4$  eV). The band gap of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  can ideally be controlled from 3.4 eV to 0.65 eV and, thus, the visible-to-near infrared solar spectrum can be used for photocatalytic overall water splitting. However, it is extremely challenging to grow the InGaN nanowires with a narrow band gap due to phase-separation issues and an increase in the number of detrimental defects. Moreover, the decrease in band gap energy of III-nitride semiconductors inevitably shifts the valence band edge potential in a more negative direction and/or the conduction band edge positions in a more positive direction, thereby resulting in a decrease in the redox ability. To mitigate these issues, multi-band InGaN/GaN nanowire photocatalysts have been developed to enhance the STH efficiency.<sup>139–141</sup> For example, sequential deposition of GaN (band gap = 3.4 eV), InGaN quantum dots (2.22 eV), and InGaN wells (2.96 eV) reduced the lattice mismatch at the hetero-interfaces and enabled the epitaxial growth of nanowire photocatalysts with a multi-band structure (Fig. 13a–c).<sup>142</sup> The HAADF image of InGaN/GaN nanowire exhibited an obvious atomic number contrast and the presence of 10 InGaN/GaN quantum dots located along the axial direction of the nanowire (Fig. 13d). InGaN/GaN nanowires with Rh/ $\text{Cr}_2\text{O}_3$  cocatalysts showed overall pure water splitting under light illumination. The high production rates of  $\text{H}_2$  ( $\sim 683$   $\mu\text{mol}$ ) and  $\text{O}_2$  ( $\sim 373$   $\mu\text{mol}$ ) were concurrently demonstrated during 18 h of reaction (Fig. 13e), indicating that the broader band light absorption induced more photogenerated charge carriers and promoted the

photocatalytic water splitting reactions compared to GaN nanowires. Furthermore, quadruple-band  $\text{In}_x\text{Ga}_{1-x}\text{N}$  nanowires consisting of continuous  $\text{In}_{0.35}\text{Ga}_{0.65}\text{N}$  (2.10 eV),  $\text{In}_{0.27}\text{Ga}_{0.73}\text{N}$  (2.40 eV),  $\text{In}_{0.20}\text{Ga}_{0.80}\text{N}$  (2.60 eV), and GaN (3.40 eV) segments have been successfully grown on an Si wafer by MBE (Fig. 13f).<sup>143</sup> The  $\text{In}_x\text{Ga}_{1-x}\text{N}$  nanowires showed an inversely tapering morphology (Fig. 13g) and 4 distinct regions with different In content (Fig. 13h). Besides, gradient doping of Mg along the lateral dimension of the nanowires induces an internal electric field, which facilitates electron–hole separation (the effect of Mg doping in InGaN nanowires will be described in Section 4.2). These advantageous optoelectronic properties of quadruple-band  $\text{In}_x\text{Ga}_{1-x}\text{N}$  nanowires greatly enhanced the photocatalytic overall water splitting and achieved a high STH (Fig. 13i).

#### 4.2. Doping of 1D nitrides

Intrinsic III-nitrides can be changed to p-type semiconductors with Mg doping. Hence, the effect of Mg dopant in GaN nanowires on light response, charge carrier transport, and photocatalytic activity of overall water splitting has been investigated. To vary the amount of Mg dopant, the Mg effusion cell temperature was changed from 190 to 315  $^\circ\text{C}$  during the MBE growth of GaN nanowires.<sup>144</sup> Low-temperature (20 K) photoluminescent spectra of pristine GaN showed a single peak at 3.435 eV, corresponding to a donor-bound exciton. With a small amount of Mg doping (200  $^\circ\text{C}$ ), GaN:Mg nanowires showed two additional peaks at 3.254 and 3.189 eV, which are attributed to the conduction band to Mg-related acceptor level (Fig. 14a). With a further increase in the amount of Mg dopant (260  $^\circ\text{C}$ ), a new broad photoluminescence peak at 2.95 eV appeared due to the donor–acceptor-pair transition between the N-vacancy deep donor states and shallow Mg acceptor states. With the intra-gap defect states which straddle the redox potential of water (Fig. 14b), GaN:Mg nanowires enable broadband light absorption and enhance the performance of overall water splitting (Fig. 14c). However, it should be noted that further incorporation of Mg dopant in GaN nanowires ( $>260$   $^\circ\text{C}$ ) drastically degrades the water splitting activity because of poor

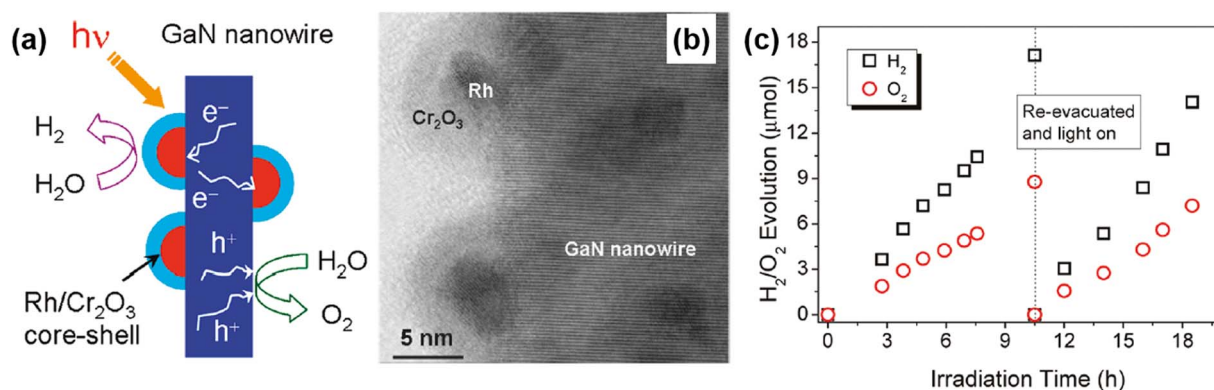


Fig. 12 (a) Schematic illustration of photocatalytic water splitting on GaN nanowire with Rh/ $\text{Cr}_2\text{O}_3$  core/shell nanoparticle cocatalysts. (b) High-resolution TEM image of Rh/ $\text{Cr}_2\text{O}_3$  cocatalysts on GaN nanowire. (c)  $\text{H}_2$  and  $\text{O}_2$  evolution under 300 W full arc xenon lamp irradiation for a duration of 18 h. Reproduced with permission from ref. 150. Copyright (2011) American Chemical Society.



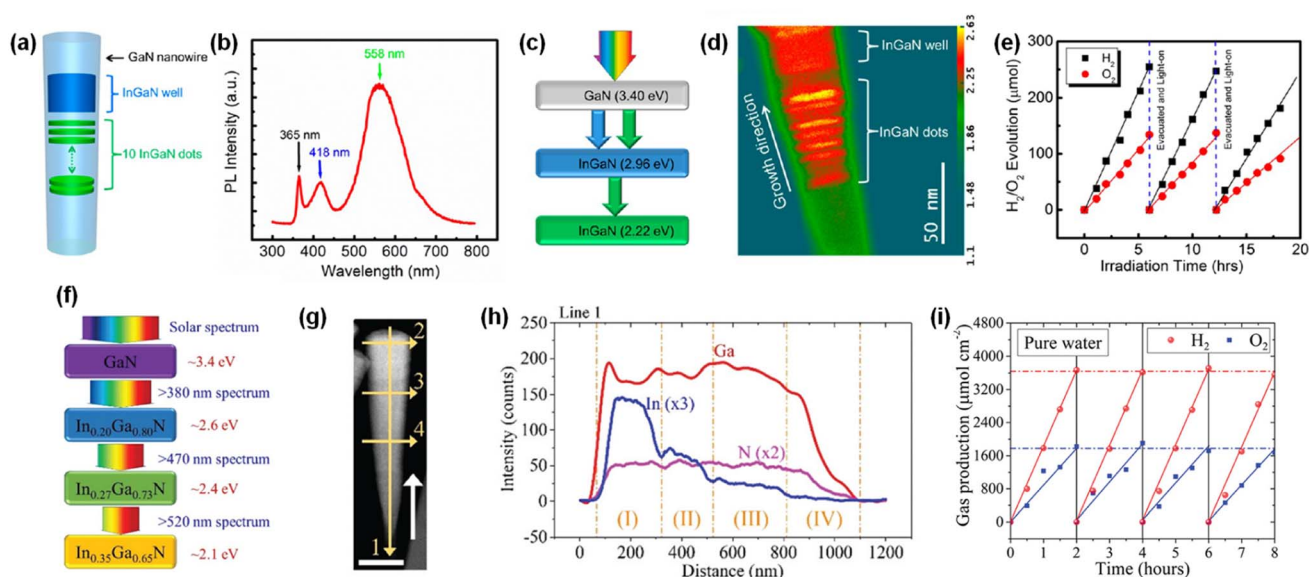


Fig. 13 (a) Schematic and (b) photoluminescence spectra of InGaN/GaN nanowires. (c) Band gap energy of each segment. (d) HAADF image in pseudocolor display of InGaN/GaN nanowire, showing the atomic number contrast between InGaN (red) and GaN (green) segments. (e) Overall pure water splitting on Rh/Cr<sub>2</sub>O<sub>3</sub>-decorated InGaN/GaN nanowires under full arc (>300 nm) 300 W xenon lamp irradiation. Reproduced with permission from ref. 142. Copyright (2013) American Chemical Society. (f) Schematic light absorption sequence and (g) TEM image of quadruple-band InGaN nanowire with various indium compositions. (h) Energy-dispersive X-ray spectroscopy line scanning showing the variation in Ga, In, and N elements along the axial direction. (i) Photocatalytic H<sub>2</sub> and O<sub>2</sub> gas evolution as a function of time. Reproduced with permission from ref. 143. Copyright (2019) Royal Society of Chemistry.

crystal quality and undesirable non-radiative recombination of photogenerated carriers. Hence, optimized doping of III-nitride photocatalysts can broaden the light-responsive wavelength and, accordingly, increase the productivity of overall water splitting under solar light irradiation.

Moreover, previous studies revealed that n-type and p-type doping of GaN surfaces results in upward and downward band bending, respectively, once water is adsorbed on the surface, which can promote the separation of photogenerated electron-hole pairs at the semiconductor/water interface.<sup>151,152</sup>

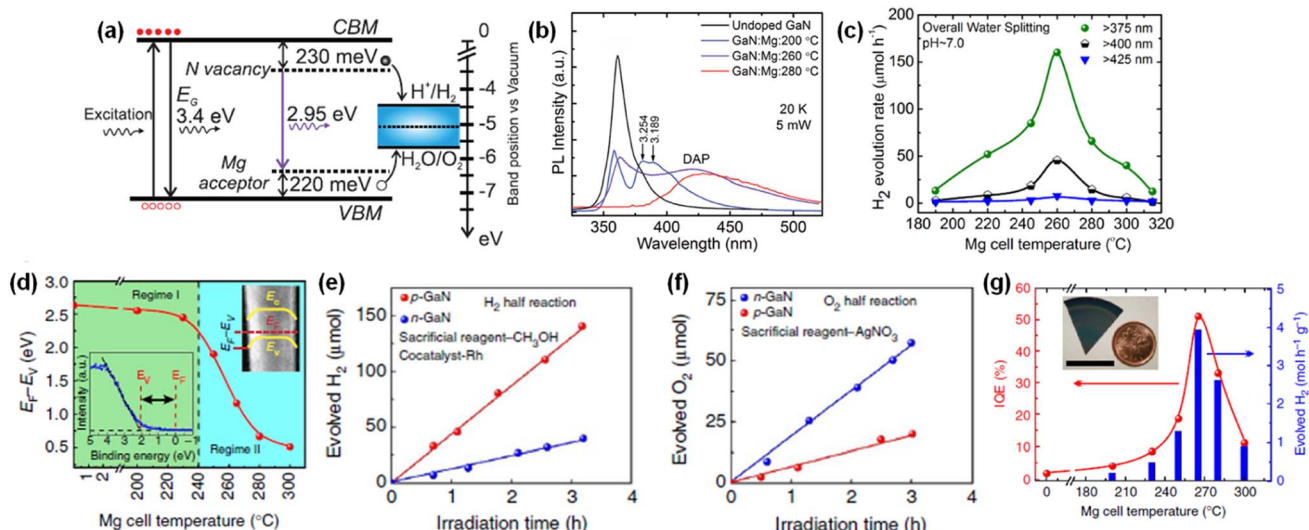


Fig. 14 (a) Schematic energy band diagram of Mg-doped GaN nanowires. (b) Low-temperature photoluminescence spectra of GaN:Mg and undoped GaN nanowires. (c) H<sub>2</sub> evolution rate from photocatalytic water splitting from the GaN:Mg samples under 300 W xenon lamp. Reproduced with permission from ref. 144. Copyright (2015) AIP Publishing. (d) Plot of  $E_f - E_v$  for different GaN:Mg nanowires. Regimes I and II indicate n-type and p-type surfaces, respectively. (e) H<sub>2</sub> and (f) O<sub>2</sub> evolution reactions from n- and p-type GaN nanowires in the presence of sacrificial reagents. (g) H<sub>2</sub> evolution rate and internal quantum efficiency for different GaN:Mg nanowires in overall pure water splitting. Reproduced with permission from ref. 145. Copyright (2014) Nature Publishing Group, a division of Macmillan Publishers Limited.



Since GaN nanowires have a weakly n-type nature with the Fermi level located higher than the redox potential of water, the fine-tuning of the p-type dopant in GaN nanowires can reduce the downward band bending and provide an opportunity to realize the balanced surface band structure for efficient photocatalytic water splitting reactions.<sup>145</sup> The amount of p-type Mg dopant was *in situ* controlled during the MBE growth of GaN nanowires by varying the Mg effusion cell temperature ( $T_{\text{Mg}}$ ). Then, the near-surface band structure of GaN:Mg nanowire was investigated by measuring the Fermi level position ( $E_{\text{F}}$ ) relative to the valence band maximum ( $E_{\text{V}}$ ) by X-ray photoelectron spectroscopy (Fig. 14d). The  $E_{\text{F}} - E_{\text{V}}$  was 2.63 eV for undoped GaN, indicating an n-type semiconductor property. However, as  $T_{\text{Mg}}$  increased over 240 °C, the near-surface  $E_{\text{F}} - E_{\text{V}}$  dramatically decreased due to the increased free hole concentration in GaN nanowires from p-type doping. To evaluate the effect of surface band bending on photocatalytic water splitting,  $\text{H}_2$  and  $\text{O}_2$  half-reactions were measured in the presence of sacrificial reagents in the electrolytes. The  $\text{H}_2$  production rate of p-type GaN nanowires was much higher than that of n-type GaN nanowires owing to downward band bending (Fig. 14e). On the other hand,

the  $\text{O}_2$  production rate of n-type GaN nanowires was significantly enhanced due to efficient hole transport by upward band bending (Fig. 14f). Hence, to demonstrate efficient overall water splitting, it is desirable to construct a nearly flat band profile at the GaN/water interface. Consequently, the optimum incorporation of p-type Mg dopants in GaN nanowires decreased the downward band bending, which led to an improvement in STH efficiency by more than two orders of magnitude compared to n-type GaN nanowires (Fig. 14g). Moreover, it is also found that this p-type doping strategy is applicable to visible-light-responsive InGaN nanowires.<sup>146</sup> A gradual decrease in near-surface  $E_{\text{F}} - E_{\text{V}}$  (gradual change from n-type to p-type) was observed with an increasing amount of Mg dopant in InGaN nanowires. With optimized InGaN:Mg nanowires, a high yield of  $\text{H}_2$  evolution ( $\sim 0.8 \text{ mol h}^{-1} \text{ g}^{-1}$ ) and STH efficiency (1.8%) were achieved with stoichiometric  $\text{O}_2$  evolution under visible light wavelength.

In addition to surface band bending, a built-in potential in bulk regions of III-nitride is highly desirable for efficient charge carrier separation. Previously, two-dimensional p-type InGaN nanosheets with gradient Mg doping were developed as

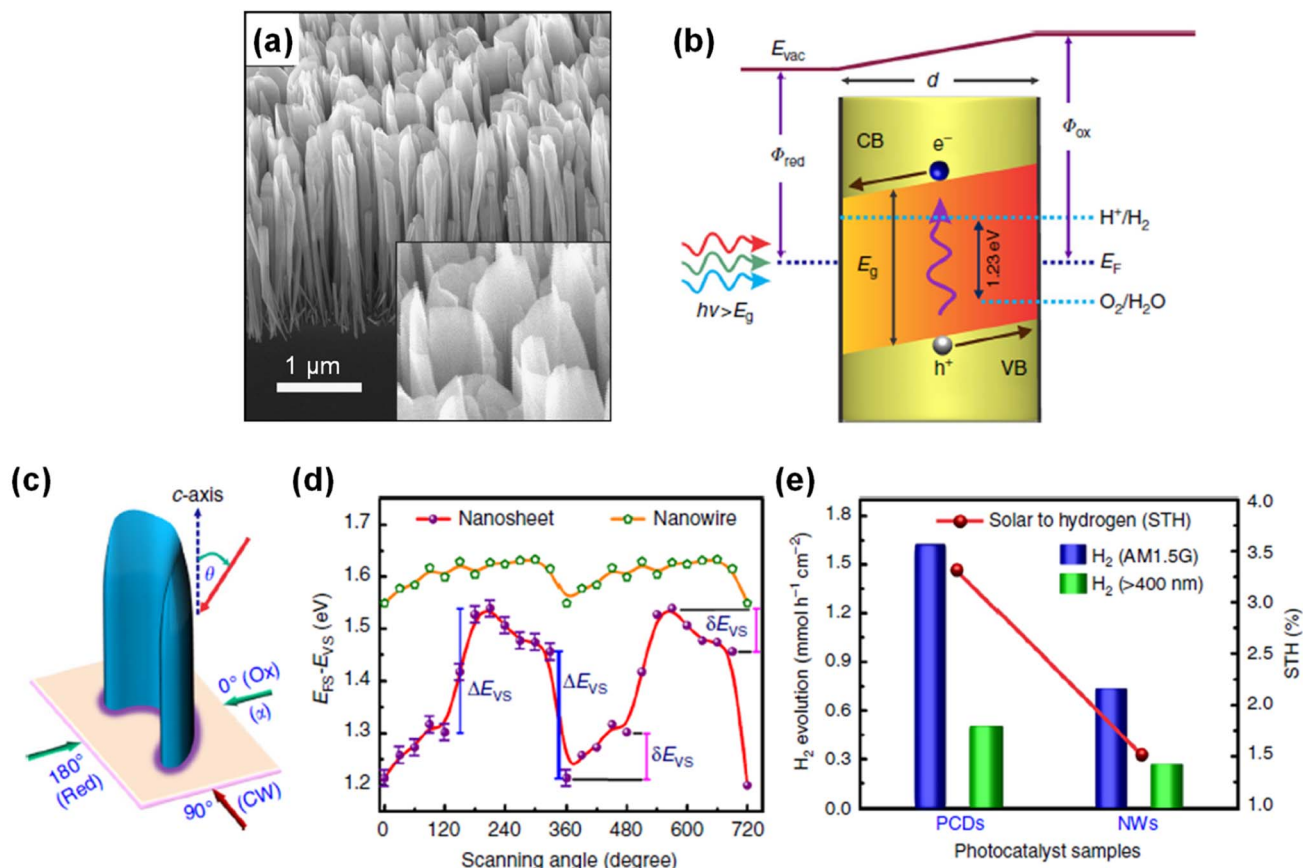


Fig. 15 (a) SEM image of Mg-doped p-InGaN nanosheets vertically grown on an Si substrate. (b) Energy-band diagram of p-InGaN nanosheet with radial thickness " $d$ " showing the built-in electric field (band-bending) that separates the electrons and holes towards opposite surfaces. (c) Schematic illustration of probing the surface valence band spectra using X-ray photoelectron spectroscopy. (d)  $E_{\text{FS}} - E_{\text{VS}}$  for Mg-doped InGaN nanosheets and nanowire arrays as a function of radial scanning angle ( $\alpha$ ). (e)  $\text{H}_2$  evolution rate in overall water splitting for photochemical diodes (nanosheets) and nanowires under different excitation conditions. All the photocatalysts were decorated with Rh/Cr<sub>2</sub>O<sub>3</sub> cocatalysts. Reproduced with permission from ref. 147. Copyright (2018) Springer Nature Limited.

photocatalysts for overall water splitting (Fig. 15a).<sup>147</sup> During the growth, Mg dopants impinged preferentially on one side, thereby leading to gradient doping of Mg along the lateral dimension of the nanosheets. This configuration induced a strong internal electric field that separated the electrons in the conduction band and holes in the valence band toward opposite surfaces with significantly suppressed non-radiative recombination (Fig. 15b). From the near-surface band structures of p-InGaN nanowires and nanosheets (Fig. 15c), a sharp change in  $E_F - E_V$  ( $\sim 300$  mV) vs. scanning angle on p-InGaN nanosheets was observed. This confirmed that there is a strong internal electric field within the nanosheet due to the Mg dopant gradient from one side to the other (Fig. 15d). In contrast, p-InGaN nanowires showed nearly constant  $E_F - E_V$  regardless of scanning angle because of the symmetric morphology of the nanowires. As a result, p-InGaN nanosheets realized remarkable enhancement in activity for the photocatalytic water splitting reaction over p-InGaN nanowires and achieved an impressive STH efficiency of  $\sim 3.3\%$  (Fig. 15e).

### 4.3. Polarity of 1D nitrides

The ionic bonds in a unit cell of crystalline III-nitride semiconductors can induce electric dipole moments, thereby resulting in positive charges on one surface and negative charges on the other, which then produces a substantial electric field directed from the positively poled regions to those negatively poled. This electric field can redistribute the photo-generated charge carriers in III-nitrides and have a great influence on photocatalytic water splitting reactions. It is well known that GaN is generally grown along the polar  $c$ -axis [0001] direction on a  $c$ -plane sapphire substrate, resulting in the exposure of the polar surface (Ga-polar or N-polar).<sup>153</sup> In order to expose the buried nonpolar plane (parallel to  $c$ -axis) to the surface, n-type GaN film was etched into nanorod arrays (Fig. 16a).<sup>148</sup> Thus, the GaN nanorod arrays have a top polar surface (Ga-polar) and a nonpolar side surface. Based on surface band bending analysis, it was found that the upward band bending of the polar surface is more pronounced than that of the nonpolar surface, which leads to spatial separation of photogenerated electrons to the nonpolar surface and holes to

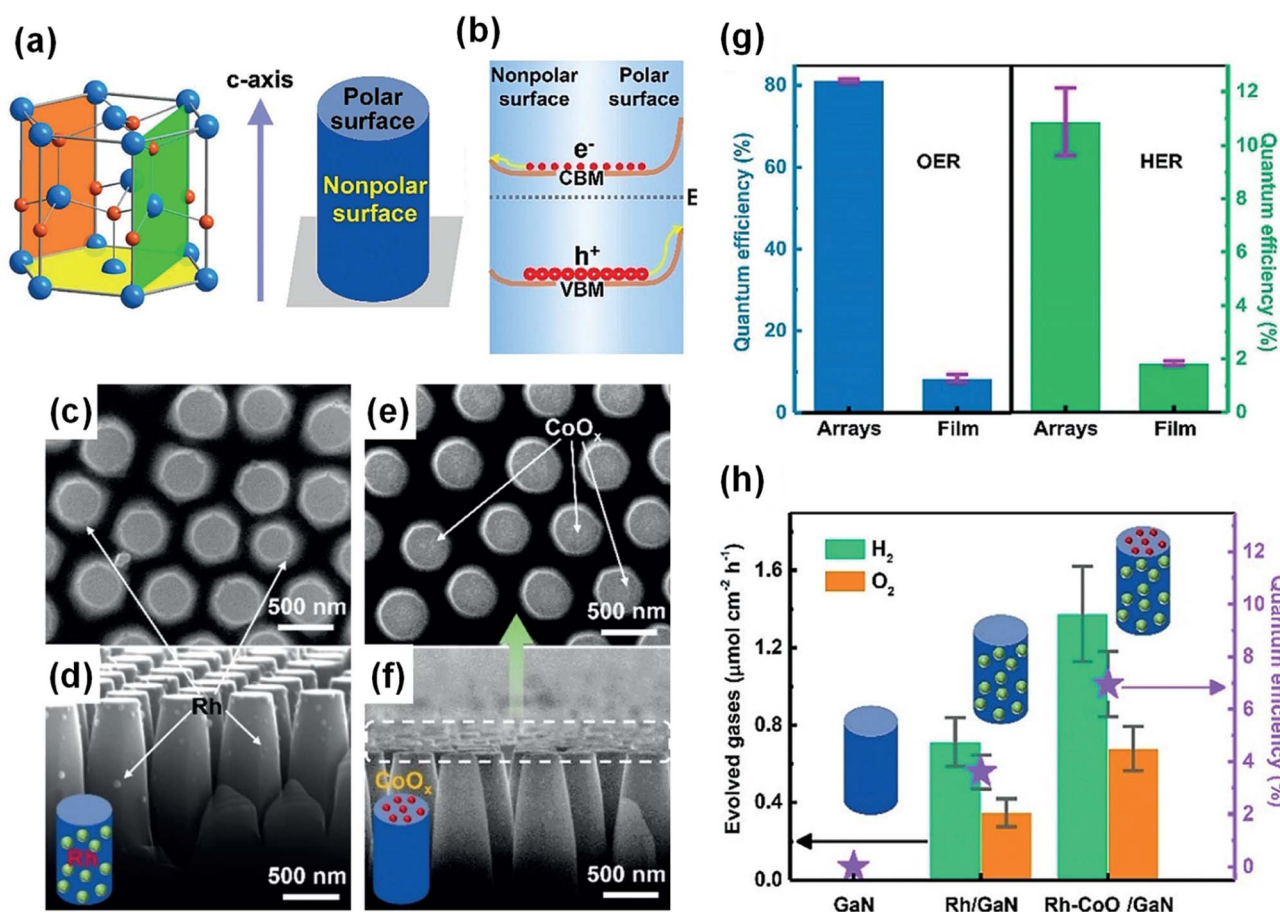


Fig. 16 (a) Schematic representation of polar  $c$ -plane (yellow), nonpolar  $a$ -plane (green), and  $m$ -plane (orange) of a GaN crystal, as well as the surface polarity of GaN nanorod arrays.<sup>148</sup> (b) Schematic representation of different band bending on polar and nonpolar surfaces and the resulting spatial charge separation. (c–f) SEM images of GaN nanorod arrays with (c and d) Rh and (e and f)  $CoO_x$  cocatalysts. (g) Photocatalytic  $O_2$  and  $H_2$  evolution reaction on GaN nanorod arrays and film coated with Rh and  $CoO_x$  cocatalysts. (h) Photocatalytic overall water splitting on GaN nanorod arrays without and with cocatalysts Rh and  $CoO_x$ . Reproduced with permission from ref. 148. Copyright (2020) John Wiley and Sons.

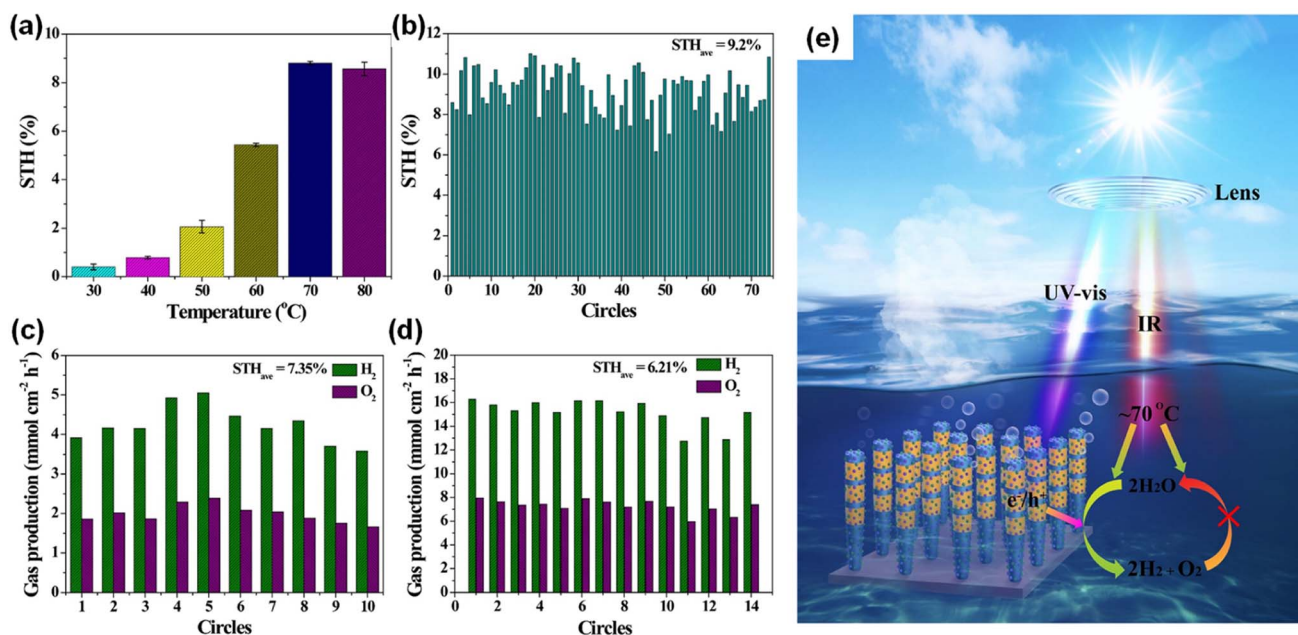


Fig. 17 (a) Temperature-dependent STH efficiency of Rh/Cr<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>-InGaN/GaN nanowires (a concentrated light of 3800 mW cm<sup>-2</sup> with AM 1.5G filter was used). (b) Stability in the self-heated photocatalytic overall water splitting system. Each circle = 1 hour. (c) Measured STH in tapwater under 3800 mW cm<sup>-2</sup>. Each circle = 1 hour. (d) STH of 4 cm × 4 cm photocatalyst under concentrated natural solar light (~16 070 mW cm<sup>-2</sup>). Each circle = 10 min. (e) Synergetic effect mechanism of promoting forward H<sub>2</sub>-O<sub>2</sub> evolution and inhibiting reverse H<sub>2</sub>-O<sub>2</sub> recombination in photocatalytic overall water splitting. Reproduced with permission from ref. 149. Copyright (2023) Springer Nature Limited.

the polar surface (Fig. 16b). The charge separation characteristics of GaN nanorod arrays can be investigated through the photochemical deposition method, in which reduced metals and oxidized metal oxides are coated on the electron-rich sites and hole-rich sites, respectively. After the photodeposition of Au, Rh, and Ag through the reduction of metal ions, metal nanoparticles were selectively coated on the nonpolar surface (side surface) (Fig. 16c and d). In stark contrast, MnO<sub>x</sub> and CoO<sub>x</sub>, deposited through an oxidation reaction, were found on the polar surface (top surface) (Fig. 16e and f). Owing to the polarity-driven electron-hole separation to redox active sites, the GaN nanorod arrays exhibited much higher photocatalytic water splitting activity compared to GaN film (Fig. 16g). In addition, the selective deposition of CoO<sub>x</sub> and Rh cocatalysts on the respective top and side surfaces greatly enhanced the overall water splitting (Fig. 16h).

#### 4.4. Temperature-dependent solar water splitting

During the photocatalytic overall water splitting, the forward reaction of H<sub>2</sub> and O<sub>2</sub> evolution (2H<sub>2</sub>O → 2H<sub>2</sub> + O<sub>2</sub>) often competes with the backward reaction of H<sub>2</sub>-O<sub>2</sub> recombination (2H<sub>2</sub>O ← 2H<sub>2</sub> + O<sub>2</sub>). Even though some cocatalysts (*i.e.*, Rh/Cr<sub>2</sub>O<sub>3</sub> core/shell nanoparticles<sup>150</sup>) loaded on InGaN/GaN nanowires have promoted the forward reaction, the catalytic activity of a III-nitride photocatalyst at higher temperature has remained unknown. Therefore, photocatalytic water splitting was conducted at different temperatures from 30 °C to 80 °C by illuminating with concentrated simulated solar light (3800 mW cm<sup>-2</sup>).<sup>149</sup> InGaN/GaN nanowires decorated with Rh/Cr<sub>2</sub>O<sub>3</sub>/

Co<sub>3</sub>O<sub>4</sub> cocatalysts exhibited a dramatic increase in STH efficiency with increasing temperature (Fig. 17a). The maximum STH efficiency of 8.8% was achieved at 70 °C. Theoretical calculation elucidated that most steps of water splitting reactions were exothermal except for the water desorption step in H<sub>2</sub>-O<sub>2</sub> recombination, meaning that H<sub>2</sub>-O<sub>2</sub> recombination is suppressed as the temperature increases. However, further increasing the temperature to 80 °C did not improve the STH efficiency because the enhanced diffusivity of H<sub>2</sub> and O<sub>2</sub> promoted mass transfer in water and accelerated H<sub>2</sub>-O<sub>2</sub> recombination. The Rh/Cr<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>-InGaN/GaN photocatalyst showed a world-record STH efficiency of 9.2% and promising stability for 74 hours at the optimized temperature of 70 °C (Fig. 17b). Moreover, the photocatalysts, evaluated in tap water (Fig. 17c) and seawater, exhibited very high STH efficiencies of 7.4% and 6.6%, respectively, showing high potential for practical use. In principle, it is possible to reduce material costs when more solar energy can be utilized in a given irradiated area. Hence, a 4 cm × 4 cm photocatalyst wafer was immersed in water and exposed to concentrated natural solar light (~16 070 mW cm<sup>-2</sup>). This outdoor test showed that the chamber could be self-heated and maintained at a high temperature (75 ± 3 °C). As a result, the highest reported STH efficiency of 6.2% was achieved under natural solar light (Fig. 17d). This work is the first demonstration that a III-nitride photocatalyst not only utilizes ultraviolet-visible light for photoexcitation of charge carriers but also benefits from the thermal energy generated by infrared light (Fig. 17e).



Table 4 III-Nitride photocathodes for photoelectrochemical CO<sub>2</sub> reduction reaction

Photocathode	Cocatalyst	Applied potential	CO <sub>2</sub> feedstock	Main products	Faradaic efficiency	Current density	Ref.
p-GaN film	Au	-1.8 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CO	CO: 83%	~2 μA cm <sup>-2</sup>	176
GaN nanowires/n <sup>+</sup> -p Si	ZnO-Cu	0.17 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CO	CO: 70%	<1 mA cm <sup>-2</sup> (8 sun illumination)	177
GaN nanowires/n <sup>+</sup> -p Si	TiO <sub>2</sub> -Pt	0.27 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CO, H <sub>2</sub>	CO: ~33%, H <sub>2</sub> : ~66%	~15 mA cm <sup>-2</sup> (8 sun illumination)	178
GaN nanowires/n <sup>+</sup> -p Si	AuPt <sub>0.2</sub>	0.17 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CO, H <sub>2</sub>	CO: ~33%, H <sub>2</sub> : ~66%	~9 mA cm <sup>-2</sup>	179
GaN nanowires/n <sup>+</sup> -p Si	Au	0.17 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CO, H <sub>2</sub>	CO: ~55%, H <sub>2</sub> : ~45%	~3 mA cm <sup>-2</sup>	180
GaN nanowires/n <sup>+</sup> -p Si	AgBr	-0.4 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CO	CO: 82%, H <sub>2</sub> : 17%	13.8 mA cm <sup>-2</sup>	181
GaN nanowires/n <sup>+</sup> -p Si	Sn	-0.53 V <sub>RHE</sub>	Pure CO <sub>2</sub>	HCOOH	HCOOH: 76.9%	~11 mA cm <sup>-2</sup>	182
GaN nanowires/n <sup>+</sup> -p Si	Bi	-0.6 V <sub>RHE</sub>	Pure CO <sub>2</sub>	HCOOH	HCOOH: 95%	~10.3 mA cm <sup>-2</sup>	183
GaN nanowires/n <sup>+</sup> -p Si	Cu	-1.5 V <sub>Ag/AgCl</sub>	Pure CO <sub>2</sub>	CH <sub>4</sub>	CH <sub>4</sub> : 18%	~30 mA cm <sup>-2</sup>	184
GaN nanowires/n <sup>+</sup> -p Si	Cu-Fe	-1.2 V <sub>RHE</sub>	Pure CO <sub>2</sub>	CH <sub>4</sub>	CH <sub>4</sub> : 51%	38.3 mA cm <sup>-2</sup>	185
GaN nanowires/n <sup>+</sup> -p Si	CuS	-1.0 V <sub>RHE</sub>	CO <sub>2</sub> with H <sub>2</sub> S	HCOOH	HCOOH: 70.2%	7.07 mA cm <sup>-2</sup>	186
GaN nanowires/n <sup>+</sup> -p Si	Au	0.17 V <sub>RHE</sub>	CO <sub>2</sub> with NO <sub>x</sub> , SO <sub>x</sub> , or O <sub>2</sub>	CO	CO: ~90%	~4 mA cm <sup>-2</sup>	187

## 5. Photoelectrochemical CO<sub>2</sub> reduction

Photosynthesis is widely known as the biochemical reaction which fixes CO<sub>2</sub> gas in the atmosphere into carbon-based species under solar light. This solar-driven biochemical process can be mimicked by semiconductors where the photo-generated charge carriers under solar light are transported to the surface, interact with CO<sub>2</sub> molecules, and catalytically convert the activated CO<sub>2</sub> molecules into other carbon products through deoxygenation and/or hydrogenation processes. Compared to the electrocatalytic CO<sub>2</sub> reduction reaction, whose efficiency is determined by the catalytic activity of the electrocatalyst, light absorption, electron-hole separation, charge carrier transport, and band alignment must be additionally considered to design an artificial photosynthetic device. Although these challenging requirements have limited the number of semiconductors, careful selection of semiconductors and catalyst materials, and optimization of device structures have realized the CO<sub>2</sub> reduction reaction.<sup>154-167</sup> Recently, 1D nanostructured semiconductor nanowires, nanorods, and nanofibers have surpassed the CO<sub>2</sub> reduction reactivity of planar structures due to enhanced light absorption, shortened charge carrier pathways, and exposure of active sites.<sup>168-175</sup> In particular, the emerging 1D III-nitrides have shown great promise for efficient and stable conversion of CO<sub>2</sub> gas into target products.

The photoelectrochemical CO<sub>2</sub> reduction reaction can convert the greenhouse CO<sub>2</sub> gas to value-added chemicals by simultaneously illumination with solar light and application of an electrical bias to semiconductor photocathodes. Despite the light absorption, charge carrier excitation, separation, and transport processes of the photoelectrochemical CO<sub>2</sub> reduction reaction being very similar to those of the photoelectrochemical hydrogen evolution reaction, the CO<sub>2</sub> reduction reaction is much more complex due to the many possible reaction pathways coming from different reaction intermediates. Depending

on the binding modes of intermediates on the surface of the electrodes, the selectivity and productivity of target chemicals can be changed. For example, an intermediate produced by CO<sub>2</sub> accepting an electron and a proton could be \*COOH with C attached to the surface or \*OCHO with O attached to the electrode. The different intermediates play a vital role in determining the final products (*i.e.*, CO, HCOOH, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, *etc.*). III-Nitride semiconductors, however, do not possess good catalytic activity toward the CO<sub>2</sub> reduction reaction, probably due to unfavorable CO<sub>2</sub> adsorption in comparison to the proton reduction reaction which can be operated with a pristine GaN photocathode. This bottleneck has been addressed by adapting appropriate cocatalysts on III-nitride photocathodes for the selective production of target chemicals, such as carbon monoxide (CO), formic acid (HCOOH), and methane (CH<sub>4</sub>) (Table 4).

### 5.1. CO production

Among the various products (*e.g.*, CO, HCOOH, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>5</sub>OH), that can be produced from CO<sub>2</sub> reduction reactions, CO and HCOOH are the kinetically most favorable products due to the simple two-proton-coupled electron transfer process. In addition, the reaction of synthetic gas (CO and H<sub>2</sub>) can produce methanol and other important chemicals and fuels through the well-established Fischer-Tropsch method.<sup>188,189</sup> Therefore, III-nitride semiconductors decorated with cocatalysts have been investigated for the photoelectrochemical reduction of CO<sub>2</sub> gas to CO. The feasibility of an Au cocatalyst has been evaluated on a p-GaN film for CO<sub>2</sub> conversion to CO.<sup>176</sup> The p-GaN photocathode coated with Au nanoparticles showed an onset potential of about 0.4 V<sub>RHE</sub>, a cathodic photocurrent density of 1.8 μA cm<sup>-2</sup> at -0.8 V<sub>RHE</sub> (Fig. 18a), and CO-to-H<sub>2</sub> ratio of 5 : 1 at -1.8 V<sub>RHE</sub> (Fig. 18b), whereas the bare p-GaN photocathode exhibited no photo-response under visible-light illumination. The drastic improvement in photoresponse can be explained by a greater collection efficiency of hot holes from plasmonic Au



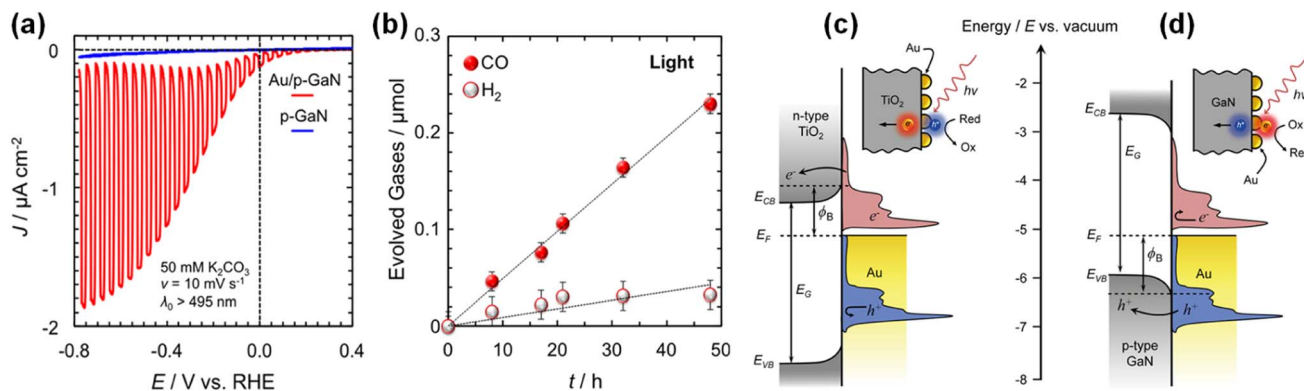


Fig. 18 (a) LSV of plasmonic Au/p-GaN and bare p-GaN photocathodes at  $10 \text{ mV s}^{-1}$  under periodic (0.5 Hz) visible-light irradiation ( $\lambda > 495 \text{ nm}$ ) at a power of  $600 \text{ mW cm}^{-2}$ . (b) CO and  $\text{H}_2$  evolution using an Au/p-GaN photocathode. (c) Energy band diagrams of Au in physical contact with an n-type semiconductor (e.g.,  $\text{TiO}_2$ ) and (d) with p-type semiconductor (e.g., p-GaN) for hot electron and hot hole collection, respectively. Reproduced with permission from ref. 176. Copyright (2018) American Chemical Society.

nanoparticles to the valence band of p-GaN. Compared to previous n-type semiconductors with good hot electron collection properties (Fig. 18c), the Au/p-GaN interface can establish a more suitable Schottky barrier for hot hole collection (Fig. 18d). Thus, remaining hot electrons in Au nanoparticles can participate in the  $\text{CO}_2$  reduction reaction. This implies the positive effect of downward band bending at the metal cocatalyst/semiconductor photocathode not only for the electron-hole separation but also for the efficient photoelectrochemical  $\text{CO}_2$  reduction reaction.

As was mentioned in the previous section, the large band gap of GaN ( $\sim 3.4 \text{ eV}$ ) cannot afford visible light absorption, which limits the photocurrent density. In addition, planar GaN has a small specific surface area capable of holding a cocatalyst. To solve these problems, 1D GaN nanowires were vertically grown on the  $\text{n}^+\text{-p}$  Si photocathode. Since the GaN nanowires have  $\sim 10$  times larger surface area than the planar structure, a large number of cocatalysts can be loaded and the catalytic activity for the  $\text{CO}_2$  reduction reaction can be greatly improved. In this configuration, the photoexcited charge carriers are mainly generated in the  $\text{n}^+\text{-p}$  Si photocathode and the photogenerated electrons migrate to cocatalysts through  $\text{n}^+\text{-GaN}$  nanowires. In order to concurrently facilitate electron transport and promote catalytic performance, Cu-ZnO cocatalysts have been deposited on GaN nanowires (Fig. 19a).<sup>177</sup> The conduction band of ZnO is located below that of GaN, so the photogenerated electrons can migrate to surface Cu catalysts without a significant energy barrier (Fig. 19b). As a result, the ZnO-Cu/GaN/ $\text{n}^+\text{-p}$  Si photocathode attained a high photocurrent density ( $\sim 10 \text{ mA cm}^{-2}$ ) (Fig. 19c) and demonstrated a higher faradaic efficiency (FE) of CO (20%) at  $-0.33 \text{ V}_{\text{RHE}}$  compared to control samples with ZnO (14.3%) and Cu (1.7%) cocatalysts (Fig. 19d). Inspired by this metal-oxide/metal cocatalyst loaded on GaN nanowires for CO production, a  $\text{TiO}_2$ -Pt cocatalyst has been evaluated on a GaN nanowires/ $\text{n}^+\text{-p}$  Si photocathode and revealed a positive onset potential of  $\sim 0.5 \text{ V}_{\text{RHE}}$  and  $\sim 2$  times higher photocurrent density compared to photocathodes with  $\text{TiO}_2$  or Pt cocatalysts (Fig. 19e).<sup>178</sup> The FE of CO was low on pristine GaN/ $\text{n}^+\text{-p}$  Si and

with individual  $\text{TiO}_2$  and Pt cocatalysts (1.7%, 5.6%, and 2%, respectively), while it increased remarkably to 32% by employing  $\text{TiO}_2$ -Pt binary cocatalysts, indicating the synergistic interaction between Pt and  $\text{TiO}_2$  for the  $\text{CO}_2$  reduction reaction (Fig. 19f). Furthermore, two metal-oxide/metal cocatalysts of ZnO-Pt and  $\text{TiO}_2$ -Pd exhibited higher CO selectivity compared to metallic Pt and Pd (Fig. 19g). To understand the mechanistic role of the metal-oxide/metal interface for  $\text{CO}_2$  reduction to CO, density functional theory calculations were carried out (Fig. 19h). It was found that  $\text{CO}_2$  is not activated on a Pt cocatalyst but strongly interacts with the  $\text{TiO}_2$ -Pt binary cocatalyst. The carbon atom of the  $\text{CO}_2$  molecule at the interface binds to the metallic atom (Pt) and one of oxygen atoms attaches to the Ti atom of  $\text{TiO}_2$ . This interaction greatly stabilizes the  $\text{CO}_2$  adsorption and facilitates the formation of  $^*\text{CO}$  via an  $^*\text{COOH}$  intermediate, thereby resulting in a thermodynamically downhill process.

Despite the GaN nanowires/ $\text{n}^+\text{-p}$  Si photocathode being able to increase CO selectivity by metal-oxide/metal cocatalysts, the true reactivity and role of GaN nanowires are largely unknown since the GaN surface covered by cocatalysts was not exposed to the electrolyte during the  $\text{CO}_2$  reduction reaction. Therefore, Au and Pt cocatalysts have been directly coated on GaN nanowires without a metal oxide passivation layer.<sup>179</sup> Au nanoparticles were prepared on top of GaN nanowires by an electron-beam evaporation method followed by thermal annealing, and Pt nanoparticles were coated on the sidewalls of GaN nanowires by a photodeposition method (Fig. 20a and b). These spatially separated Au and Pt cocatalysts preferentially convert  $\text{CO}_2$  to CO and  $\text{H}^+$  to  $\text{H}_2$ , respectively. Control of the product distribution (*i.e.*, CO/ $\text{H}_2$  syngas ratio) can be realized by tuning the composition ratio of Au and Pt cocatalysts. As the ratio of Pt increased in  $\text{AuPt}_x/\text{GaN}/\text{n}^+\text{-p}$  Si, the FE of  $\text{H}_2$  gradually increased from  $\sim 10\%$  to  $\sim 99\%$  with a decreased FE for CO from  $\sim 90\%$  to nearly zero (Fig. 20c). By adjusting the cocatalyst composition on GaN nanowires, the syngas ratio of CO/ $\text{H}_2$  could be varied over a wide range from 1 : 99 to 10 : 1. Furthermore, the size effect of Au nanoparticles was studied for syngas

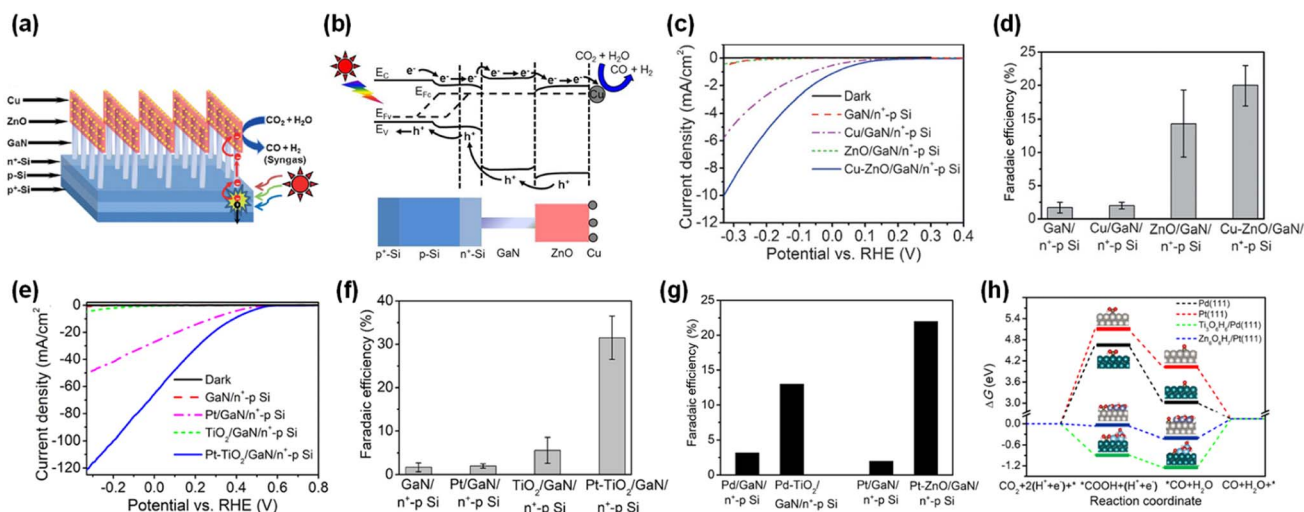


Fig. 19 (a) Schematic and (b) energy band diagram of Cu-ZnO/GaN/n<sup>+</sup>-p Si photocathode under light illumination. (c) LSV curves and (d) FE of CO at -0.33 V<sub>RHE</sub>. Reproduced with permission from ref. 177. Copyright (2016) John Wiley and Sons. (e) LSV curves and (f) FE of CO for pristine GaN/Si and GaN/Si with Pt, TiO<sub>2</sub>, and Pt-TiO<sub>2</sub> cocatalysts. (g) FE of CO at 0.27 V<sub>RHE</sub> for GaN/Si photocathodes with Pd, Pd-TiO<sub>2</sub>, Pt, and Pt-ZnO cocatalysts. (h) Calculated free energy diagrams for CO<sub>2</sub> reduction to CO. Green, Pt: gray, Ti: blue, Zn: purple, O: red, C: brown and H: white. Reproduced with permission from ref. 178. Copyright (2018) American Chemical Society.

production on a GaN/n<sup>+</sup>-p Si photocathode.<sup>180</sup> A gradual increase in CO selectivity with decreasing H<sub>2</sub> selectivity was observed with increasing particle size at 0.17 V<sub>RHE</sub> under solar irradiation (Fig. 20d). As the size of Au nanoparticles with an icosahedral structure increases, the ratio of facet sites increases and, at the same time, the portion of edge and corner sites decreases (Fig. 20e). From theoretical calculation, it was found that H<sub>2</sub> evolution, the major competitive reaction, becomes much easier on the corner and edge sites than on facet sites (Fig. 20f). Therefore, the facet sites of large Au nanoparticles (16 nm) are responsible for the reduction reaction of CO<sub>2</sub> into CO while dominant corner and edge sites of small Au nanoparticles (3 nm) are active for the H<sub>2</sub> evolution reaction.

In addition to crystal facet engineering, Ag and Ag halide cocatalysts have been modified using phase engineering on vertically grown GaN nanowires by a photoelectrochemical anodization method (Fig. 20g).<sup>181</sup> Compared to the metallic Ag nanoparticles, AgCl and AgBr cocatalysts greatly improved the selectivity and productivity of CO compared to H<sub>2</sub> (Fig. 20h). This indicates that fine control over the material composition of cocatalysts can alter the surface electronic properties and consequent catalytic activity for CO<sub>2</sub> conversion. Moreover, GaN/n<sup>+</sup>-p Si photocathodes with AgBr cocatalysts showed a very high photocurrent density of ~92 mA cm<sup>-2</sup> at -1.0 V<sub>RHE</sub> under concentrated solar light (3 sun illumination) (Fig. 20i). Stable and continuous production of CO could be achieved for 12 h without losing catalytic activity.

## 5.2. HCOOH production

HCOOH is an energy-dense liquid fuel and a building block for modern chemistry. There have been extensive developments of metallic electrocatalysts, such as Pb, Hg, Cd, Pd, In, Sn, and Bi, for the selective conversion of CO<sub>2</sub> into HCOOH in aqueous

electrolytes.<sup>190-198</sup> However, the cost of expensive metals (Pd and In) and the toxicity of heavy metals (Pb, Cd, Hg) are a hindrance to practical application. Hence, the environmentally benign metals Sn, Bi, and their compounds have been spotlighted.<sup>199-201</sup> Previously, Sn nanoparticles were electrochemically deposited on GaN nanowires grown on n<sup>+</sup>-p Si for the photoelectrochemical CO<sub>2</sub> reduction reaction to HCOOH (Fig. 21a).<sup>182</sup> Compared to the negligible productivity (2.1 μmol cm<sup>-2</sup> h<sup>-1</sup>) of HCOOH on the Sn/n<sup>+</sup>-p Si photocathode, the productivity (201 μmol cm<sup>-2</sup> h<sup>-1</sup>) of Sn/GaN/n<sup>+</sup>-p Si was nearly two orders of magnitude higher (Fig. 21b). This indicates that 1D GaN nanowires not only function as a support for cocatalysts and an electron-migration channel but also participate in the CO<sub>2</sub> reduction reaction. Density functional theoretical calculation elucidated that the CO<sub>2</sub> molecule can be easily activated and readily dissociated into \*CO *via* a covalent-like Ga-C bond and an ionic-like Sn-O bond over the Sn/GaN interface, respectively (Fig. 21c). Then, the reduction of a key intermediate of CO\* to HCOOH follows an energetically favorable reaction pathway (Fig. 21d). It is of scientific interest to find that III-nitride integrated with cocatalyst results in beneficial synergy for CO<sub>2</sub> activation and HCOOH production.

Metallic Bi can also play a role as an efficient cocatalyst for photoelectrochemical CO<sub>2</sub>-to-HCOOH conversion when it is integrated with a GaN/n<sup>+</sup>-p Si electrode.<sup>183</sup> A simple one-step thermal evaporation of Bi cocatalysts on GaN nanowires induces uniformly distributed Bi/Bi<sub>2</sub>O<sub>3</sub> nanoparticles (Fig. 21e). Noticeably, a Bi/GaN/Si photocathode showed a high FE of HCOOH > 95% at -0.3 V<sub>RHE</sub> whereas Bi/Si exhibited a low FE of HCOOH < 70% and a relatively small photocurrent density (Fig. 21f). The reasons for the high HCOOH selectivity were the lowered catalytic energy barrier originating from Bi<sub>2</sub>O<sub>3</sub>/GaN interfacial interaction (Fig. 21g) and efficient transport of

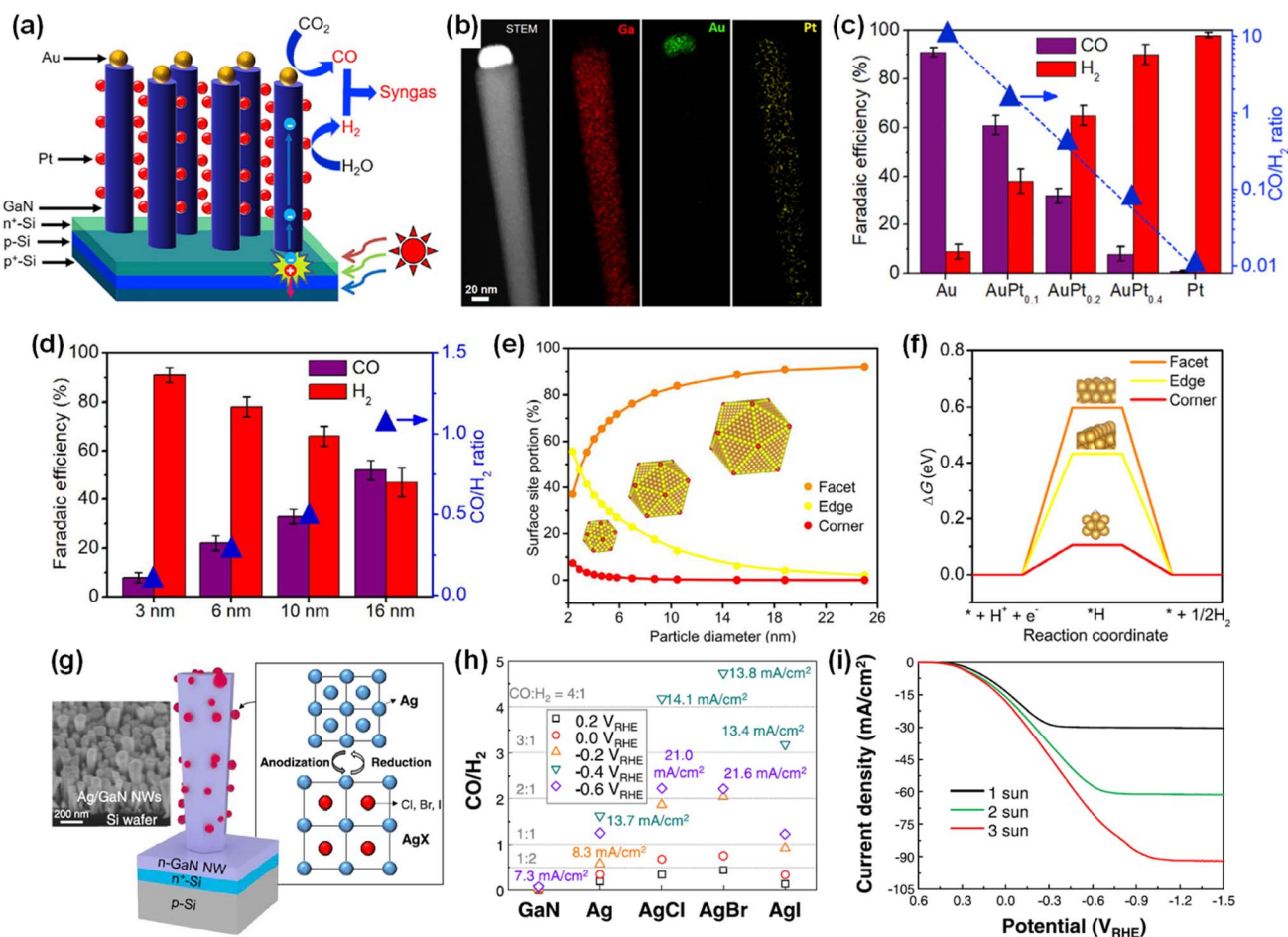


Fig. 20 (a) Schematic of an AuPt<sub>x</sub>/GaN/n<sup>+</sup>-p Si photocathode under light illumination. (b) STEM-energy dispersive X-ray spectroscopy elemental mapping images. (c) FE of CO and H<sub>2</sub> for AuPt<sub>x</sub>/GaN/n<sup>+</sup>-p Si photocathodes at 0.17 V<sub>RHE</sub>. Reproduced with permission from ref. 179. Copyright (2020) Elsevier. (d) Size dependence of photoelectrochemical CO<sub>2</sub> reduction performance on Au nanoparticles at 0.17 V<sub>RHE</sub>. (e) Portion of surface sites on icosahedron Au nanoparticles vs. particle size. (f) Free energy diagram of proton reduction into H<sub>2</sub> on facet, edge, and corner sites of Au nanoparticles. Reproduced with permission from ref. 180. Copyright (2022) Elsevier. (g) SEM image of Ag-decorated GaN nanowires and schematic fabrication processes of Ag halide cocatalysts. (h) Plots of the CO/H<sub>2</sub> ratio for the photocathodes at different potentials from 0.2 to -0.6 V<sub>RHE</sub>. (i) LSV curves of AgBr/GaN/Si under concentrated solar light. Reproduced with permission from ref. 181. Copyright (2022) American Chemical Society.

photogenerated electrons from GaN to Bi<sub>2</sub>O<sub>3</sub> due to conduction band alignment (Fig. 21h). This work showed a promising insight that a strong electronic interaction between cocatalyst and 1D III-nitride can shift the intrinsic catalytic activity and realize a new class of material for an efficient photoelectrochemical CO<sub>2</sub> reduction reaction.

### 5.3. CH<sub>4</sub> production

Electrochemical production of CH<sub>4</sub> from CO<sub>2</sub> faces challenges of sluggish kinetics and a competitive proton reduction reaction. Cu and its alloys are known to be state-of-the-art catalysts for converting CO<sub>2</sub> to high-order products.<sup>202-204</sup> Therefore, Cu nanoparticles have been decorated on GaN/n<sup>+</sup>-p Si for a photoelectrochemical CO<sub>2</sub> reduction reaction to CH<sub>4</sub>.<sup>184</sup> A small amount of CO was produced on pristine GaN nanowires and CH<sub>4</sub> product was not detected by gas chromatographic measurement (Fig. 22a and b). In stark contrast, Cu cocatalysts

on both GaN/n<sup>+</sup>-p Si and n<sup>+</sup>-p Si boosted the photocurrent density, positively shifted the onset potential, and increased the FE of CH<sub>4</sub>. More interestingly, the Cu cocatalysts loaded on GaN nanowires showed higher selectivity for CH<sub>4</sub> (~18%) than those on the Si photoelectrode (~4%). To enhance the catalytic activity of photocathode, binary Cu-Fe cocatalysts have been developed on GaN/n<sup>+</sup>-p Si.<sup>185</sup> From theoretical calculation, it was found that a Cu and Fe binary catalyst activates the inert CO<sub>2</sub> molecule by bending the O-C-O angle from 180° to 126.05° and by elongating the C-O bond length (Fig. 22c and d). The thermodynamic energy barrier of the potential-determining step (*i.e.*, \*CO → \*CHO) for CO<sub>2</sub>-to-CH<sub>4</sub> conversion was reduced from 0.85 to 0.51 eV by incorporating Fe into Cu catalysts (Fig. 22e). The binary Cu-Fe showed better onset potential and higher photocurrent density compared to single Cu or Fe catalysts on GaN/n<sup>+</sup>-p Si. Moreover, FE of CH<sub>4</sub> increased to 51%, which is superior to that of the Cu cocatalyst (~19%) under identical measurement conditions (Fig. 22f). Rational design of



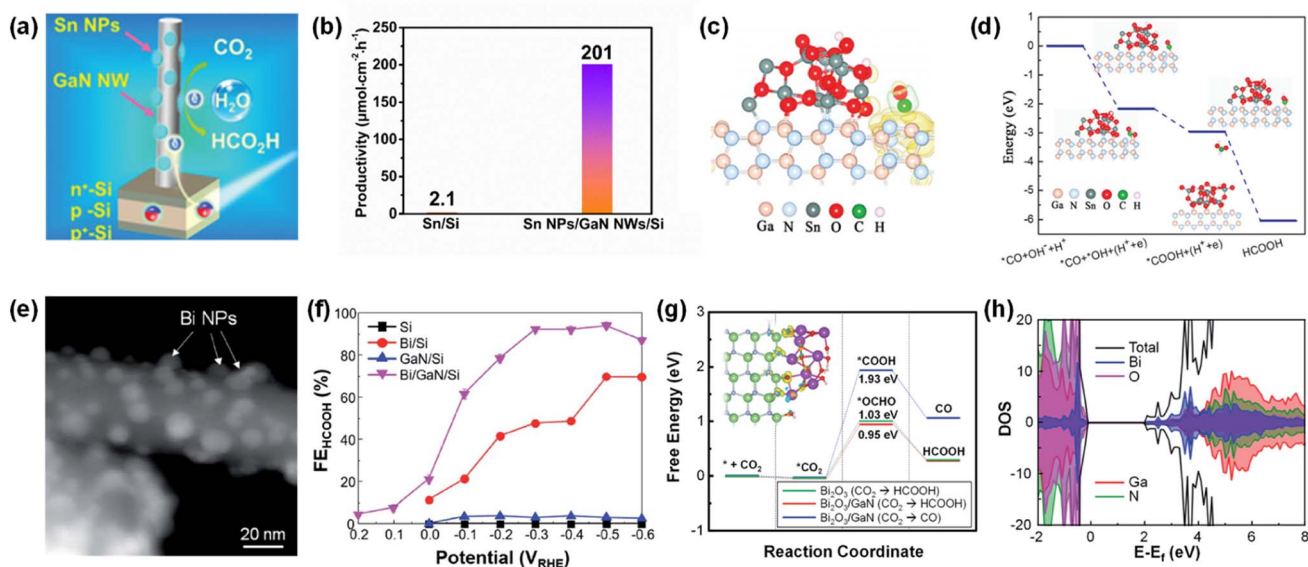


Fig. 21 (a) Schematic of Sn nanoparticles/GaN nanowires/ $n^+$ - $p$  Si for photoelectrochemical  $\text{CO}_2$  reduction with  $\text{H}_2\text{O}$  to  $\text{HCOOH}$ . (b) Productivity of  $\text{HCOOH}$  for Sn/Si and Sn/GaN/Si photocathodes. (c) Calculated differential charge density for  $^*\text{CO}/\text{Sn}_{13}\text{O}_{26}/\text{GaN}$ . (d) Potential energy diagram of reducing  $\text{CO}_2$  to  $\text{HCOOH}$  at the Sn/GaN interface. Reproduced with permission from ref. 182. Copyright (2019) Royal Society of Chemistry. (e) HAADF STEM image of Bi nanoparticles/GaN nanowires. (f) FE of  $\text{HCOOH}$  for photocathodes. (g) Free-energy profiles for the  $\text{CO}_2$  reduction reaction to  $\text{HCOOH}$  and  $\text{CO}$  on  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3/\text{GaN}$ . (h) Density of states of  $\text{Bi}_2\text{O}_3/\text{GaN}$  near the band gap. Reproduced with permission from ref. 183. Copyright (2022) Royal Society of Chemistry.

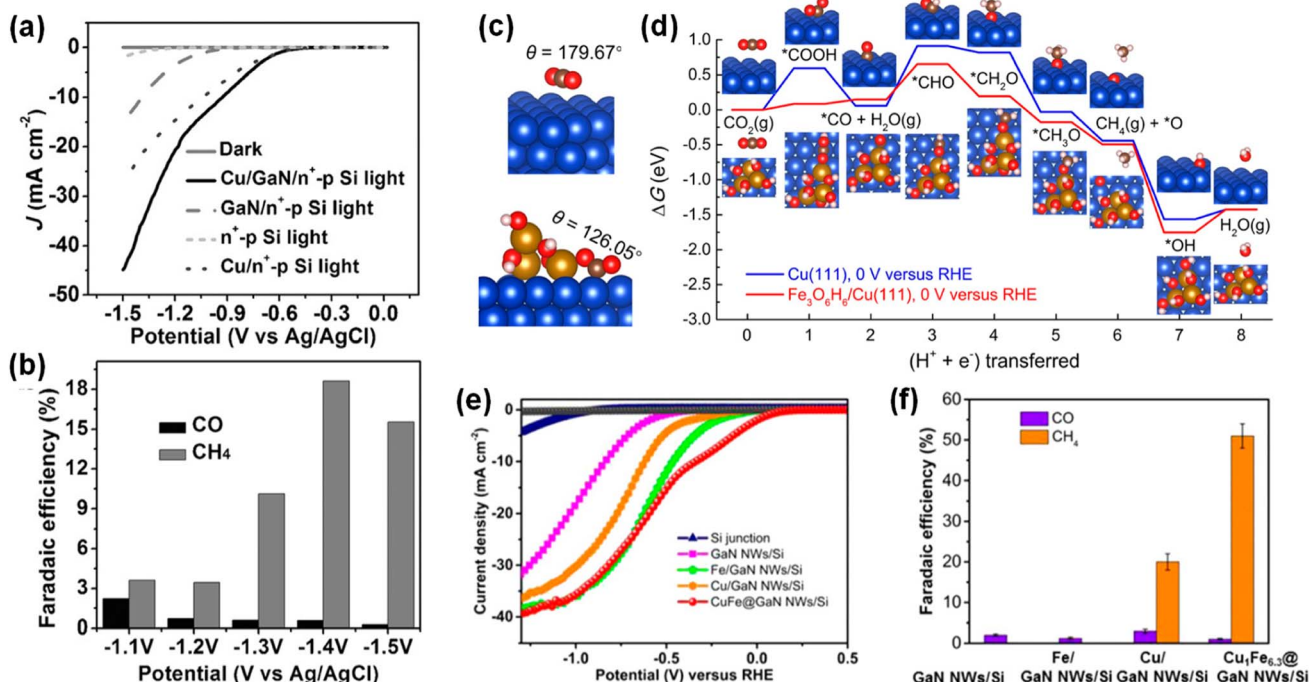


Fig. 22 (a) LSV curves of  $n^+$ - $p$  Si and GaN nanowires/ $n^+$ - $p$  Si photocathodes with/without Cu cocatalysts. (b) FE of  $\text{CO}$  and  $\text{CH}_4$  produced from a Cu/GaN/Si photocathode. Reproduced with permission from ref. 184. Copyright (2016) John Wiley and Sons. (c) The optimized configurations of the  $\text{CO}_2$  molecule on Cu(111) and  $\text{Fe}_3\text{O}_6\text{H}_6/\text{Cu}(111)$ . Blue, orange, red, brown, and white spheres represent Cu, Fe, O, C, and H atoms, respectively. (d) Free-energy diagrams for  $\text{CO}_2$  reduction to  $\text{CH}_4$  on Cu and the  $\text{Fe}_3\text{O}_6\text{H}_6/\text{Cu}$  interface. (e) LSV curves and (f) FE of  $\text{CO}$  and  $\text{CH}_4$  for GaN/Si photocathodes with Fe, Cu, and Cu-Fe cocatalysts. Reproduced with permission from ref. 185. Copyright (2020) National Academy of Science.

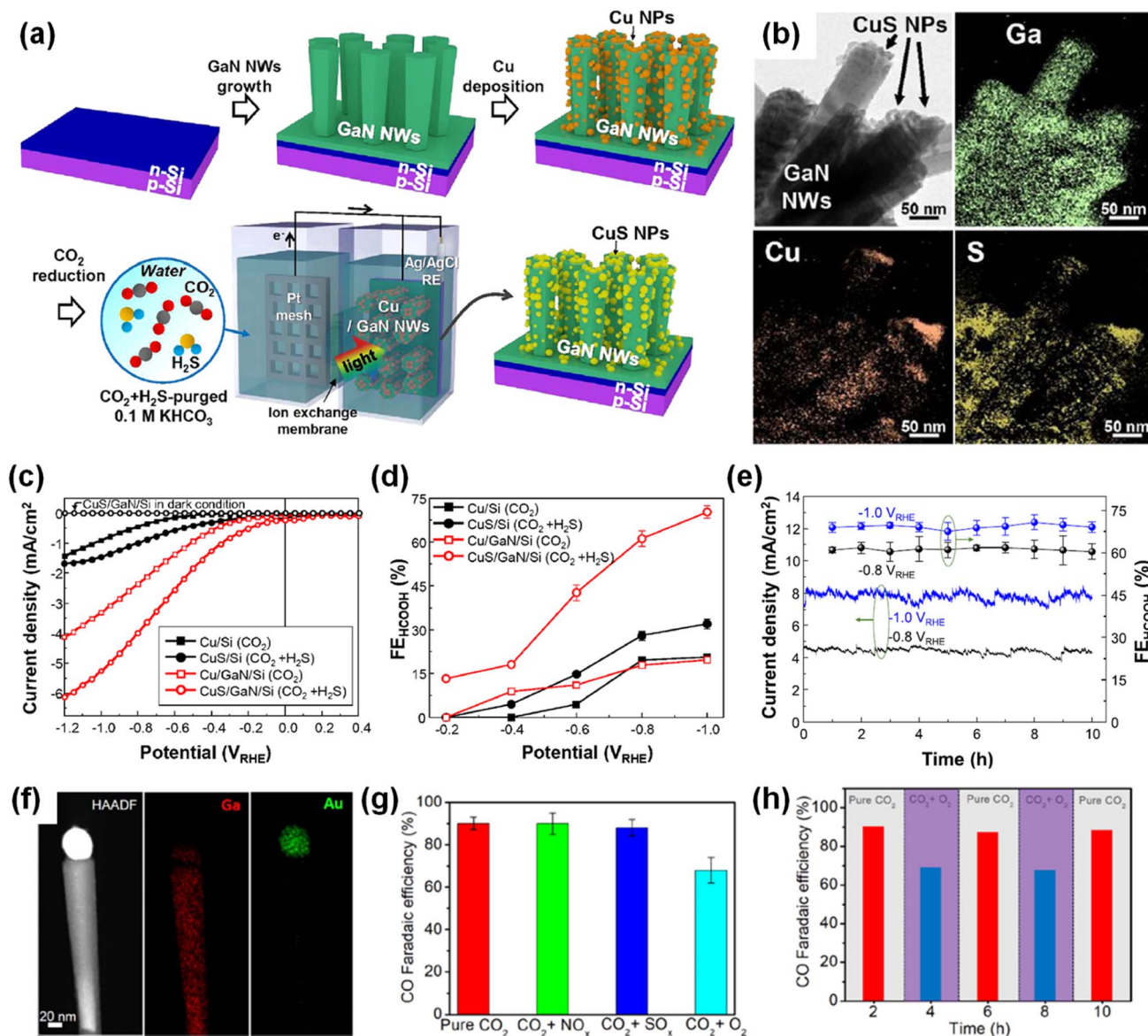


Fig. 23 (a) Schematic fabrication process of CuS/GaN/Si by MBE growth of GaN nanowires on  $n^+$ -p Si, electron-beam deposition of Cu nanoparticles, and spontaneous transformation of Cu to CuS cocatalysts. (b) TEM analysis of CuS nanoparticles on GaN nanowires. (c) LSV curves and (d) FE of HCOOH for photocathodes measured in  $\text{CO}_2$ - or  $\text{CO}_2 + \text{H}_2\text{S}$ -purged electrolytes. (e) Stability of CuS/GaN/Si photocathode at  $-0.8$  and  $-1.0$   $V_{\text{RHE}}$ . Reproduced with permission from ref. 186. Copyright (2021) American Chemical Society. (f) Structural characterization of Au/GaN/Si. (g) FE of CO at  $0.17$   $V_{\text{RHE}}$  measured with impurities of  $\text{NO}_x$ ,  $\text{SO}_x$ , and  $\text{O}_2$  mixed in  $\text{CO}_2$  gas. (h) Time-dependent CO FE with or without  $\text{O}_2$  impurity gas. Reproduced with permission from ref. 187. Copyright (2022) Elsevier.

cocatalysts and 1D III-nitrides with high catalytic activity for  $\text{CO}_2$ -to- $\text{CH}_4$  conversion is found to be essential for the efficient and selective photoelectrochemical synthesis of high-order products such as  $\text{CH}_4$ .

#### 5.4. Flue gas $\text{CO}_2$ reduction

Until now, most studies have focused on the development of photocathodes using a pure  $\text{CO}_2$  feedstock. However, for practical application, their compatibility with flue-gas  $\text{CO}_2$  should be considered. Flue-gas  $\text{CO}_2$  usually contains many impurities, such as  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ , and  $\text{H}_2\text{S}$  compounds. Hence, it is of

great interest to convert impurity-containing flue-gas  $\text{CO}_2$  into value-added chemicals without a costly purification process.<sup>205–207</sup> Recently, a photocathode consisting of a CuS cocatalyst loaded on GaN nanowires/ $n^+$ -p Si has been presented as a promising architecture for the efficient and stable conversion of an  $\text{H}_2\text{S}$ -containing  $\text{CO}_2$  mixture gas to HCOOH.<sup>186</sup> Cu nanoparticles were firstly deposited on GaN nanowires and then spontaneously transformed to CuS nanoparticles by  $\text{H}_2\text{S}$  impurity dissolved in the electrolyte during the  $\text{CO}_2$  reduction reaction (Fig. 23a). After the photoelectrochemical  $\text{CO}_2$  reduction reaction, CuS compounds can be clearly seen on GaN

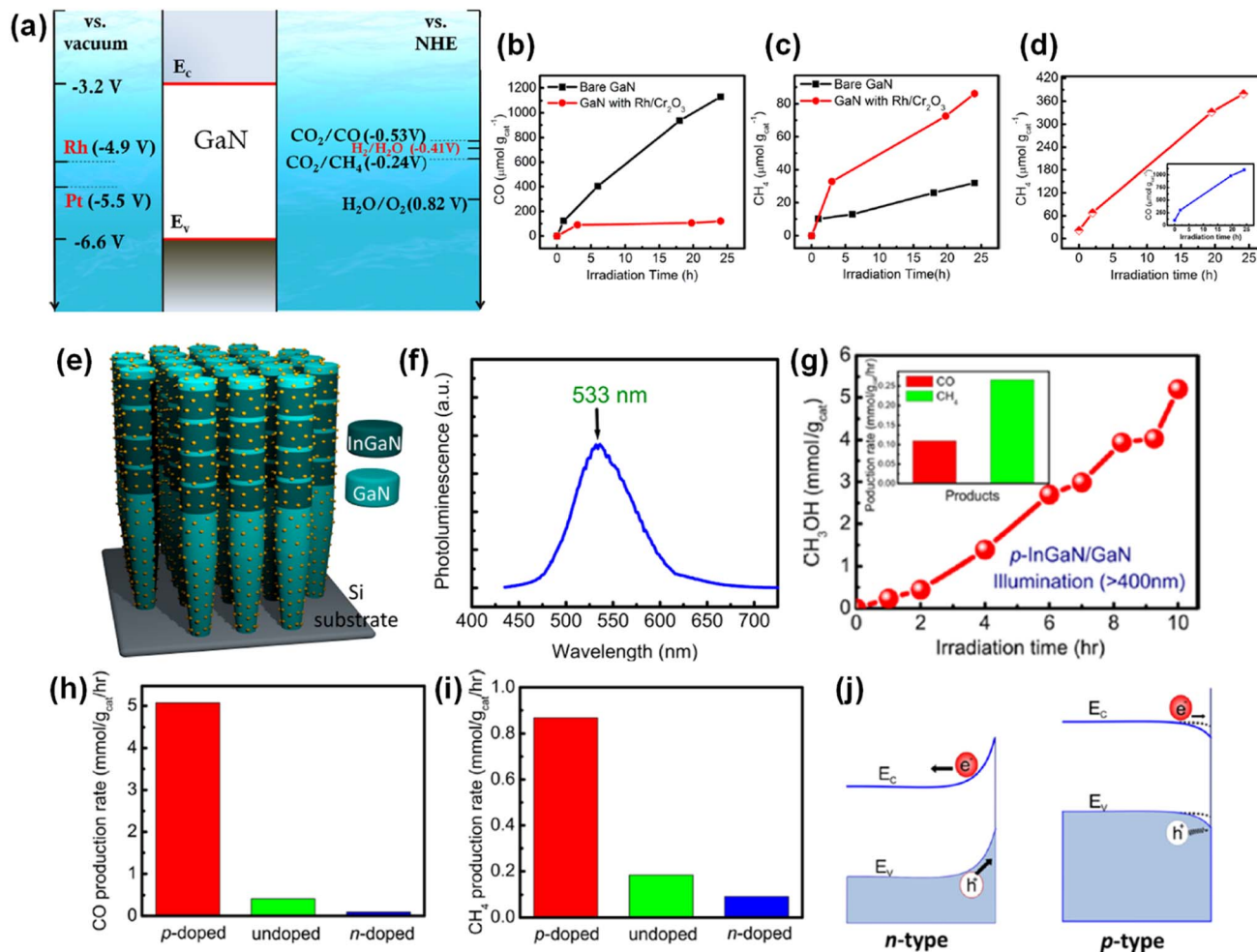


Fig. 24 (a) Band edge positions of GaN in comparison with the work function of Rh and Pt.  $\text{CO}_2/\text{CO}$  and  $\text{CO}_2/\text{CH}_4$  reduction potentials vs. normal hydrogen electrode for  $\text{pH} = 7$  are shown together. Photocatalytic  $\text{CO}_2$  reduction reaction to (b) CO and (c)  $\text{CH}_4$  by Rh/ $\text{Cr}_2\text{O}_3$  cocatalysts. (d)  $\text{CH}_4$  evolution over Pt-decorated GaN nanowires and the inset shows CO generation. Reproduced with permission from ref. 208. Copyright (2015) American Chemical Society. (e) Schematic of p-InGaN/GaN nanowire photocatalysts decorated with Pt nanoparticles. (f) Photoluminescence spectrum of InGaN/GaN photocatalysts. (g)  $\text{CH}_3\text{OH}$  evolution over Pt-decorated p-InGaN/GaN nanowires under visible light illumination (>400 nm). The inset shows the production rates of CO and  $\text{CH}_4$ . Doping-type-dependent production rate of (h) CO and (i)  $\text{CH}_4$  of InGaN/GaN nanowires. (j) Schematic of charge carrier transfer illustrated on n- (p-) doped semiconductors with upward (downward) surface band bending. Reproduced with permission from ref. 209. Copyright (2016) American Chemical Society.

nanowires (Fig. 23b). In order to evaluate Cu and CuS cocatalysts on photocathodes, a photoelectrochemical  $\text{CO}_2$  reduction reaction was conducted in  $\text{CO}_2$ - or  $\text{CO}_2 + \text{H}_2\text{S}$ -purged electrolyte, respectively. Cu and CuS cocatalysts integrated with GaN nanowires grown on  $\text{n}^+\text{-p}$  Si (GaN/Si) showed a substantial improvement in onset potential and photocurrent density compared to those of Cu/Si and CuS/Si (Fig. 23c). An increase in

the selectivity for HCOOH was observed from  $\sim 21\%$  to  $\sim 32\%$  when Cu cocatalysts were converted to CuS on an  $\text{n}^+\text{-p}$  Si photocathode at  $-1.0 V_{\text{RHE}}$  (Fig. 23d). Impressively, the transformation of Cu to CuS nanoparticles on GaN nanowires greatly increased the FE of HCOOH from  $\sim 20\%$  to  $\sim 70\%$  under the same conditions. This demonstrates that  $\text{H}_2\text{S}$  impurity mixed in the  $\text{CO}_2$  gas can enhance, rather than degrade, the performance

Table 5 III-Nitride photocatalysts for photocatalytic  $\text{CO}_2$  conversion reaction

Photocatalyst	Cocatalyst	Reactant	Light source	Performance	Ref.
GaN NWs	Pt	$\text{CO}_2 + \text{vaporized H}_2\text{O}$	300 W Xe lamp	$\text{CH}_4 \sim 14.8 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	208
p-InGaN/GaN NWs	Pt	$\text{CO}_2 + \text{H}_2 + \text{vaporized H}_2\text{O}$	300 W Xe lamp with 400 nm long-pass filter	$\text{CH}_3\text{OH} \sim 0.5 \text{mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	209
InGaN/GaN NWs	Au@ $\text{Cr}_2\text{O}_3$	$\text{CO}_2 + \text{vaporized H}_2\text{O}$	300 W Xe lamp	Syngas of $1.08 \text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	210



of the photoelectrochemical CO<sub>2</sub> reduction reaction. CuS/GaN/Si revealed constant photocurrent densities of ~4.5 and ~7.8 mA cm<sup>-2</sup> and consistently produced high FE of ~60% and ~70% at -0.8 and -1.0 V<sub>RHE</sub>, respectively (Fig. 23e). This outstanding stability is likely due to the chemical stability of the unique N-rich GaN surface which can withstand oxidation or sulfurization by impurities in the flue-gas CO<sub>2</sub>.

The influence of various impurities (0.1% NO<sub>x</sub>, 1% SO<sub>x</sub>, and 5% O<sub>2</sub>) on the photoelectrochemical CO<sub>2</sub> reduction performance was also tested using Au nanoparticles deposited on top of GaN nanowire arrays on n<sup>+</sup>-p Si (Fig. 23f).<sup>187</sup> The effects of NO<sub>x</sub> and SO<sub>x</sub> on CO<sub>2</sub> reduction reaction to CO were negligible (Fig. 23g). In contrast, the presence of O<sub>2</sub> impurity decreased the FE of CO from 90% to 68% due to the more favorable O<sub>2</sub> reduction reaction. Although the O<sub>2</sub> impurity led to a temporary decrease in the FE of CO, it could be fully recovered when a pure CO<sub>2</sub> feedstock was purged, indicating the negligible long-term impact of O<sub>2</sub> on the photocathodes (Fig. 23h). From these results, it was found that 1D GaN nanowires are chemically stable against impurity gases mixed in flue-gas CO<sub>2</sub> and function as a good photocathode platform for the CO<sub>2</sub> reduction reaction.

## 6. Photocatalytic CO<sub>2</sub> reduction reaction

1D III-nitride photocathodes can drive a half-reaction of the CO<sub>2</sub> reduction reaction and the other oxidation reaction takes a place at the counter electrode. In contrast, both CO<sub>2</sub> reduction and oxidation reactions occur at the surface of 1D III-nitride photocatalysts during photocatalytic CO<sub>2</sub> conversion reaction. During photocatalytic CO<sub>2</sub> reduction, intermediates on the surface can be reduced or simultaneously oxidized to produce a variety of chemical products that are rarely obtainable with cathodic half-reactions alone. In addition to the requirements of conventional photocatalysts (*i.e.*, band edge positions, charge carrier separation, and transportation), the kinetic balance between the CO<sub>2</sub> reduction and oxidation reactions is mandatory for the selective production of target chemicals. Because GaN nanowires fulfill the requirements of band edge positions (the conduction band positions are higher than the reductive potential of CO<sub>2</sub> reduction and the valence band is located lower than the water oxidation reaction) (Fig. 24a), 1D III-nitrides are desirable platforms for the photocatalytic CO<sub>2</sub> reduction reaction, as demonstrated by several experiments (Table 5). In addition, GaN nanowires can readily activate the adsorbed CO<sub>2</sub> by bending the linear O-C-O bonds, thereby resulting in the effective CO<sub>2</sub> reduction reaction toward CO even without a cocatalyst (Fig. 24b).<sup>208</sup> However, pristine GaN nanowires cannot efficiently produce CH<sub>4</sub> since the CO<sub>2</sub>-to-CH<sub>4</sub> conversion is kinetically and thermodynamically unfavorable because of the high reaction barrier and complicated 8H<sup>+</sup>/8e<sup>-</sup> process. This limitation can be overcome by employing Rh/Cr<sub>2</sub>O<sub>3</sub> cocatalysts on the GaN nanowires. When the CO<sub>2</sub> reduction reaction was carried by vaporized water and CO<sub>2</sub> gas under concentrated solar light, the production rate and selectivity of

CH<sub>4</sub> were enormously improved by suppressing the competing CO evolution reaction (Fig. 24c). The Pt cocatalyst exhibited a further increase in the production rate of CH<sub>4</sub> (Fig. 24d), which is 4.2 times higher than that of Rh/Cr<sub>2</sub>O<sub>3</sub>, indicating once again that the rational design of cocatalysts on 1D nitrides can drastically boost the productivity of target chemicals.

InGaN nanowires with narrower band gap can broaden the wavelength of light absorption and enhance the production rate compared to GaN nanowires. Hence, p-InGaN/GaN nanowires were grown on an Si substrate with the decoration of Pt nanoparticle cocatalysts for the photocatalytic CO<sub>2</sub> conversion reaction (Fig. 24e).<sup>209</sup> Photoluminescence spectroscopy measurement identified that the p-InGaN/GaN nanowire photocatalyst is capable of harvesting visible light (<533 nm) (Fig. 24f). The photocatalyst achieved a conversion rate of CO<sub>2</sub> into CH<sub>3</sub>OH of ~0.5 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> under visible light illumination (>400 nm). Moreover, the role of dopants in the photocatalytic CO<sub>2</sub> reduction reaction was investigated (Fig. 24g). Mg-doped InGaN nanowires presented much higher CO, CH<sub>4</sub>, and CH<sub>3</sub>OH production rates than the undoped and Ge-doped InGaN nanowires (Fig. 24h and i) because of the reduced surface potential barriers by downward band bending as well as the activation of the CO<sub>2</sub> molecule (Fig. 24j). A mechanistic understanding of the origins for the enhanced photocatalytic activities provides insights into the important function of dopants and surface band bending of III-nitrides.

Recently, Au/Cr<sub>2</sub>O<sub>3</sub> core/shell nanoparticle cocatalysts have shown promising photocatalytic CO<sub>2</sub>-to-CO conversion reactivity on 1D InGaN/GaN nanowires (Fig. 25a).<sup>210</sup> Under solar irradiation, CO<sub>2</sub> and H<sub>2</sub>O reactants were effectively converted to CO and H<sub>2</sub> syngas with a production rate of 1.08 mol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and a ratio of 1 : 1.6 (Fig. 25b). Au/Cr<sub>2</sub>O<sub>3</sub> cocatalysts significantly outperform the single-component cocatalysts of Au and Cr<sub>2</sub>O<sub>3</sub>, evidencing the synergistic interaction between Au and Cr<sub>2</sub>O<sub>3</sub> for photocatalytic reactions. Density functional calculation revealed that the CO<sub>2</sub> molecule barely interacts with Au and the Cr<sub>2</sub>O<sub>3</sub> surface while it is easily activated by bending the O-C-O angle to 116.5° on Au/Cr<sub>2</sub>O<sub>3</sub>, thus significantly reducing the reaction energy barrier (Fig. 25c). In addition, the energy barrier for the H<sub>2</sub> evolution reaction was also lowest on the Au/Cr<sub>2</sub>O<sub>3</sub> interface, exhibiting high catalytic activity for both CO and H<sub>2</sub> evolution reactions and thus syngas synthesis (Fig. 25d and e).

## 7. Challenges, prospects, and conclusions

III-Nitrides, *e.g.*, InGaN, have tunable band gap energy and ideal band edge positions for water splitting and CO<sub>2</sub> reduction. Moreover, the emerging 1D III-nitride nanostructures have greatly improved the performance of photoelectrodes and photocatalysts compared to the planar structures. In this review, we describe the fabrication methods of 1D III-nitrides and their application to photoelectrochemical and photocatalytic water splitting and CO<sub>2</sub> reduction reactions, along with efficiency-enhancement strategies. There have been key challenges to artificial photosynthesis, such as (1) low optical

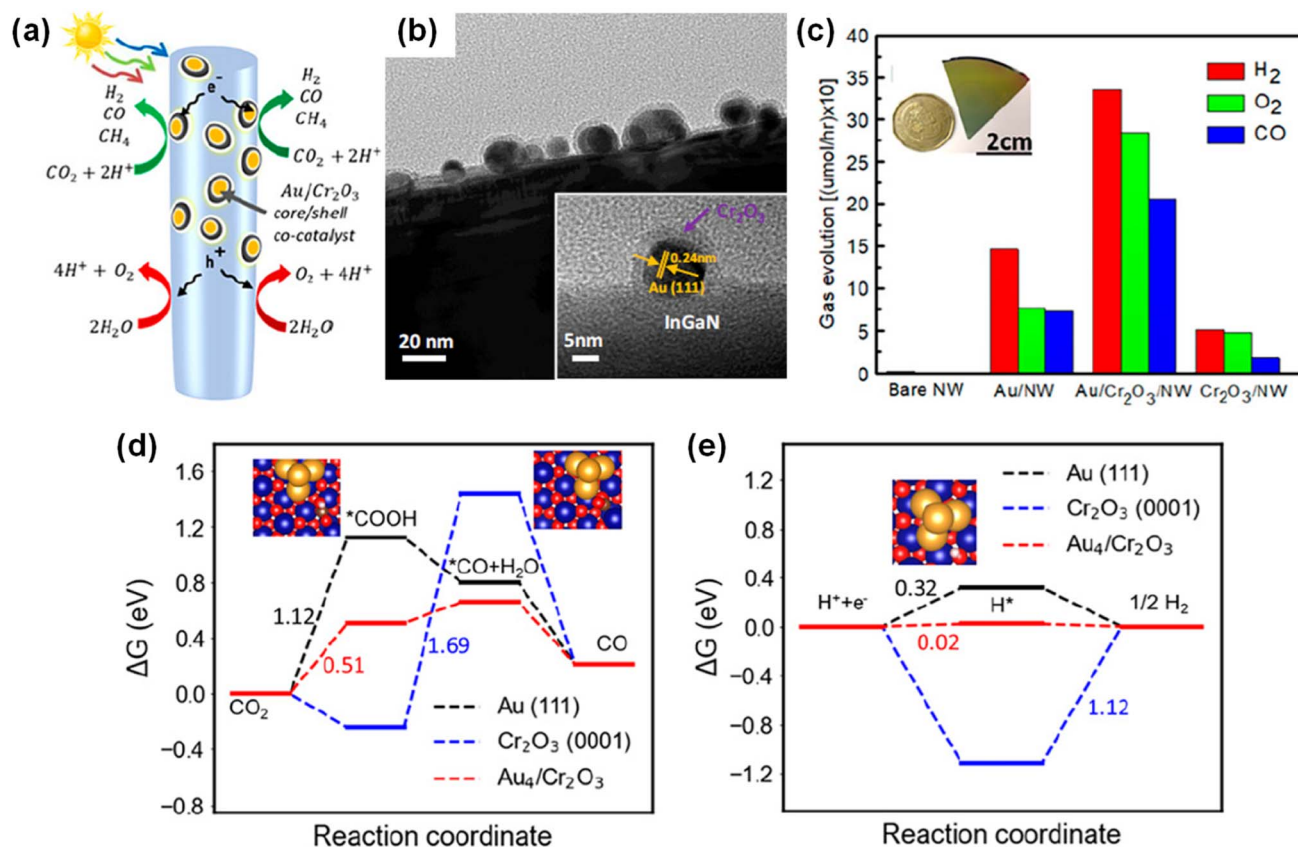


Fig. 25 (a) Schematic illustration of photocatalytic overall CO<sub>2</sub> reduction reaction over Au/Cr<sub>2</sub>O<sub>3</sub>-decorated InGaN/GaN nanowires. (b) Structural analysis of Au/Cr<sub>2</sub>O<sub>3</sub> core/shell cocatalysts on InGaN/GaN nanowires. (c) Output gas evolution with various cocatalysts. Calculated free energy diagrams for (d) CO<sub>2</sub> reduction reaction and (e) H<sub>2</sub> evolution reaction on different photocatalysts. Au, gold; Cr, blue; C, brown; and O, red. Reproduced with permission from ref. 210. Copyright (2022) National Academy of Science.

absorption, (2) severe electron-hole recombination, (3) poor catalytic activity, and (4) poor stability. Thus, tuning of band gap energy for broadband light absorption is a primary concern to achieve a high yield of target products. In this context, indium incorporation into GaN nanowires and heterogeneous tandem stacking of dual- or triple-band III-nitrides have been demonstrated. Preventing the recombination of photogenerated electrons and holes is another critical issue for the efficient utilization of charge carriers. Therefore, electrical conductivity, surface band bending, and charge carrier transport properties have been finely controlled by n- or p-type doping of III-nitrides. The intrinsic catalytic activity and selectivity of III-nitrides could be enhanced by decoration with suitable cocatalysts, which sometimes show unprecedented synergy at the interface of the III-nitride/cocatalyst and realize a unique catalytic performance for water splitting and CO<sub>2</sub> reduction reaction. Moreover, N-terminated top and lateral surfaces of GaN nanowires showed record-high stability over 3000 h for photoelectrochemical water splitting under solar light irradiation. Recent studies identified that the partial substitution of nitrogen by oxygen on the nonpolar lateral surface of GaN nanowire not only improves the catalytic activity for the H<sub>2</sub> evolution reaction but is also responsible for the excellent stability against harsh reaction conditions.

Nevertheless, the state-of-the-art growth methods of high-crystal-quality III-nitrides are limited to wafer-scale fabrication techniques (*e.g.*, MBE or MOCVD), which may pose limitations on the large-scale application of photocatalysts or photoelectrodes. Recent studies, however, found that concentrated solar light irradiation on wafer-scale 1D III-nitrides drastically improves their photocatalytic activity, which outperforms photocatalyst particles dispersed in the solution.<sup>149</sup> Hence, the utilization of thermal energy obtained from phonon vibration or non-radiative recombination under concentrated sunlight has been attracting attention. The thermal energy generally degrades the optoelectronic properties of semiconductors but promotes the chemical reactions by providing additional energy to overcome the activation barriers. Considering these trade-offs, the rational design of III-nitrides and the careful utilization of the photoexcited charge carriers with photoinduced thermal energy will represent a significant opportunity. In addition, fast reaction kinetics under concentrated solar light will lead to a vigorous generation of products and consumption of reactants near the electrode, which will change the local reaction environment and affect catalytic activity and stability. The local shift in reaction condition near the III-nitrides may oxidize the specific crystal planes, leading to new composites on the surface. An understanding of the material, optoelectronic,

and catalytic properties of the reconstructed surface compounds will guide us to design more efficient and stable III-nitride devices. Gas bubbles generated in the solution have the physical force to remove 1D III-nitrides from the substrate by surface tension. When the reaction rate increases under concentrated sunlight, the physical stability will become a more severe issue, and a strategy to anchor 1D nitride nanostructures on supports will be required. The stability of the photo(electro) catalyst is also largely dependent on the stability of the cocatalyst, and the separation of the cocatalyst from III-nitrides during the reaction has been a major reason for degradation. In general, since metallic nanoclusters or single-atom catalysts tend to be stably located in the N-vacancy of the nitride materials,<sup>211</sup> the method of forming the N-vacancy and subnanometer cocatalysts on the surface of the III-nitride semiconductors as well as catalytic activity should be studied to hold the cocatalysts on the surface and to maintain high efficiency. To date, the growth of high-crystal-quality 1D III-nitrides has been limited to a few types of substrate due to lattice mismatch and high-temperature compatibility of the substrate. Overcoming challenges in the growth method could potentially solve the efficiency bottleneck by integrating 1D III-nitrides with other highly efficient semiconductors (e.g., III-V semiconductors).

The fact that 1D III-nitrides are efficient and stable materials for water splitting and CO<sub>2</sub> reduction reactions implies that these nanostructured semiconductors can also be used for various other chemical reactions, including ammonia (NH<sub>3</sub>) synthesis, methane (CH<sub>4</sub>) oxidation, and urea synthesis. Recently, studies related to the conversion of N<sub>2</sub> or NO<sub>3</sub><sup>-</sup> into NH<sub>3</sub> in an aqueous solution are attracting great attention in order to replace the conventional energy-intensive and CO<sub>2</sub>-emissive synthetic process. However, the initial activation of these reactants is extremely difficult due to the difficulties of N≡N bond or N=O bond cleavage. This problem could be resolved if 1D III-nitrides with an appropriate amount of N-vacancies, that readily interact with N-containing reactants to activate and promote the catalytic reaction, could be realized.<sup>212</sup> Moreover, unique metal-support interactions, found in the cocatalyst-III-nitride system, will broaden the application of 1D III-nitrides to solar-driven CH<sub>4</sub> oxidation. Several promising results of CH<sub>4</sub> oxidation to CH<sub>3</sub>OH<sup>213</sup> and benzene production<sup>214</sup> via C-C coupling have been reported using 1D III-nitride artificial photosynthetic devices. Therefore, III-nitrides hold great potential for many solar-powered catalytic reactions by enhanced N≡N and N=O bond cleavage, C-H bond activation, C-C and C-N coupling reactions, and aromatization.

In summary, various physical/chemical studies on 1D III-nitride semiconductors have led to the successful demonstration of artificial photosynthetic devices. A deeper understanding of the mechanism at the atomic scale with the assistance of experimental evaluation, catalyst characterization, operando analysis, advanced molecular dynamics and first-principles density functional calculations will provide further fundamental guidelines on the rational design of the device. In the near future, research on III-nitrides which can operate in extreme environments (i.e., high temperature, concentrated

solar light, etc.) will be required to increase yield as well as efficiency and stability. Finally, since III-nitrides are one of the most commonly used semiconductor materials in the industry, commercialization is expected to be easier than for other competing materials if the III-nitride artificial photosynthesis device achieves an appropriate level of efficiency and lifetime.

## Conflicts of interest

Some IP related to this work was licensed to NS Nanotech, Inc. and NX Fuels, Inc., which were co-founded by Z. Mi. The University of Michigan and Mi have a financial interest in NS Nanotech.

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