Quasi-1D Aligned Nanostructures for Solar-Driven Water Splitting Applications: Challenges, Promises, and Perspectives

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1. Introduction

Excessive usage of fossil fuels already crosses the threshold boundaries of environmental sustainability due to intensive release of greenhouse gases, with the subsequent generation of CO$_x$, NO$_x$, and SO$_x$-based environmentally toxic substances. Therefore, there is a great need for clean energy harvesting from green chemical methods. In particular, photocatalytic water splitting has attracted the interest of scientists from various disciplines over the last few decades. While sunlight offers a considerable alternative to fulfill the required global energy demands, the lethal environmental impact can be countered by developing successful energy harvesting tools for solar energy harvesting. Solar energy is a readily available, inexhaustible, and decentralized natural resource. The magnitude of the solar radiation striking the Earth’s surface is nearly equivalent to 130 million 500 MW power plants at each instant. However, due to the intermittent nature of solar energy, it is quite challenging to use it in a more appropriate manner such as fossil fuels. Industries based on solar energy utilization are still in their initial stages, and a lot of work has yet to be done to achieve the ultimate means by which we can store, carry, and convert this energy efficiently. The development of efficient solar energy harvesting devices with high efficiency and that are cost-friendly is the worldwide target to realize the potential of solar energy.

Photoresponsive materials are prone to solar light based on their optoelectrical characteristics and, hence, could trap part of any solar radiation upon interaction. The chemical bonds store the solar energy to mimic natural photosynthesis, where green leaves trap sunlight through chlorophyll for the preparation of glucose and oxygen. Thus, using these nanomaterials, artificially mediated photosynthesis could be a desirable and intended goal to produce clean energy. Most of these photoactive materials are based on semiconductors. However, metal oxides and...
earth metals,[13,14] coordinate complexes,[15,16] and even conjugated polymers,[17,18] are also used. In particular, semiconductors are preferred due to their innate characteristics, such as light absorption, desirable charge separation, and stability toward photocorrosion. These materials are used as electrodes (photoanodes or photocathodes) in artificial solar devices for energy harnessing. One of these modifications is adopted for the photoelectrolysis of water, which produces oxygen and hydrogen in the two- or three-electrode electrochemical cell. Oxygen and hydrogen molecules can store an immense amount of energy.[19] Enhanced photoelectrochemical (PEC) water splitting into usable hydrogen has already knocked on the industrial doors that would provide clean fuel, whose only waste product upon utilization is water.[19] Jia et al. already achieved an enthralling 30% solar-to-hydrogen (STH) efficiency by combining the photovoltaic (PV) process with the electrochemical process.[20] To be precise, a viable and cheaper electrochemical cell contains electrodes, suitable electrolytes, and artificial solar radiation at the required potential, which are the main requirements for the successful demonstration of PEC water splitting. Within the electrochemical cell, the working electrode is the component where the photoactive materials, i.e., semiconductors, could be used, and the water splitting takes place on the interface. The PV device can also perform water splitting once directly connected to the electrolyzers and/or engineered catalytic electrodes, but the fabrication requires intense care and the cost is usually significant. On the other hand, a PEC water splitting cell design is cost-effective and facile. In addition to this, PEC water splitting takes place directly at the surface of the semiconductor.[5,22]

Fujishima and Honda successfully demonstrated the PEC water splitting experiment initially in the early 1970s at the laboratory scale using bare TiO$_2$ as a working electrode and simulated ultraviolet (UV) solar radiation.[21] The purpose of using UV light lies in the wide bandgap of TiO$_2$, which is $>3.0$ eV and, hence, can only absorb in the UV region. After their seminal discovery, a large number of research groups are inclined toward the concept of generating hydrogen as a clean fuel from water splitting. The primary purpose was to substitute or modify TiO$_2$ with a highly efficient material that is stable toward photocorrosion, could absorb the visible spectrum, as it constitutes a significant portion of available sunlight, and was economically feasible. Researchers have developed a considerable number of advanced nanostructures to evaluate their water-splitting performance. Photoresponsive materials, which are generally based on semiconductors, should have desired properties, such as 1) swift charge transfer at a semiconductor/electrolytic solution interface; 2) displaying longstanding stability and resilience at high voltage and pH of the electrolytic solution; and 3) can competently capture a large percentage of the solar spectrum, especially the visible region.[22–24] These properties can be achieved by modification of the bulk physicochemical properties of pristine semiconductor materials via various approaches. These include formulation of their nanocomposites,[25,26] heterostructures,[17,27,28] doping via non-metals, such as oxygen,[29] nitrogen,[25,29–31] and sulfur,[32,33] creating defects,[29] and oxygen vacancies;[34–36] addition of cocatalysts;[37,38] and gleaming plasmonic metal, such as Ag, Au, etc.[39–42] In addition to those listed earlier, other physical properties, such as surface area,[43] crystallinity,[44] and morphology,[24,45–47] also affected the PEC water splitting performance of the materials, because the optical properties also depend on these factors.[48]

It is evident that the development of electrode materials for PEC water splitting is a crucial aspect of PEC water splitting and depends on many factors, such as surface area, optoelectronic properties, thin-film quality, visible light absorbance, nanoscale morphology, etc. Therefore, this review will particularly emphasize the geometry of aligned semiconductor materials and their nanoarchitecture and high-quality macroscopic films of these aligned nanostructured electrodes for PEC water splitting. Different synthesis methods for aligned nanomaterials, such as hydrothermal/solvothermal, sol–gel, and physical vapor deposition (PVD) methods, with their crucial reaction parameters and nature of reaction precursors will be highlighted. A few case studies will be provided to shed some light on the performance of aligned semiconductor nanorays (NAs) with the support of mechanistic aspects. In addition to this, a comparative analysis will be provided (in terms of photocurrent densities) to compare the aligned and other morphologies under similar conditions.

2. Basic Principles, Mechanism, and Benchmarks of PEC Water Splitting

2.1. Principles of PEC Water Splitting

Water splitting into hydrogen and oxygen with the combined effect of solar light and electric potential and photoelectrocatalyst is called PEC water splitting. It is an uphill reaction, and the thermodynamic free energy change ($\Delta G^\circ$) for one water molecule to split into hydrogen and oxygen is $+237 \text{kJ mol}^{-1}$. The positive $\Delta G^\circ$ indicates that the reaction is non-spontaneous and requires energy to be added to the system. This energy can be converted to electron volts (eV) using the Nernst equation, shown in Equation (1), i.e., $\approx 1.23 \text{eV}$.\[49 $
\Delta G^\circ = -nFE^\circ$
\]

Thus, $\Delta E^\circ = 1.23 \text{eV}$ of energy is required per electron transfer, which is very high; 1.23 eV can be converted to wavelength by simple mathematical calculations, as shown in Equation (2) and (3).

$E^\circ = \frac{hv}{hc/\lambda}$

$\lambda = \frac{hc}{E^\circ}$

where $\lambda = 1.2398 \text{eV nm}/1.23 \text{eV} \approx 1008 \text{nm}$. Thus, for effective water splitting with solar light alone, $\approx 1000 \text{nm}$ of energy is required, and the semiconductor should have an absorption capacity in this range. The water splitting reaction can be broken down into two half-cell reactions. Scheme 1 demonstrates these two reactions.

OER and HER half-reactions require a minimum of 1.23 V versus reversible hydrogen electrode (RHE) overpotential and complete water splitting of one water molecule.[50] The equations also indicate that the HER requires a minimum of two $e^-$ holes $^+$ (h$^+$) pairs to produce one molecule of hydrogen. These electrons come from the OER half-reaction step. Semiconductor materials

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are suitable for water splitting, because they possess tunable bandgaps, as compared with metals (with zero bandgaps) and insulators (with very large bandgaps), where the bandgap is the distance between the valence band (VB) and the conduction band (CB). The VB and CB positions of semiconductor materials straddle the OER and HER band positions and, thus, can drive these reactions under illumination.

2.2. The Optical Requirements and Typical Mechanism

Optical properties more effectively describe the photocatalytic nature of the material. Insight into the bandgaps, band edges, and solar spectrum absorption is the key to design a suitable photocatalyst for PEC water splitting. These properties are usually measured via UV–vis, diffuse reflectance spectroscopy (DRS), photoluminescence (PL), etc. These characterization techniques evaluate the absorption capacity, bandgap, and photoexciton properties of the examined material. The aligned NAs material with absorption in the visible range has a lower bandgap, because they are related to each other by Equation (2) and (3). DRS is an important technique that is usually used for solid materials, especially powders. The basic working principles for UV–vis and DRS are the same. PL is an important luminescence technique to extract information about the lifetime of the excitons in addition to their light absorption capacity. Normally, the high and low intensity bands of PL spectra signify that the excitons possess a long or short lifetime, respectively, which ultimately influences the charge recombination rates of the excited states.

The most acceptable mechanism for these reactions on the surface of a semiconductor is shown in Figure 1. Semiconductor materials upon absorption of higher energy photons \((E(h\nu) > \text{bandgap})\) create holes in the VB, as electrons are excited to CBs. Photogenerated electrons/holes pairs drive the OER and HER reactions on the surface of the semiconductor. The former takes place at VB, whereas the latter occurs at CB, respectively (Figure 1a). The band position is critical to realize the reaction to occur more readily. Figure 1b shows that certain catalysts are appropriate for HER, whereas others for the OER reaction, based on their band positions. In a one-electrode system, the working electrode can behave as a cathode or anode, depend on its optical nature (Figure 1c,d). Besides this, in a tandem configuration (Figure 1e), n- and p-type photoelectrodes can be used to achieve OER and HER simultaneously.

**Scheme 1.** The water splitting reaction shown as two half-cell reactions.

**Figure 1.** Energy illustrations of PEC water splitting: a) single-step excitation, b) Z-scheme-based two-step excitation, c) working electrode as a photoanode, d) working electrode as a photocathode, and e) tandem cell configuration. Reproduced with permission. Copyright 2014, Royal Society of Chemistry.
When photoelectrodes are immersed in an electrolyte, the Fermi level is repositioned, and therefore, overpotential comes into act. The overpotential can be overcome via an external power supply to reduce the threshold value of water splitting. The power source is also required for compensation of energy for the generation of hydrogen from the semiconductor material, whose band position is not straddled with HER potential and vice versa. The absorbing materials decide the band edge potential of a semiconductor at the interface; i.e., the Fermi energy of the semiconductor can change the applied bias, but the band edge potential cannot change by the same. Thus, by engineering the surface of the photoelectrode and applying external potential, the behavior of working electrodes can be tuned accordingly. Figure 2 provides the band position diagram for some important photoactive materials. Three main categories can be distinguished in the diagram. The first category contains those photocatalysts whose band position is straddled with HER and, thus, is efficient for hydrogen generation. The second category represents photocatalysts whose band position fits with the OER level and, hence, is suitable for PEC water oxidation. The third category comprises special kinds of photocatalysts, which can undergo PEC hydrogen and oxygen generation, as their VB and CB levels straddle both OER and HER.

3. Parameter Benchmarking

PEC water splitting depends on various internal and external factors. Therefore, the actual performance of a photocatalytic material for water splitting needs diverse subject knowledge of all parameters. From the electrochemical cell and photoelectrode design to data interpretation, every step should be carried out with a proper understanding. As discussed in the earlier section, PEC water splitting is carried out in a two- or three-electrode cell, supported by a potentiostat and solar simulator (to provide artificial light). The photocatalysts (normally nanoparticles) should be deposited over a conducting surface such as indium tin oxide (ITO) or fluorine doped tin oxide (FTO) with homogeneous uniformity. Various methods can be used for this purpose, which includes electrochemical anodization (especially in the case of metal foils), the doctor-blade method, the spin coating method, the solution casting method, particle/seed transfer, and direct film growth over the conducting surface during synthesis on the electrode surface. Once the photocatalytic materials are uniformly deposited, the photoelectrodes are ready for water splitting. These electrodes are immersed in the cell containing the opposite electrolytic solution. The selection of the electrolytic solution (pH) is as crucial as electrode preparation, and an optimized concentration should be used after several repetitions.

Various electrical parameters can be studied to investigate water splitting, which include cyclic voltammery (CV), linear sweep voltammery (LSV), and chronoaomperometric analysis. The first two give a current with voltage scan, whereas the latter provides a current versus time plot under light and dark. Electronic impedance spectroscopy (EIS) is also required to see the interfacial charge transfer efficiency in semiconductor electrode materials. The efficiency of the photoelectrode is also considered very important, and therefore, benchmarking is carried out in terms of incident photon charge carrier efficiency (IPCE), STH, and quantum efficiency (QE). Equation (4)–(6) are mostly used for this purpose.

\[
IPCE(\lambda) = \frac{\text{electrons cm}^{-2} \text{s}^{-1}}{\text{photons cm}^{-2} \text{s}^{-1}} = \frac{[j_{ph}(\text{mA cm}^{-2})]}{P_{mono}(\text{mW cm}^{-2}) \times \lambda(\text{nm})}
\]

where \(j_{ph}\) is the current, and \(P_{mono}\) is the illumination power.

\[
\text{STH} = \frac{\text{Output energy as } H_2}{\text{Energy of incident solar light}} = \frac{r_{H_2} \times \Delta G}{P_{sun} \times S}
\]

where \(P_{sun}\) is the energy flux of the sunlight, \(S\) is the area of the reactor, and \(r_{H_2}\) is the rate of \(H_2\) generation.

\[
nQE = \frac{N_{\text{eff}}}{N_{\text{total}}}
\]

where \(N_{\text{eff}}\) is the number of generated electron–hole pairs (effective) under solar irradiation, and \(N_{\text{total}}\) is the number of incident photons.

The typical interpreted data for PEC water splitting are shown in Figure 3.

4. Aligned NAs, Synthesis, and Their Water Splitting

4.1. Aligned NAs Materials

As discussed in the earlier part of this review, certain physicochemical characteristics are important to make semiconductor materials suitable for overall water splitting. One of those characteristics is morphology. Indeed, morphology impacts the performance of photoelectrode materials for PEC water splitting. Nanostructures with various morphologies have been reported for efficient water splitting. Khan et al. synthesized pseudo-flower-shaped BiVO₄ and studied their PEC water splitting behavior. The same group also reported a hierarchical morphology for Bi₂O₃/WO₃ nanocomposite with efficient water splitting oxidation, nanoflower, nano flakes.
nanospheres, nanocubes, nanowires (NWs), nano-rods (NRs), and nanotubes (NTs) morphologies widely reported for their role in water splitting reactions. The controlled growth of NAs in a well-organized manner can effectively enhance PEC water splitting performance. The aligned morphology facilities the light absorption, charge separation, and transport and, therefore, suppresses charge recombination, which leads to good PEC performance. The good distribution and organization of NAs lead to alignment, and therefore, these materials are also called aligned NAs owing to their ordered arrangement (mostly 1D). Figure 4 provides a typical NA morphology of Ta$_3$N$_5$ prepared by nanoinprinting and mask anodization. The NR arrays (NRAs) are aligned and arranged in a highly parallel aligned order as discussed.

Aligned NAs semiconductors are auspicious aspirants for next-generation optoelectrical devices. Alignment and proper orientation endorse many exceptional characteristics in these photoactive materials. For instance, for ideal PV devices, the NAs need preferably to be aligned vertically with respect to the photoelectrodes. Similarly, in piezoelectric devices, the NAs provide the required reversible flexibility for the generation of electrical energy from mechanical energy or vice versa. This alignment will create an incessant pathway for the conduction of the charge carriers. While numerous synthetic techniques...

Figure 3. Typical PEC water splitting plots obtained from modified α-Fe$_2$O$_3$ NAs under light and dark: a) LSV plot. b) Transient photocurrent measurement as a function of variable applied potential. c) Chronoamperometric current versus time plot at a constant voltage. d) % IPCE plot. e) Chronoamperometric current versus time stability plot. f) EIS or Nyquist plots. Reproduced with permission.[72] Copyright 2015, Royal Society of Chemistry.

Figure 4. SEM images of Ta$_3$N$_5$ NRAs. a) 30°-tilted and b) cross-sectional view. Reproduced with permission.[91] Copyright 2014, IOP Science.
have been demonstrated for aligned NAs, it is still very challenging to achieve these structures due to high cost, slow growth, and lack of reproducibility. Various groups are explicitly working on aligned heterostructure NAs for enhanced photocatalytic and PEC applications. Yang and co-workers reported various 1D nanowire arrays (NWAs)\(^{[100\textbf{-103}]}\). Similarly, Yong and co-workers also explicitly designed aligned heterostructure NAs for various optical applications\(^{[104\textbf{-109}]}\). Later, our research group has focused on the design of highly aligned pristine heterostructure NAs for sensing, water splitting, and piezoelectric applications\(^{[10,42,34,90,110,111]}\).

5. Synthesis of Aligned NAs

Many successful attempts have been reported for the synthesis of aligned NAs materials in the form of rods, wires, tubes, etc. The literature reveals the use of external modulators such as applied current, and slow solvent evaporation could lead to an aligned orientation of NAs. These methods, however, are quite stumpy, robust, and time-consuming. Therefore, strategies that are more facile, fast, and less energy-intensive would be appreciated. To reach this goal, different materials can be used to synthesize nanomaterials of various morphologies under controlled reaction conditions. The tuning of various reaction parameters is always important to achieve aligned NAs structures. The vapor deposition method is extensively practiced for the synthesis of aligned nanomaterials and heterostructure NAs. The raw materials are vaporized under specific conditions in this technique. It is broadly divided into two classes, i.e., PVD\(^{[112]}\) and chemical vapor deposition (CVD).\(^{[113]}\) In the first case, condensed phase materials are vaporized in a vacuum through a laser or another alternating current or direct current power source. In CVD, these vapors are chemically reacted to produce the desired product before deposition. PVD and CVD are used for the synthesis of thin films and other condensed-phase products. These techniques are well regarded for the synthesis of well-aligned NAs semiconductor materials. Ahsanulhaq et al. utilized atomic layer deposition (ALD) (a subclass of vapor deposition) for the synthesis of square-shaped ZnO NRAs over silicon (Si) wafer, using a diethyl zinc (C\(_2\)H\(_5\)Zn) precursor.\(^{[111]}\) Scanning electron microscopy (SEM) simulated with a field-emission (FE) electron gun, and a nanomask pattern generator were used for patterning the ZnO/Si wafers with diverse sizes and forms at the nanoscale level. These patterned ZnO/Si wafers were used to grow aligned ZnO NRAs (Figure 5).

Wu et al. successfully achieved aligned TiO\(_2\) NRNs and nanowalls (NWs) without using any template via the CVD technique. They deduced that the bandgaps alter with the crystallinity and reported 3.0 and 3.2 eV for rutile and anatase NRs, respectively.\(^{[114]}\) Core-shell WO\(_3\)-NRs/BiVO\(_4\) photoactive nanocomposite was engineered via a glancing angle deposition (GLAD) technique. A descriptive synthetic scheme is provided in Figure 6.\(^{[84]}\) where a high vacuum was developed before the growth of WO\(_3\) NRs over stacked ITO/PT/ITO substrate via glancing angle sputtering. The crystallinity was achieved through the calcination of WO\(_3\) NRs at 575 °C for 4.5 h. The BiVO\(_4\) was electrochemically deposited from an electrolytic solution of 1 × 10\(^{-2}\) M Bi(NO\(_3\))\(_3\) in 35 × 10\(^{-3}\) M VOSO\(_4\). After this, the photoanode was subjected to annealing again at 500 °C for 2 h. The crystalline monoclinic phase was achieved. The Co–Pi cocatalyst was also deposited by a photoassisted electrodeposition (PED) technique to enhance photocactivity.

In addition to vapor deposition, other synthetic techniques, such as simple hydrothermal, solvothermal, sol–gel, electrochemical anodization, deposition, and lithography, have been used for the synthesis of NAs. In most of these cases, the distribution of the seeds over the support is highly critical in achieving aligned growth. A list of these techniques is provided in Table 1 with relevant examples and reaction conditions\(^{[30,115–121]}\).

6. PEC Water Splitting by Aligned NAs Materials

Alignment of NAs and size reduction of materials into the nanometer regime can advance device performance and lead to novel performance. For example, the size of transistors has shrunken over the years, and more transistors can be accommodated in a small silicon area, which ultimately enhanced the performance of these devices with a massive decrease in power consumption.\(^{[122]}\) Specific size-dependent characteristics are possessed by 1D nanomaterials, including photon emission and absorption,\(^{[13,14]}\) quantized or ballistic transport properties, and metal-to-insulator conversion in materials.\(^{[115]}\) Besides the opportunity to investigate and evaluate the novel physical properties of 1D materials, the controlled fabrication of high-quality NWs and their growth mechanisms has attracted tremendous attention. These material classes include metallic elements, oxides, nitrides, carbides, and sulfides.\(^{[122]}\) Owing to such excellent optoelectrical characteristics, 1D aligned NAs have been explored by many research groups for PEC and photocatalytic water splitting applications. The NAs are suitable for overall water splitting applications; therefore, their PEC-assisted OER and HER characteristics are reported in the literature. The following classes of materials have well-established aligned NAs morphologies.

6.1. Titania (TiO\(_2\))-Based Aligned NAs

Titanium dioxide (TiO\(_2\))\(^{[21,123]}\) has been extensively explored in photocatalytic and PEC applications, based on their effective photoresponse and electrical characteristics. Though TiO\(_2\) can be found in a variety of morphologies, however, more recent attention has been dedicated to its 1D aligned growth, which was also found to be useful for PEC applications due to their desirable characteristics. In particular, aligned NTs have been extensively reported in the literature for PEC water splitting applications.\(^{[42,124–126]}\) Table 1 provides some of the conventional techniques for the growth of NAs; however, in the case of TiO\(_2\) NAs, electrochemical anodization techniques are used extensively. This fabrication method effectively controls NTS orientation and morphology. The electrochemically anodized 1D TiO\(_2\) NT arrays (NTAs) possess distinctive characteristics compared with NAs grown by other routes, as the NTs formed are highly ordered, well organized, and perpendicularly oriented on the Ti substrate surface. Using different varieties of fluoride-based etching electrolytes, such as NaF, NH\(_4\)F, and hydrogen fluoride, in addition to others\(^{[127–130]}\) and a variable range from 10
to 150 V,\textsuperscript{[42,58,125,131]} NTAs with controlled size and length can be fabricated.

In addition to normal NTAs, when the voltage is kept lower for the initial reaction interval and then increased slowly to the desired value, a bamboo-shaped double-walled NT forms (Figure 7).\textsuperscript{[132,133]}

Allam et al. engineered the bandgap of TiO$_2$ by manipulating pristine TiO$_2$ with Pd in aligned NAs morphology.\textsuperscript{[134]} The Pd (0.25\%–Ti foil was anodized and annealed in an ammonia environment for 5 h at various temperatures. Nitrogen treatment was used to grow oxynitride photoanode, which was then subjected to PEC water oxidation. The maximum photocurrent density of $\approx$2 mA cm$^{-2}$ and $\approx$0.82\% IPCE was achieved for Ti–Pd, which was annealed at 550 °C in the ammonia environment.

Deliberately controlled deposition of TiO$_2$ nanoparticles (NPs) on the half surface of Si arrays was found to be a useful way to enhanced light absorption in the visible region, whereas the bare Si provides the visible absorption center to the catalyst, thus enhancing the overall water splitting. Under 1 sun light, a photo-generated electron from the conduction band of Si and holes in the VB of TiO$_2$ moves to the interface of the catalyst to perform PEC water splitting (Figure 8).

The ternary mixed oxide form of Ti–Mo–Ni NTAs was found critical for HER\textsuperscript{[136]} by the same group. Likewise, the electrochemical anodization technique was adopted for the synthesis of NTAs using NH$_4$F and H$_3$PO$_4$ as an electrolyte in a two-electrode cell. The as-anodized substrates were subjected to annealing under air at 450 °C for 4–16 h. Different parameters were optimized before getting the best photoanode for HER. They found that the substrate annealed for 16 h had the highest photocurrent efficiency of 1.1\% with $\approx$2.2 mA cm$^{-2}$ photocurrent density at 1.1 V versus RHE. More recently, our group explored the enhanced water splitting capacity of hematite photoanodes by combining their properties with TiO$_2$ NTs and

Figure 5. Low (left) and high (right) magnification FE SEM images of ZnO NRAs grown selectively on pre-patterned Si substrates with the diameters of a,b) 2 μm, c) 500 nm, and d) 50–100 nm, respectively. Reproduced with permission.\textsuperscript{[111]} Copyright 2017, IOP Science.
Table 1. Distinct crafting techniques for the synthesis of aligned NAs of various shapes and morphologies.

| S No. | Synthetic strategy | Precursors | Reaction conditions | 1D NAs morphology | References |
|-------|--------------------|------------|---------------------|-------------------|------------|
| 1     | GLAD and anodization | Tungsten metal target, Bi(NO$_3$)$_3$, VOSO$_4$, and CoPi | Specific angle sputtering, followed by annealing | Stacked NRAs | [84] |
| 2     | ALD                | Diethyl zinc (C$_2$H$_5$)$_2$Zn | | ZnO NRAs | [111] |
| 3     | CVD                | Titanium acetylacetonate (Ti(C$_{10}$H$_{14}$O$_5$)) | 200–230 °C to vaporize | TiO$_2$ NRs and nanowalls | [114] |
| 4     | Magnetron sputtering and hydrothermal | (Zn(NO$_3$)$_2$·6H$_2$O), NH$_4$OH, and Co(NO$_3$)$_2$·6H$_2$O | 5–10 nm ZnO sputtered substrate in autoclave (pH = 11) at 95 °C for 24 h | Co$_3$O$_4$ tip-coated ZnO NWs | [104] |
| 5     | Electrospinning method | Polyethylene glycol 8000, polyvinylpyrrolidone, tetrabutyl titanate | Stirring and sonication of precursors to get the gel followed by electrospinning | TiO$_2$ nanofibers | [116] |
| 6     | Thermal evaporation and hydrothermal | Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), NH$_4$OH, and zinc powder | Autoclaved and treat at 60–90 °C (pH = 10.1–10.45) | ZnO NRs | [117] |
| 7     | Ultrasonic-assisted hydrothermal method | Sodium tungsten dehydrate (Na$_2$WO$_4$·2H$_2$O), ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$) | 80–180 °C for 0.5–20 h and calcined at 450 °C | WO$_3$ aligned nanoplate arrays | [115] |
| 8     | Non-hydrolytic sol–gel method | Titanium isopropoxide in acetic acid and 1-hexadecylamine | The mixture was gradually heated to 270 °C for 20 min and kept at this temperature for 2 h | TiO$_2$ NRs | [118] |
| 9     | Interfacial nanosphere lithography followed by hydrothermal growth | Monolayer colloidal crystals (MCCs) template, TiO$_2$ gel, polystyrene (PS), FTO substrate | MCC template transferred onto TiO$_2$ sol, leading to the deposition at PS sphere. The film deposited on FTO, calcined | TiO$_2$ NR@nanobowl arrays | [121] |
| 10    | Electrochemical deposition | Aqueous solution of ZnCl$_2$ and KCl (0.1 M) saturated with oxygen gas | 2 × 2 cm$^2$ FTO surface was used as an electrode. ZnO NWAs were electrodeposited at 80 °C under 1 V constant potential | ZnO NWAs | [119] |

Figure 6. a,b) SEM supported schematic diagram of WO$_3$-NRs/BiVO$_4$ core–shell photoanode engineered by glancing angle deposition (GLAD). Reproduced under the terms and conditions of the Creative Commons Attribution license 4.0.[84] Copyright 2015, The Authors, published by Springer Nature.
Figure 7. a) Bamboo-shaped TiO$_2$ NTAs developed by a stepping voltage anodization technique. b) Branched NTs. c) Double-walled NTAs. d) Overgrown NTs. Reproduced with permission.$^{[132]}$ Copyright 2018, John Wiley and Sons.

Figure 8. Schematics of tree-like Si–TiO$_2$ heterostructures growth. (top box) The Aligned TiO$_2$ NWs (blue) on half of a Si NW (grey), and insets display electron-hole pairs at the semiconductor-electrolyte interface for solar-driven water splitting supported by cocatalysts (yellow and grey dots). (down box) Energy band diagram for water splitting. Reproduced with permission.$^{[135]}$ Copyright 2013, American Chemical Society.
plasmonic Ag. The electrochemical incorporation of hematite and Ag into TiO$_2$ efficiently decreased the bandgap from 3.24 to $\approx$2.5 eV, which led to a shift of absorption toward a visible light and elevated photocurrent density of $>$2.50 mA cm$^{-2}$. This enhancement was ascribed to lower charge recombination, the swift charge transfer due to type-II heterojunction formation, and resilience toward photocorrosion. Figure 9 shows the stepwise electrochemical anodization growth of TiO$_2$ and the incorporation of hematite and Ag with a water splitting mechanism, respectively.

The preceding discussion indicates that the aligned morphology is pretty useful to introduce enhanced optoelectrical characteristics within aligned TiO$_2$-based photocatalysts, which can improve their overall water splitting performance many fold.

6.2. Zinc Oxide (ZnO)-Based Aligned NAs

Owing to similar semiconductor characteristics and its UV photoactive nature, similar to TiO$_2$, ZnO has been equally explored by researchers for PEC water splitting in recent years. However, the photocorrosion of ZnO has restricted its potential use for the cited purpose.$^{[137]}$ Therefore, surface modification is highly desired to improve its photocurrent generating capacity and photo-stability. The NAs-based modifications are acquired via various synthetic protocols. Figure 10 shows some ZnO-based aligned NAs morphologies reported by various researchers.$^{[104,105,107]}$

ZnO NAs could be engineered on FTO, ITO, or other conducting surfaces by simple wet chemistry techniques, unlike TiO$_2$ NAs where electroanodization is predominantly used. Various research groups have reported high crystalline hexagonal ZnO NAs fabrication. Like the reaction parameters the post-treatment of as-synthesized ZnO NAs is equally important to sustain the alignment of the NAs. The post-synthesis gentle washing of the NAs sample and temperature treatment (annealing) should be carefully implemented.$^{[54]}$

Well-aligned ZnO NRAs have been developed on the surface of the metal-plated polymer by a wet chemistry reaction in a sophisticated continuous reactor to achieve wire-shaped photoanodes.$^{[138]}$ The growth was controlled with computational flow-field simulation, which yields wire-shaped ZnO NAs photoanodes having better PEC performance. The length of ZnO NRAs approached a few micrometers in the continuous reactor. The diameter and length of ZnO NA can be controlled by the time for growth. It is reported that the ZnO NRs grew up to 570, 934, and 1 280 nm in length and 138, 230, and 236 nm in diameter at the reaction times of 4, 6, and 8 h, respectively.$^{[139]}$ Similarly, the role of surfactants, zinc precursors, and post-reaction treatment also influences the length and morphology of the ZnO NAs. The length and morphology have significant consequences over the optoelectrical characteristics and, hence, the PEC performance of the ZnO-based photoelectrodes.$^{[140,141]}$

The composite and heterostructures of ZnO NAs with other materials have been found to have exceptional potential for PEC water splitting. In the past few years, hybrid ZnO NAs materials, such as TiO$_2$/ZnO,$^{[142]}$ ZnO/CdS,$^{[143]}$ GaON/ZnO,$^{[10]}$ Ga$_2$O$_3$/ZnO,$^{[144]}$ Au/ZnO/CdS,$^{[145]}$ Au/FeOOH decorated ZnO/CdS,$^{[146]}$ etc., have been explored for PEC water splitting and

![Figure 9](https://www.advancedsciencenews.com/content/2000741/sol_rrl/figures/flowchart.png)

**Figure 9.** Electrochemical growth of Ag/Fe$_2$O$_3$/TiO$_2$ NTAs (top), FESEM (down) of (a,b) electrochemically fabricated TiO$_2$ NTAs and (c,d) Fe$_2$O$_3$/TiO$_2$ NTAs. Reproduced with permission.$^{[141]}$ Copyright 2018, American Chemical Society.
showed promising photocurrent densities. Ibrahim et al. successfully developed the GaON/ZnO NRAs composite by ultrasonically assisted hydrothermal mixing. The composite showed exceptional PEC water splitting performance with the photocurrent density approaching 1.2 mA cm$^{-2}$ at 1.0 V (vs RHE), and the photoanode was stable and also effectively demonstrated transient photocurrent under periodic simulated irradiations. The computational analysis through DFT revealed that the GaON/ZnO NRAs composite showed more affinity toward water molecule adsorption compared with bare GaON and ZnO, which is the main reason for enhancement of the water splitting reaction. As mentioned earlier, modulation and proper tuning of light trapping through the assemblage of 3D structures and compositional and structural alteration with semiconductors having a narrow bandgap deliver an improved PEC performance; 3D-branched ZnO NWAs impregnated with cadmium sulfide (CdS) NPs have been fabricated by wet chemical routes. Bai et al. demonstrated the fabrication of 3D-branched ZnO NWA with CdS NPs (Figure 11). Under the full solar spectrum, the 3D-branched ZnO/Cds NWAs showed an STH conversion efficiency up to 3.1%. This efficiency can be attributed to the tremendous carrier collection competence and the light-trapping ability of 3D-branched ZnO NWAs, which is further enhanced by the photocatalytic activity of CdS NPs. To enhance the stability of the photoanodes, an interfacial TiO$_2$ protective layer is filmed over its surface.

By introducing Au and FeOOH NPs cocatalysts into ZnO/CdS NAs, an excellent photocurrent density of 5.38 mA cm$^{-2}$ at 1.23 V versus RHE has been accomplished by Liu et al. The PEC performance enhancement of the Au and FeOOH cocatalysts-modified ZnO/CdS (AZCF) heterojunction photoanode could be ascribed to enhanced solar light absorption, improved charge transfer, and photoexciton separation. More specifically, this is due to the long light pathway of 1D ZnO NRs, the visible light absorption capacity of CdS due to the small bandgap, and bidirectional kinetics due to dual FeOOH and Au NPs cocatalysts. The cocatalysts promote charge separation and, hence, minimize their recombination, which enhances

Figure 10. SEM images of the ZnO-based aligned heterostructure NAs at a) low and b) high magnification for hierarchical ZnO NWs on WO$_x$ nanowhiskers, reproduced with permission. Copyright 2011, American Chemical Society; c,d) 30° tilted view of bare-ZnO NWs and CuInS$_2$ (CIS)/CdS/ZnO NWs, reproduced with permission. Copyright 2014, Royal Society of Chemistry; and e,f) tilted view of Co$_3$O$_4$-coated ZnO NW, reproduced with permission. Copyright 2008, American Chemical Society, respectively.
the PEC water splitting performance of the photocatalyst. Figure 12a provides a schematic of AZCF NRAs heterojunction formation, and Figure 12b shows the PEC water splitting mechanism.

Likewise, ZnO NTAs have also shown some promising PEC water splitting results. As in the case of the ZnO/CdS/Au NTAs heterojunction, a maximum photocurrent density of 21.53 mA cm\(^{-2}\) with 3.45% STH efficiency was observed under visible light, which is the highest reported value for such systems.\(^{143}\)

Similar to aligned TiO\(_2\)-based NAs, ZnO-based aligned NAs photocatalyst shows exceptional PEC characteristics, when
compared with other morphologies. However, it is worth mentioning that further studies are needed to engineer more aligned ZnO-based NAs morphologies to explore their improved PEC performance.

6.3. WO$_3$- and BiVO$_4$-Based Aligned NAs

WO$_3$ and BiVO$_4$ are considered to be relatively new entrants to the group of PEC catalysts. The narrow bandgap, photocorrosion stability, and potentially low cost make these materials suitable for PEC water splitting applications. Like their NPs, the WO$_3$ and BiVO$_4$ NAs are also found useful in PEC and photocatalytic applications.

Like their NPs, the WO$_3$ and BiVO$_4$ NAs are also found useful in PEC and photocatalytic applications.

Metal-supported aligned WO$_3$ NAs synthesized via porous alumina-assisted electrochemical anodization, and various aligned morphologies, have been determined. These materials exhibited improved semiconducting properties due to their aligned morphology, as indicated from previous discussion. They induce significant oxygen vacancies in WO$_3$, which are regarded as electron donors, and, thus, lead to deviation from the expected Mott–Schottky plot. This indicates the formation of suboxide, which can be critical for photocatalytic applications. In addition, the EIS measurements also showed several orders of difference for air- and vacuum-annealed WO$_3$ NAs, confirming the existence of the WO$_3$ and suboxide WO$_{2.9}$ phases, respectively, at the tops of the NRs.

Similarly, AuNPs (≈24 nm) dispersed BiVO$_4$ nanopramidal arrays (NPAs) were assembled by a simple electrostatic approach, which enhanced the photocurrent density from 0.42 mA cm$^{-2}$ (for pristine BiVO$_4$) up to 0.93 mA cm$^{-2}$ at 1.23 V (vs RHE) during the PEC water splitting reaction. In a similar way, Bi cocatalyst decorated BiVO$_4$ NAs were found useful to enhance the overall water splitting performance.

However, more researchers are using heterostructures and nanocomposites comprised of WO$_3$ and BiVO$_4$-based NAs. As an example, a facile single-step hydrothermal strategy was adopted for the fabrication of WO$_3$-BiVO$_4$ NWAs width ≤100 nm and length 200–400 nm at relatively low temperature (110 °C). The bandgap tuning was observed during heterostructure
formation, as the value shifted from 2.8 and 2.4 eV for pristine WO₃ and BiVO₄, respectively, to 2.1 eV for WO₃-BiVO₄ NWAs.¹¹⁰

Pihosh et al. used photoanodes based on vertically WO₃ NRs capped with very thin BiVO₄ layers, developed by GLAD and sputtering techniques (as mentioned earlier). The oxygen evolution Co–Pi cocatalyst was added to enhance the photocurrent density from 3.2 to 5.1 mA cm⁻² at 1.23 V (vs RHE) in Na₂SO₄. The particulate BiVO₄ thin layer provides an excellent solar absorption medium for WO₃ NRs, which plays a vital role in the effective water splitting, whereas Co–Pi is best known as an oxygen evolution catalyst (OEC).⁸² WO₃/BiVO₄ NRs core–shell was impregnated with Co–Pi to achieve a near theoretical water splitting efficiency. The NRs heterostructure photoanode exhibits the highest water splitting photocurrent of 6.72 mA cm⁻² for such systems at 1.23 V (vs RHE), equivalent to ≈90% of the theoretical value of BiVO₄, as given in Figure 14.⁸⁴

Alternatively, BiVO₄ and TiO₂ combinations have also been tried for efficient PEC water splitting. A TiO₂/BiVO₄ NRs core/shell photoanode is combined with a perovskite solar cell (CH₃NH₃PbI₃-based). This combination was found useful, as unassisted solar water splitting is observed when the

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**Figure 13.** SEM images of anodized WO₃: a) nanocapsules with partly etched tops, b,c) nanocapsules with fully opened tops, and d) open-top NTs incorporated in the alumina overlayer. Reproduced with permission.¹⁵⁵ Copyright 2016, Royal Society of Chemistry.

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**Figure 14.** PEC performance of CoPi-WO₃/BiVO₄ NA: a) % IPCE at 25°C (blue) and 50°C (red). b) I–V graph under chopped light at 1 sun, 25°C and at 3 sun, 50°C. c,d) Faradaic efficiencies (rectangles), gas production rates (circles), and theoretical gas production rates (dashed lines) of H₂ (red) and O₂ (black) for c) 1 sun, 25°C and d) 3 sun, 50°C with simultaneously recorded J–t profiles. Reproduced under the terms and conditions of the Creative Commons Attribution license 4.0.⁸⁴ Copyright 2015, The Authors, published by Springer Nature.
photocurrent density approached almost 1.3 mA cm$^{-2}$ with an STH efficiency of 1.24% under irradiation.$^{[154]}$ Similarly, TiO$_2$ NRs (as a 1D electron transport tunnel) and BiVO$_4$ (as an efficient light harvester), with Co–Pi (a cocatalyst), are pooled in TiO$_2$/BiVO$_4$/Co–Pi NRAs photoanode over FTO substrate. The PEC water splitting measurements indicated that the loading of BiVO$_4$ and CoPi affects the efficiency of the catalyst until 1.86 mA cm$^{-2}$ photocurrent at 1.0 V (vs RHE) is achieved, having a small onset potential of 0.3 V (vs RHE) and an IPCE of 26% (at 450 nm), which corresponds to $\approx$7.31 $\mu$mol cm$^{-2}$ h$^{-1}$ hydrogen gas production.$^{[147]}$ More recently, Li et al. demonstrated adequate PEC water splitting using Ta-modified BiVO$_4$/TiO$_2$ aligned nanoforests (NFs) morphology (nanoporous groves). Intense enhancement of photocurrent density was observed at the heterojunction interface. The spectroscopic and electrochemical measurements of Ta-doped TiO$_2$ indicated the proper alignment of bands and, hence, a high photocurrent density of 1.77 mA cm$^{-2}$ at 1.23 V (vs RHE) under visible light.

The remarkable features of WO$_3$, and BiVO$_4$-based NAs are worthwhile to achieve enhanced PEC performance in terms of high photocurrent density, IPCE, and STH. However, the photostability of these catalysts is a major concern and can be further improved by achieving non-compromised NAs alignments. Moreover, modifications to the mechanism of fabrication could be useful to obtain robust NAs morphology in these cases.

### 6.4. Miscellaneous Semiconductor Oxides Aligned NAs

Besides well-established TiO$_2$, ZnO, BiVO$_4$, and WO$_3$ aligned NAs, a similar morphology is also reported for other semiconductors. A few exciting examples are discussed as follows. ZrO$_2$ NTAs were developed by the ALD protocol, whereas ZrN ultrathin layers were deposited to tune the photoactivity of zirconia NTs in ZrO$_2$/ZrN NTAs photoanode for visible solar radiation-mediated PEC water splitting.$^{[156]}$ The nitridation effectively enhanced the visible light absorption capacity of the photoanodes and, hence, increased the overall PEC water splitting. The highest photocurrent density of $\approx$1.25 mA cm$^{-2}$ was achieved for the optimized composition of the ZrO$_2$/ZrN NTAs nanocomposite with excellent interfacial charge transfer. The OER is a critical step in PEC water splitting to produce hydrogen.

Iron oxide is a well-known photocatalyst for water splitting.$^{[142,155–161]}$ However, its conventional shape, morphology, and composition could lead to severe photocorrosion and charge recombination phenomena, which negatively affect the PEC water splitting process. Therefore, researchers have tried to use the NAs morphology by combining other photoactive materials to enhance their efficiency for the target application. Phosphorus-doped Fe$_2$O$_3$ NAs photoanodes were successfully used for this purpose with improved photogenerated charge separation capacity.$^{[160]}$ Gradient phosphorous incorporation upsurges the width of optical band bending in hematite NAs, which is vital for endorsing the charge separation in the doped product. The quantitative photoconversion efficiency of the grad-P:Fe$_2$O$_3$/Co–Pi photoanode is calculated to be 0.32% at 0.92 V, whereas for pristine Fe$_2$O$_3$, homo, and grad-P:Fe$_2$O$_3$ NAs, the efficiencies were in the range of 0.05, 0.09, and 0.12%, respectively, at 1.05 V (Figure 8). Furthermore, the IPCE at wavelengths extending from 350 to 650 nm in 1 m potassium hydroxide (KOH) solution is found to be the maximum for grad-P:Fe$_2$O$_3$/Co–Pi photoanodes, which suggested the effective utilization of photons by doped photoanodes as compared with other species.

Tantalum-based NAs materials have also been widely used by various researchers for PEC applications in recent times due to their distinctive photoresponse and optical tuning characteristics. Tantalum nitride (Ta$_3$N$_5$) is well known for the NRs or NWs morphology and exceptional PEC water splitting characteristics.$^{[83,115,163–167]}$ Figure 15 shows the Ta$_3$N$_5$ NAs morphologies reported by various research groups. The NA morphology is found useful in the case of Ta$_3$N$_5$, as it enhanced its PEC performance many fold as compared with traditional custom morphologies. The Domen group reported 3.8 mA cm$^{-2}$ at 1.23 V (vs RHE) for a vertically aligned Ta$_3$N$_5$ NRs photoanode, which was fabricated by through-mask anodization followed by nitridation. The IPCE activity was found to be $\approx$41% at 440 nm, which was the highest reported at that time.$^{[83]}$ This record was improved with CoPi/Co(OH)$_2$, and NiFe(OH)$_2$-coated Ta$_3$N$_5$ NRs photoanode with a photocurrent density of 6.3 mA cm$^{-2}$ at 1.23 V versus RHE due to the efficient effect of Ni–Fe–layered double cocatalysts, which not only enhanced the photocurrent density, but also affected the photostability of the photoanode positively.$^{[168]}$

Later on, a phenomenal photocurrent density was achieved for Ni(OH)$_2$/ferrhydrite (hole-storage layers), Co cubane, and Ir complex (molecular catalysts) that mediate interfacial charge transfer from Ta$_3$N$_5$, and TiO$_2$ modified (a blocking layer) hierarchical Ta$_3$N$_5$ photoanode, which reached 12.1 mA cm$^{-2}$, almost in the same range as the theoretical value, i.e., 12.9 mA cm$^{-2}$.$^{[165]}$ Although a near theoretical limit photocurrent density value has achieved, Ta$_3$N$_5$-based photoanodes encounter two critical issues, i.e., poor photostability and low photovoltage, and remain critical challenges, which need to be fixed to make their practical application possible.$^{[167]}$ Later, our group has developed interesting nanopencil-shaped tin oxide arrays and indium oxide NWs by an electroanodization process.$^{[169,170]}$ It is expected that these materials could be effective for photinduced electrochemical applications. Moreover, we also achieved the quasi-aligned GaON/ZnO NRAs by a simple sonochemical-assisted hydrothermal route, which showed remarkable water oxidation behavior compared with conventional morphologies.$^{[10,171]}$ Table 2 summarizes some well-known aligned nanostructure materials of various NAs morphologies with their reported photocurrent densities and IPCE values. It is predicted from Table 2 that morphology greatly influences the optoelectronic properties of the nanomaterials, as stated earlier.

### 7. Water Splitting Performance Comparison with Typical Morphologies

The morphology, electrode film thickness, and concentration of the photoelectrode materials considerably affect the overall water
splitting performance of the photoelectrode for HER and OER. These parameters affect the charge transfer, charge scattering, charge separation, and charge recombination properties of these materials significantly. Morphology should be given great importance, as it controls most of these characteristics. The comparison of PEC water splitting efficiency by aligned NAs and other morphology can be judged by various factors, such as % IPCE, STH, and current density. Herein, we provide this comparison in terms of the last parameter, i.e., current density. The photocurrent densities of various aligned NAs are compared with other morphologies and summarized in Table 3. Considering the example of TiO₂, the photocurrent density for the aligned nanostructure is 2.0 mA cm⁻², whereas for branched TiO₂, the value is reported at 0.85 mA cm⁻². Similarly, for ZnO aligned nanopencils, the photocurrent density is 1.3 mA cm⁻², whereas for ZnO NPs and nanocorals, the values drop to 0.142 and 0.25 mA cm⁻², respectively. In nearly all reported cases, a similar trend is observed for other nanostructures as well. As with a pristine nanostructure, the composite also exhibits higher photocurrent densities than other morphologies; e.g., RGO/ZnO NWAs possess more current density (1.55 mA cm⁻²) than oxygen-deficient ZnO/graphene NPs (0.05 μA cm⁻²). Similarly, WO₃/BiVO₄ helix NAs exhibit the highest current density among all morphologies proposed for the same composite. These observations suggest that alignment plays an important role in controlling the optoelectrical properties of the photoactive materials, as discussed earlier. The enhanced photocurrent density in the case of aligned nanostructures can be attributed to the vectorial charge transport through the long axis of the aligned NAs and the limited losses caused by electron–hole recombination and surface trapping.

8. Conclusion and Future Perspective

From the synthetic method used to electrode engineering, noteworthy efforts have been devoted to the pursuit of visible light-driven photocatalysts with aligned NAs morphologies. More attention has been devoted to the creation of more active centers on the aligned photocatalyst surfaces by modifying their textural properties. In addition, significant attention has been paid toward the determination of exact reaction mechanisms, which involve morphological transformations to achieve the desired morphology with less effort. Certain synthetic techniques, such as magnetron sputtering, sol–gel, lithography, etc., have been used for this purpose with special amendments. Significant efforts have been made in the last few years to design aligned NAs for PEC water splitting, as shown in Table 2. However, there is still a lot more to be done in this field, as the desired photocurrent density, STH, and % IPCE are still to be achieved.

The earliest estimations suggest that roughly 10 000 "solar plants" (5 km × 5 km per plant with 10% solar conversion efficiency) would be needed to provide one-third of energy needs in 2015. The total proposed area is just 1% of the total deserts and would produce ≈570 tons of H₂ per day. Such a large quantity of this gas would be effectively available for many important domestic and industrial processes. In addition to effective water splitting, the separation of product gases, i.e., H₂ and...
Table 2. Reported photocurrent densities of some important aligned NAs photoelectrodes for PEC water splitting with % IPCE.

| Materials                        | Aligned nanostructures | Characteristics                                                                 | Substrate electrolyte                        | Photocurrent density [mA cm⁻²] at 0.50 V | % IPCE | References |
|---------------------------------|------------------------|---------------------------------------------------------------------------------|---------------------------------------------|------------------------------------------|--------|------------|
| Titania NAs-based PEC materials | TiO₂ NTAs              | Increased crystallinity of the NTs walls, and reduction of grain boundaries slows down the charge carrier recombination | Anodized Ti foil 1 M KOH                   | 20 mA cm⁻² at 0.50 V                     | 10%    | [172]      |
|                                 | Heterostructured TiO₂  | Hierarchical arrayed, the rutile/anatase phase junction, large surface area, etc. | FTO 1 M NaOH (pH = 13.6)                   | 1.24 mA cm⁻² at 1.23 V                   | 77%    | [116]      |
|                                 | NR@nanobowl arrays     |                                                                                   |                                             |                                          |        |            |
|                                 | Hyperbranched TiO₂     |                                                                                   |                                             |                                          |        |            |
|                                 | TiO₂ NTs transferred on FTO |                                                                                   |                                             |                                          |        |            |
|                                 | TiO₂ NRs               |                                                                                   |                                             |                                          |        |            |
|                                 | TiO₂/CoO₂ core/shell   |                                                                                   |                                             |                                          |        |            |
|                                 | TiO₂/CoO₂ core/shell   |                                                                                   |                                             |                                          |        |            |
|                                 | Carbon layer silicon (C@Si) NWs/TiO₂ non-shell |                                                                                   |                                             |                                          |        |            |
|                                 | Hierarchical TiO₂–CIS core–shell NAs |                                                                                   |                                             |                                          |        |            |
|                                 | Ti–Pd mixed oxynitride NTAs |                                                                                   |                                             |                                          |        |            |
|                                 | Ti–Mo–Ni NTAs          |                                                                                   |                                             |                                          |        |            |
|                                 | CdS/TiO₂ B-NRAs        |                                                                                   |                                             |                                          |        |            |
| Zinc oxide NAs-based PEC materials | ZnO nanocylinder | Unique structure with an abrupt shrinkage in diameter between the tip and the pencil holder | FTO 0.5 M Na₂SO₄ (pH of 7.0)         | ≈1.3 mA cm⁻² at 1.00 V                  | 18%    | [180]      |
|                                 | ZnO NWs                |                                                                                   |                                             |                                          |        |            |
|                                 | ZnO NWs/nanodiscs (NDs) |                                                                                   |                                             |                                          |        |            |
|                                 | ZnO NWs with ultrathin titania shells |                                                                                   |                                             |                                          |        |            |
|                                 | Nitrogen-doped ZnO NRs |                                                                                   |                                             |                                          |        |            |
|                                 | Nitrogen and cobalt co-doped zinc oxide NWs |                                                                                   |                                             |                                          |        |            |
|                                 | Reduced graphene oxide (RGO)/ZnO NWAs |                                                                                   |                                             |                                          |        |            |
|                                 | ZnO–ZnGaON NWAs        |                                                                                   |                                             |                                          |        |            |
|                                 | ZnO/CdS NWAs           |                                                                                   |                                             |                                          |        |            |

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O₂ is a great challenge and will require significant efforts to develop facile technologies for this purpose. A unique reactor has already been proposed by James et al.\textsuperscript{[206]} There is significant improvement needed for such aligned array photoelectrodes; their heterostructures and nanoarchitectures such as surface passivation can be easily developed on the top surface to enhance the charge separation. Cocatalyst deposition on aligned heterostructure photoanodes can potentially improve performance, as cocatalyst can offer additional oxidation or reduction active sites, enhance the surface reaction by reducing activation energy, and suppress the recombination process. One of the important advantages of aligned nanostructures is that they can be processed on large-scale electrodes (a few inches in area) to a scale-up device, which avoids thin-film fabrication by
Table 3. The comparative water splitting performance of some aligned NAs with various morphologies.

| Materials       | 1D aligned NAs, i.e., NRAs, NWAs, and NTAs | Other morphologies, i.e., irregular shapes, nanoparticles, nanosheets, nanoflowers, etc. |
|-----------------|-------------------------------------------|----------------------------------------------------------------------------------------|
|                 | Nanostructure shape | Photocurrent | Ref. | Nanostructure shape | Photocurrent | References |
| Pristine TiO₂   | TiO₂ NTs | 2.0 mA cm⁻² at 1.23 V | [174] | TiO₂ branched | 0.85 mA cm⁻² at 0.65 V | [198] |
| Pristine ZnO   | ZnO nanopencils | 1.3 mA cm⁻² at 1.00 V | [180] | ZnO NPs | 0.142 mA cm⁻² at 1.00 V | [199] |
| RGO/ZnO        | RGO/ZnO NWAs | 1.55 mA cm⁻² at 1.00 V | [54] | Oxygen-deficient ZnO/graphene | 0.05 μA cm⁻² at 0.5 V | [201] |
| WO₃            | Hexagonal nanoflower WO₃ | 1.3 mA cm⁻² at 1.23 V | [189] | WO₃ nanoflakes | 0.88 mA cm⁻² at 1.00 V | [203] |
| WO₃/BiVO₄      | WO₃/BiVO₄ helix NAs | 5.35 mA cm⁻² at 1.23 V | [191] | WO₃/BiVO₄ nanoflakes | 0.08 mA cm⁻² at 0.33 V | [74] |
| Hematite       | Fe₂O₃ NAs | 1.56 mA cm⁻² at 1.23 V | [162] | Fe₂O₃ mesoporous | 0.56 mA cm⁻² at 1.23 V | [204] |

drop-casting screen printing, etc. These techniques develop high resistance, which is not useful for ameliorated performance in PEC water splitting. Also, in the near future, these nanostructured arrays could be used for other promising PEC reactions, such as carbon dioxide reduction, H₂O₂ reduction, and other promising solar-to-chemical reactions. Undoubtedly, a highly efficient photocatalyst with desirable characteristics is required to achieve overall water splitting in the visible range. Significant research is in progress in this regard, and we are expecting that sooner or later we will be able to achieve the desired goal of water splitting on an industrial level.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aligned nanoarrays, nanocorals, nanorods, nanowires, photo-electrochemical water splitting

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