TOPICAL REVIEW

Electrochemically anodized one-dimensional semiconductors: a fruitful platform for solar energy conversion

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Abstract

One-dimensional (1D) semiconductors have garnered considerable attention in solar energy harvesting and conversion since they possess a long axis to absorb incident light yet a short radial distance for fast separation of photogenerated charge carriers. Among the diverse 1D semiconductors, metal oxides arrays prepared by electrochemical anodization technique demonstrate unique structure merits for efficient charge separation and transfer; nevertheless, thus far, recent process on the photoelectrochemical (PEC) and photocatalytic applications of electrochemically anodized 1D semiconductors has not yet been elucidated. In this review, basic principle, classification, and developments of electrochemical anodization technique were systematically introduced. Great attention was paid to summarize the predominant 1D metal oxides arrays fabricated by anodization approach and their wide-spread photocatalytic and PEC applications. Moreover, modification strategies used for boosting the photocatalytic and PEC performances of 1D anodized metal oxides nanostructures were further comprehensively elucidated. Finally, future perspectives and challenges in triggering the future innovative ideas on fabricating a large variety of promising anodized semiconductor-based nanomaterials are envisaged. It is anticipated that our review could provide enriched information on the rational design and construction of electrochemically anodized 1D semiconductors for solar energy conversion.

1. Introduction

The world is currently facing an urgent energy crisis owing to the continuously increasing demand for sustainable energy source and depletion of natural fossil fuels [1]. Solar energy harvesting and conversion have been considered as one of the most promising ways to satisfy the ever-growing demand for human beings as the energy from the sun is abundant and clean without exerting detrimental influence on the environment [2]. In particular, photo-electrochemical (PEC) water splitting with the assistance of solar light for hydrogen production has been deemed as a rather promising route to ameliorate the increasing energy crisis since the pioneer work launched by Honda and Fujishima in 1972, who judiciously harnessed TiO₂ powder electrode to achieve water splitting under UV light irradiation [3, 4]. Thereafter, semiconductor-based photocatalysis and photoelectrocatalysis, which allow direct conversion of solar energy to chemical energy via a renewable route, have been deemed as the most viable long-term solution to address the environmental and energy issues [5]. In recent years, one-dimensional (1D) semiconductors-based photocatalysts or photoelectrodes have been gaining tremendous attention by virtue of their unique structural advantages compared with bulk counterparts, including fast and long-distance charge transport, large specific surface area and pore volume, as well as enhanced light absorption and scattering properties [6]. More significantly, charge transfer efficiency of 1D semiconductors can be markedly improved along the vectorial direction, which substantially boosts the separation of photogenerated electron–hole pairs.
Up to date, various synthetic strategies have been developed to prepare 1D semiconductors such as direct hydrothermal method \[7\], sol–gel method \[8\], or template method \[9\]. Among which, of particular note is electrochemical anodization approach which has been well-established to be an efficacious technique to fabricate spatially periodically ordered nanostructures consisting of highly ordered 1D semiconductors arrays \[10\]. Especially, 1D semiconductor nanomaterials prepared by electrochemical anodization are featured by smooth surface in conjunction with regularly aligned nano-architectures growing perpendicularly from the foil, which is beneficial for efficient charge separation and transfer. More intriguingly, carrier diffusion length on the anodized 1D semiconductors is much shorter than that on the bulk counterparts, which considerably minimizes the energy loss caused by the electron transition among nanoparticles (NPs). Alternatively, size of the 1D semiconductors (e.g. nanotubes) can be precisely controlled by tuning the anodization parameters such as applied voltage, anodization time, ingredient percentage in electrolyte (e.g. ammonium fluoride, water) \[11–13\]. Although various 1D semiconductors have been successfully fabricated by anodization method in the past few years, predominant attention is focused on the conventional TiO2 nanotube arrays (TNTAs) and investigations on other electrochemically anodized 1D semiconductors as photocatalysts or photoanodes are still far from satisfactory. Therefore, we believe it is the right time to comprehensively and systematically sum up the latest developments of quintessential electrochemically anodized 1D semiconductors besides the typical TNTAs along with their wide-spread applications in the fields of photocatalysis and photoelectrocatalysis. Furthermore, there are still lack of review articles that specifically introduce the electrochemical anodization technique for fabricating a collection of 1D semiconductors (e.g. Fe2O3, Ta2O5, WO3, ZrO2, etc), which is of paramount importance for those who engage in these booming research fields.

In this review article, latest research progress on electrochemical anodization technique for constructing spatially hierarchically ordered 1D semiconductors arrays was rationally summarized. Moreover, photocatalytic and PEC applications of these periodically ordered anodized 1D semiconductors including photocatalytic environmental remediation, photocatalytic water splitting, photocatalytic CO2 reduction, PEC water splitting and PEC CO2 reduction were specifically elucidated and summarized. Finally, future outlooks and perspectives in this booming research field were envisaged. It is anticipated that our review article could provide enriched information on the fabrication and utilization of various electrochemically anodized 1D semiconductors for solar energy harvesting and conversion.

2. History of electrochemical anodization technique

Anodization is an electrochemical oxidation method to increase the thickness of metal (e.g. Al, Ti, Fe, W, Zr, Nb, etc) or semiconductor (e.g. Si, GaAs, etc) surface oxide layer \[14\]. As shown in figure 1, anodization technique was first presented in the preparation of alumina. In general, anodic oxidation of aluminum can produce two different types of oxide depending on the property of the electrolyte used. That is, normally, neutral electrolyte produces tight and non-porous barrier oxides while porous oxides can be produced in an acidic electrolyte \[15\]. In the past decade, porous metal oxide layers made by anodization in an acidic electrolyte endows periodically ordered 1D semiconductors with well-defined architecture, tunable thickness, and good corrosion resistance. Consequently, currently, preparation of porous materials via electrochemical anodization approach has still been attracting enormous attention, especially in fabricating highly ordered nanoporous materials.

In 1991, Zwilling and co-workers \[16\] firstly reported the anodic oxidation of titanium (Ti) in fluorinated electrolyte under ambient conditions, by which spatially highly ordered titanium dioxide (TiO2) film with porous surface was fabricated. Since then, articles concerning 1D semiconductor materials are emerging in an
endless stream. For instance, Gong et al [17] reported the construction of uniform TNTAs with a thickness of ca. 0.5 \( \mu \)m in a hydrofluoric acid (HF) electrolyte by anodization method. In 2005, Cai and co-authors prepared TNTAs with a vertical length of 6.4 \( \mu \)m using a fluoro-containing solution by changing the pH and electrolyte concentration [18]. In the next following years, length of TNTAs can reach up to ca. 1000 \( \mu \)m by using an anhydrous polar organic electrolyte such as formamide, dimethyl sulfoxide, ethylene glycol or diethylene glycol [19–23]. In recent years, fabrication of TNTAs in fluorne-free electrolytes has been achieved, which makes precise control over the shape, length, pore size and wall thickness of nanotubes accessible [18, 24, 25]. Apparently, composition and category of electrolyte plays crucial roles in determining the morphology and size of the anodized nanotube arrays.

Inspired by the fabrication of well-defined periodically ordered Al2O3 and TiO2 nanotube arrays, anodic oxidation techniques were further extended to prepare a large variety of other 1D semiconductor arrays. For instance, transition metal foils including Fe [26, 27], Ni [28], Cu [29], Zn [30–33], Zr [34], Nb [35], Hf [36], Ta [37, 38], W [39], etc have been utilized as the metal precursors to prepare corresponding anodized metal oxides such as Fe2O3, NiO, Cu2O, and ZnO nanotube arrays. Moreover, some hybrid metal nanotube arrays can also be fabricated by using the metal alloy foils, e.g. TiAl [40], TiNb [41], or Ti6Al4V [42], most of which are featured by highly ordered nanostuctures and remarkably enhanced photocatalytic and PEC performances. Despite the developments of anodization technique in the past one decade, category of transition metal oxides prepared by anodization is still relatively limited compared with conventional alumina and titania nanotube arrays, which suggests future development of electrochemical anodization is fraught with infinite possibilities.

3. Electrochemical anodization mechanism and influencing factors

3.1. Anodization mechanism

Figure 2 exhibits the typical anodization device for fabricating self-aligned highly ordered 1D semiconductor nanotube arrays. Specifically, metal foil is directly connected to the positive electrode of DC power source as working electrode and conducting mediums such as platinum, graphite or metal is used as counter electrode. In this way, a thin metal oxides layer can be produced by a simple electrochemical oxidation of metal foil under ambient conditions. Generally, electrochemical anodization mechanism dictating the formation of self-aligned metal oxide arrays can be mainly divided into five stages including: (1) metal electropolishing, (2) formation of compact anodic metal oxides, (3) generation of self-ordered metal oxides (nanotubes or nanopores), (4) production of disordered oxide nanotubes, (5) organization of ordered nanoporous layers [43].

By taking TNTAs as a quintessential example, electrochemical anodization process can be generally divided into four steps: (1) At the beginning of anodization, metal Ti4+ interacts with O2− or OH− in the electrolyte to form an initial oxide layer on the surface under an electric field, during which these anions continuously migrate through the oxide layer to the metal/oxide interface and react with the metal at the interface [44]. (2) Subsequently, Ti4+ anions rapidly migrate from the metal/oxide interface to the oxide/electrolyte interface under an applied external electric field. (3) Afterwards, Ti–O bonds are weakened under the auxiliary electric field to promote the dissolution of the metal ions at the oxide/electrolyte interface, thereby causing dissolution
of Ti$^{4+}$ to the electrolyte solution and promoting reaction with the free O$^{2-}$ [45–47]. (4) Finally, when chemical dissolution rate of metal oxide is in equilibrium with the anodization rate, thickness of the oxide film no longer increases. It should be emphasized that interaction between surface Ti$^{4+}$ ions and O$^{2-}$ in the electrolyte solution dictates the formation of initial oxide layer at the beginning of anodization [48], which can be expressed as follows:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^{-} + 4\text{H}^{+},$$

$$\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2.$$  \hfill (1)  \hfill (2)

Besides, noteworthy, field-assisted dissolution dominates the chemical dissolution in the initial stage of anodization due to relatively large electric field on the thin oxide layer [47]. Local dissolution of the oxide yields small dimples on the surface and they serve as the center of the hole, after which these pits become larger and are evenly distributed on the metal surface. The local chemical dissolution equation of the oxide can be expressed as follows:

$$\text{TiO}_2 + 6\text{F}^{-} + 4\text{H}^{+} \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}.$$  \hfill (3)

On the other hand, it is worth mentioning that the presence of F$^{-}$ ions in the chemical dissolution of metal oxides under acidic electrolytes plays a crucial role in forming nanotube rather than nanopore structures [49].

### 3.2. Influencing factors of anodization process

Anodization as an electrochemical film growth technique has been attracting tremendous interest over the past few decades owing to its cleanliness and easy availability. In particular, growth of self-ordered metal oxide films involves transport of matter and charge between different phases such as metal, oxide and anodizing medium. Hence, as displayed in figure 3, anodization parameters exert profound impact on the structure of anodized metal oxide layers.

#### 3.2.1. Anodization voltage

As reflected by the electrochemical anodization mechanism, formation of TNTAs in essence is a result of electrochemical equilibrium between oxidation of Ti to TiO$_2$ and dissolution of TiO$_2$ in fluorine-containing electrolytes [30]. The oxidation voltage is an important factor in the electrochemical anodization process. For example, Cai and co-workers [18] fabricated TNTAs within the voltage profile of 10–30 V in a KF electrolyte and the authors revealed that nanotube diameter increases from 40 to 110 nm with boosting the applied anodizing voltage. In another work, Grime’s group [17] prepared well-aligned TNTAs in a HF electrolyte at an anodic oxidation voltage of 10–40 V and the pore size of nanotube increases from 25 to 65 nm with increasing the voltage. However, there is an anodizing voltage window for specific electrolyte and this voltage window depends heavily on the chemical and physical properties of the electrolyte as well as pH. Thus, anodization voltage is closely associated with the pore size of nanotube. Normally, pore size of anodized nanotube is proportional to applied voltage within the appropriate voltage range.

#### 3.2.2. pH value

It has been evidenced that pH value of electrolyte exerts important influence on the structure of anodized nanotubes. Generally, acidic condition is essential for nanotube formation and electrolyte with lower pH results in nanotube with length of a few hundred nanometers, while higher pH produces longer nanotubes. For
instance, Cai and co-workers [18] prepared TNTAs with pore size of a few hundred nanometers using electrolyte with pH of 1–2 and the length of the nanotubes can increase to 4.4 μm by increasing the pH to 5.6. Apparently, pH value of electrolyte directly affects the chemical corrosion process of the nanotubes. More specifically, hydrolysis extent aggravates with the increase of pH value, which substantially reduces the chemical dissolution rate, thus resulting in long nanotubes in the electrolyte with higher pH value to maintain the acidity. Consistently, as demonstrated by Mor’s group, pH profile within 3–5 is beneficial for the formation of relatively long nanotubes, while lower pH facilitates the formation of shorter ones [49].

3.2.3. Water content

It has been well-established that water content in the electrolyte is critical to the dissolution of oxides during the electrochemical anodization process and an appropriate reduction in water content can increase the length of nanotubes [51]. In a typical example, Sun and colleagues [32] systematically explored the effect of water content on the length of TNTAs in an ethylene glycol (EG) electrolyte containing NH₄F. According to their results, average length of anodized TNTAs prepared using 1 vol% water in EG was ca. 7.3 μm and tube length reaches to ca. 10.6 μm when the water content increases to 2 vol%. However, tube length of TNTAs decreases remarkably upon further increasing the water content. For example, average nanotube length of TNTAs can be reduced to ca. 2.2 μm by using electrolyte containing 10 vol% water. This is mainly ascribed to the fact that diffusion of H⁺ and F⁻ is suppressed when an organic electrolyte containing low water content is used during the anodization, thus retarding the formation of ordered nanotubes. On the contrary, diffusion of H⁺ and F⁻ is accelerated and concentration of H⁺ increases upon utilizing the electrolyte containing high water content, by which chemical dissolution rate is faster than the field-assisted oxidation rate, resulting in decrease in the length of nanotubes.

3.2.4. Electrolyte temperature

Influence of electrolyte temperature on the structure of nanotubes is mainly reflected by the wall thickness of nanotubes. For example, Grime’s group [51] evidenced that TNTAs prepared using the same electrolyte (10 V, 0.5% HF and acetic acid with a ratio of 1:7) but with different temperature (5 °C, 25 °C, 35 °C and 50 °C) demonstrate almost the same pore size (ca. 22 nm), suggesting electrolyte temperature exerts negligible influence on the pore size of TNTAs. However, the authors unveiled that wall thickness of TNTAs increases from 9 to 34 nm as electrolyte temperature decreases from 50 °C to 5 °C, disclosing the correlation of electrolyte temperature with the structure of anodized TNTAs. On the other hand, it should be noted that effect of electrolyte temperature on the structure of anodized nanotubes is different for aqueous and non-aqueous electrolytes. For instance, Wang et al. [53] verified electrolyte temperature exert no influence on the structure of TNTAs in aqueous electrolytes, while electrolyte temperature significantly affects the size of TNTAs in non-aqueous electrolytes.

3.2.5. Anodization time

The effect of anodization time on the morphology of anodized metal oxides depends on the type of electrolyte medium. For instance, utilizing glycerol as a medium modifier in NH₄F-containing electrolyte with small water content, nanotube openings change aligned along the grooves for short anodization time, whereas nanotube appears in the form of bundles after long-time anodization with a higher exposure of the more deeper areas of the film [17].

4. Categories of anodized 1D semiconductors

4.1. α-Fe₂O₃

Hematite (α-Fe₂O₃) possesses a bandgap of ca. 2.1 eV and can absorb substantial visible light with wavelength approaching to ca. 600 nm, which accounts for 40% of solar spectrum [54]. Furthermore, note that flat band potential of hematite is more positive than the hydrogen reduction potential (0 V versus NHE) and hence it cannot be used for photocatalytic hydrogen production but rather oxygen production in terms of its more positive valence band (VB) than the oxygen production potential (1.23 V versus NHE) [55]. There have been many ways to prepare Fe₂O₃ nanostructures including ultrasonic spray pyrolysis [56], template-involving method [57], chemical vapor deposition [58], atomic layer deposition [59], sol–gel deposition [60], and electrochemical anodization [26]. Among which, electrochemical anodization has been attracting the most tremendous attention since its morphology and size can be precisely controlled by the anodization parameters.

For typical example, Grime’s group first reported the preparation of self-organized nanoporous Fe₂O₃ by potentiostatic anodization of Fe foil utilizing two-electrode system [26], in which Fe foil was utilized as anode and platinum foil as counter electrode in the presence of a mixed electrolyte consisting of 1% HF + 0.5% ammonium fluoride (NH₄F) + 0.2% 0.1 M nitric acid (HNO₃) in glycerol (pH = 3). In this way, self-aligned
Fe$_2$O$_3$ nanotubes with pore diameter of 50–250 nm and length of 300–600 nm can be fabricated depending on the anodization conditions, such as anodization voltage, electrolyte temperature/composition and anodization time. Zhang’s group found that Fe$_2$O$_3$ of different nanostructures can be fabricated by anodizing Fe foil in electrolyte containing different water content [27]. As shown in figures 4 (a)–(e), α-Fe$_2$O$_3$ with different structures can be prepared in EG electrolyte (0.3% NH$_4$F) with water content ranging from 0% to 4%. Contrarily, anodization of Fe foil in EG electrolyte without water shows a flat surface, whereas morphologies of α-Fe$_2$O$_3$ change to NPs, nanorods, nanoporous and nanoleaflet structures with water content increasing to 1%, 2%, 3%, and 4%, respectively. Moreover, the authors unraveled that α-Fe$_2$O$_3$ nanotube exhibits enhanced photoactivities in degrading azo dyes and photocatalytic water splitting in comparison with nanoporous α-Fe$_2$O$_3$ counterpart under visible light irradiation [61, 62]. Alternatively, Grime’s group prepared highly ordered Fe$_2$O$_3$ nanotubes over a potential profile of 30–60 V in EG electrolyte (0.2–0.5 wt% NH$_4$F, 2%–4% DI H$_2$O 45 °C–75 °C) [63]. It is unveiled by the authors that nanotube formation is strongly dependent on the anodization bath temperature and fluoride concentration. This is understandable since growth rate of the nanotubes increases at a high temperature which is essential for increment of F$^-$ ion concentration to obtain nanotube. Besides the water bath temperature and the fluoride ion concentration, other anodization conditions such as anodization voltage, water content and thermal treatment temperature all strongly affect the structure of Fe$_2$O$_3$. Consistently, Xie and co-workers investigated the influence of anodization parameters on the structure of anodized Fe$_2$O$_3$ [64] and their results indicate that highly quality Fe$_2$O$_3$ nanotube arrays can be fabricated under the optimized anodization conditions.

Figure 4. FESEM images of anodized α-Fe$_2$O$_3$ in EG with water percentage of (a) 0, (b) 1, (c) 2, and (d) 3, and (e) 4% along with corresponding (f) EDS pattern. (Reprinted with the permission from [27]. Copyright 2010, Elsevier).
4.2. ZrO\textsubscript{2}

Zirconium dioxide (ZrO\textsubscript{2}) as a typical transition metal oxide has been widely applied as thermal catalysts and photocatalysts \cite{66,67}. Recently, many research works are focused on the preparation of nanosized ZrO\textsubscript{2} nanomaterials using various methods such as templating techniques \cite{68} and atomic layer deposition \cite{69}. However, morphologies of the ZrO\textsubscript{2} are mainly confined to NPs or nanoporous structures with their size and shape hard to be finely control. However, electrochemical anodization provides an effective way to fabricate highly ordered ZrO\textsubscript{2} nanostructures with size finely controlled by electrolyte composition. For example, Tsuchiya and co-authors \cite{70} fabricated self-organized sponge-like porous ZrO\textsubscript{2} layer by electrochemical anodization in an electrolyte containing NH\textsubscript{4}F and H\textsubscript{2}SO\textsubscript{4}, which is the first report on the preparation of controllable self-organized porous ZrO\textsubscript{2} nanotube arrays by anodization. More intriguingly, highly self-aligned ZrO\textsubscript{2} nanotubes with a diameter of ca. 50 nm and length of ca. 17 μm corresponding to an aspect ratio of more than 300 can be fabricated by adding (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} buffer solution in the electrolyte \cite{34}, which is distinct from the methods used for preparing other anodized metal oxides. In another case, Guo et al \cite{71} reported the preparation of nanoporous WO\textsubscript{3} with an average pore diameter of 100 nm were prepared by utilizing NaF as the electrolyte \cite{39}. Moreover, it was revealed that nanoporous WO\textsubscript{3} demonstrates much enhanced incident photon conversion efficiency than the compact counterpart (figure 6). As shown in figure 5, anodized ZrO\textsubscript{2} NTs were prepared by Xue’s group \cite{65} in glycerol-based electrolyte (glycerol, NH\textsubscript{4}F, H\textsubscript{2}O) at 80 V for 1 h, resulting in ZrO\textsubscript{2} NTs with outer and inner layers. Intriguingly, it was found that double-walled ZrO\textsubscript{2} NTs demonstrate enhanced photoactivity in comparison with single-walled ZrO\textsubscript{2} NTs toward organic dye degradation.

4.3. WO\textsubscript{3}

Tungsten oxide (WO\textsubscript{3}) has been deemed as an important sector of semiconductor with relatively small bandgap of ca. 2.4–2.8 eV, which has wide-spread photocatalytic and PEC applications \cite{74}. Nanoporous WO\textsubscript{3} was first prepared by galvanostatic anodization in a 0.25 M oxalic acid electrolyte, but its structure is not uniform and regular \cite{75}. In the following work, self-organized nanoporous WO\textsubscript{3} with an average pore diameter of 100 nm were prepared by utilizing NaF as the electrolyte \cite{39}. Moreover, it was revealed that nanoporous WO\textsubscript{3} demonstrates much enhanced incident photon conversion efficiency than the compact counterpart (figure 6(a)). Consistently, as displayed in figures 6(b), (c), Li and co-authors \cite{73} corroborate the nanotube array-like WO\textsubscript{3}/W photoanode (NAs-WO\textsubscript{3}/W) exhibits substantially improved photocurrent of in comparison with standard WO\textsubscript{3} under visible light irradiation (λ > 420 nm). Figure 6(d) shows that NAs-WO\textsubscript{3}/W exhibits the
smallest semi-circle arc radius compared with standard WO_3 implying the most efficient charge transfer efficiency in the interfacial region of a photoelectrode-electrolyte. The results imply that unique nanoporous/nanotube structure of WO_3 is beneficial for boosting the charge separation and transfer in PEC water splitting.

Besides the pure anodized WO_3, hybrid WO_3–TiO_2 nanotube arrays have also been prepared by anodization approach. For typical example, Nah and co-authors first reported the construction of WO_3–TiO_2 structures by electrochemical anodization [76]. Compared with pure TiO_2 nanotubes, composite WO_3–TiO_2 nanotubes shows greatly significantly enhanced PEC water splitting performances, unraveling the cooperativity of WO_3 and TiO_2 arising from their suitable band alignment and intimate interfacial integration. Although nanoporous WO_3 have been prepared and extensively utilized for PEC applications, WO_3 electrodes are still lack of cycling photostability [77]. Therefore, synthesis of robust self-organized and highly ordered WO_3 nanotube arrays is highly desirable for maximizing solar energy conversion [78].

4.4. Ta_2O_5

Tantalum oxide (Ta_2O_5) has been attracting increasing interest as photocatalysts or photoelectrodes. In a typical example, Allam and co-authors [81] first synthesized vertically oriented Ta_2O_5 NTs via anodization in an aqueous electrolyte containing HF, H_2SO_4, and low-concentration EG. They found that self-standing, robust nanotubes can be prepared under the optimized conditions in an electrolyte containing HF and H_2SO_4 (1:9) along with dimethyl sulfoxide (DMSO, 5%). Additionally, the authors revealed that morphology of Ta_2O_5 film depends heavily on the applied potential and electrolyte composition. In another similar work, Momeni and co-authors [82] demonstrated the fabrication of a high surface-volume Ta_2O_5 NTs with an external diameter of ca. 55 nm and a thickness of ca. 2 μm in an electrolyte containing H_2SO_4 and fluoride ion. Alternatively, freestanding Ta_2O_5 NTs can be prepared by adjusting the electrolyte temperature during the anodization in an electrolyte containing H_2SO_4, H_2O, and HF [79]. The results indicated that when electrolyte temperature decreases during the anodization in a sulfuric acid solution, adherence of Ta_2O_5 nanotubes to the Ta substrate increases. On the other hand, it should be emphasized that thermal treatment of the freestanding Ta_2O_5 NTs below 750 °C (figure 7(a)) results in an amorphous structure which exhibits low photoactivity, whereas annealed at 800 °C (figure 7(b)), orthorhombic crystalline of Ta_2O_5 NTs show the optimal photoactivity for hydrogen generation under UV radiation. This is mainly ascribed to the high crystallinity and low surface contamination of the freestanding Ta_2O_5 NTs. Despite anodized Ta_2O_5 nanostructures exhibit desirable photoactivities, its
wide bandgap (ca. 3.8–4.0 eV) substantially limits its light-harvesting capability in the visible region [83]. To solve this problem, more recently, as demonstrated by Su and co-workers [80], vertically aligned Ta3N5 NTs with a length of ca. 7.7 μm was prepared by annealing Ta2O5 NTs in a NH3 atmosphere. Moreover, it was significant to unveil that thus-obtained Ta3N5 NTs demonstrate markedly increased PEC water splitting performances after decoration of co-pi co-catalyst by electrodeposition under visible light irradiation (figure 7(d)).

4.5. Nb2O5
Niobium has been widely explored for fabricating fiber optics, catalytic and biocompatible materials [86]. Especially, porous niobium oxide (Nb2O5) has intriguing potential applications as gas sensors [87], catalysts [88] and electrochromic devices [89]. Self-organized porous Nb2O5 NTs was first fabricated by Schmuki’s group by anodization in a mixed H2SO4/HF electrolyte [35]. Although formation of thicker layers is easily hampered by dissolution process (figure 8(a)), dissolution of the formed oxide can be retarded by adding appropriate amount of H3PO4 (figure 8(b)) [84]. With a view to further controlling the chemical dissolution of the formed metal oxide in fluorinated electrolytes, Kim’s group [85] synthesized self-ordered nanoporous Nb2O5 NTs with double layers by anodization-annealing-anodization method. As displayed in figures 8(c), (d), first anodization was carried out in H3PO4 (1 wt%, 1 M) at 2.5 V for 1 h. After annealing (150 °C) and second anodization, double-layered nanostructure with a thickness of more than 500 nm was formed. In this way, outside oxide layer can efficiently protect the inside oxide from chemical dissolution in fluorinated electrolyte. Recently, Kang’s group successfully prepared anodized Nb2O5 NTs in an anhydrous glycerol electrolyte containing 10 wt% K2HPO4 at 10 V for 10 min [90], by which nanostructure of oxide layer was carefully modulated to be discorded or branched in low or high applied potential.

4.6. HfO2
It is well-known that hafnium oxide possesses promising applications as coating materials and gas sensors [92, 93]. Notably, anodized nanoporous HfO2 nanostructures remarkably broaden the applications of hafnium oxide. Tsuchiya and co-workers first fabricated the self-organized nanoporous HfO2 via anodization in an electrolyte containing 1 M H2SO4 + 0.2 wt% NaF at room temperature [36]. They revealed that morphologies and structures of porous HfO2 layers were strongly depended on the applied potential. Afterward, Schmuki’s group optimized the synthesis conditions to obtain the robust self-ordered nanoporous HfO2 in glycerol electrolyte (0.35 M NH4F, 1 vol% of H2O, 60 V) [94]. Interestingly, such-anodized nanoporous HfO2 can be
transformed into HfO$_2$ nanotubes by altering the water content in the electrolyte. In another work, Mozalev and co-worker prepared self-organized HfO$_2$ films with nanostructured 3D architectures and variable dimension ($10$–$400$ nm) by anodizing the thin Al/Hf metal layers in phosphoric, malonic, and oxalic acid electrolytes (figure 9) \cite{91}. It is worth pointing out that this nanostructured 3D morphology, graded chemical composition, crystallization, and phase transition behavior of the films are expected to significantly improve charge transport in photocatalysis.

4.7. ZnO
Zinc oxide (ZnO), as a direct bandgap semiconducting material with wide bandgap (3.37 eV) and large excitation binding energy (60 meV), has been widely investigated for photocatalytic applications \cite{96}. Physicochemical properties of ZnO are strongly dependent on its structures. Thus far, various ZnO nanostructures such as NPs, nanofilm and nanotube have been prepared by multifarious methods including chemical vapor deposition \cite{97}, sol–gel method and electrochemical approaches \cite{98, 99}. However, there are few reports on the fabrication of nanostructured ZnO by anodization due to rich defect chemistry of ZnO and its very easy dissolution in acidic or basic mediums \cite{100}. Nevertheless, preparation of ZnO nanowires in NaOH and HF solutions by anodic oxidation was reported in many literatures in the past few decades \cite{101}. For example, highly oriented ZnO nanoneedle arrays were prepared by anodization of Zn foil in zincate saturated aqueous solution at room temperature \cite{102}. Besides, as reported by Basu and co-authors, nanoporous ZnO thin films can also be prepared by electrochemical anodization in oxalic acid with different concentration at a constant potential of 10 V \cite{103}. They claimed that crystal and pore size of nanoporous ZnO film can be controlled by oxalic acid concentration during the anodization particularly in the presence of UV light. As aforementioned before that field-assisted dissolution and electric field driven oxidation are synchronized during the anodization progress and the etching speed was accelerated by UV light. In another work, as reported by Choi’s group, ZnO nanowires can be prepared by anodization in electrolytes containing fluoride ions \cite{100}, in which H$^+$ ions mainly contribute to the dissolution process at a low potential and neutral (NH$_4$F) condition and it is beneficial for decreasing the corrosion process. Alternatively, ultra-long ZnO nanowire arrays were fabricated by anodizing Zn foil in KHCO$_3$ aqueous solution (5–50 mM) within a voltage profile of 10–20 V, by which ZnO nanowires with length reaching to 100 $\mu$m can be prepared \cite{104}. Similarly, Mattia and co-worker...
systematically investigated the correlation of morphology with the photoactivities of anodized ZnO nanowires. Furthermore, as displayed in figure 10, microscale arrangement (light absorbance capacity) and nanoscale structure (crystal size and orientation) of the anodized ZnO nanowires can be finely tuned by anodization. Although preparation of ZnO nanowires, nanofilms and nanowires by anodization have been achieved, fabrication of highly ordered nanoporous or nanotubes nanostructure is still seldom reported due to the instability of ZnO in acid or alkali conditions and under high voltage. Therefore, it is still a challenge to explore the appropriate experimental conditions for anodization technique to prepare spatially highly ordered ZnO nanostructures.

4.8. CuO
Copper oxide (CuO), as an important p-type metal-oxide semiconductor with narrow bandgap of ca. 1.2–2 eV, has been wide-spread employed as photocatalysts or photoelectrodes owing to its strong redox capability, abundance and non-toxicity [106]. Preparation of CuO nanostructures by anodization is a facile and low-cost method and, more importantly, it guarantees precise control of surface roughness and nanostructures [107]. Wu and co-workers [108] first developed an electrochemical anodization method without involving any template and additive to synthesize 1D CuO nanostructures on the surfaces of copper foil in KOH aqueous solution under constant current density of 1.5 mA cm⁻². The thus-obtained Cu(OH)₂ nanoneedles after anodization can be converted to nanotubes by appropriately increasing the temperature and KOH concentration of. More specifically, Cu(OH)₂ nanoneedles were annealed in a N₂ atmosphere to promote the crystallization resulting in 1D CuO nanostructures. In the following works, researchers investigated the influence of anodization
parameters on the growth of CuO nanostructures. For instance, Li and co-authors [109] probed the effect of annealing atmosphere on the growth of CuO nanowires and their results suggest that CuO nanowires are produced exclusively in the N2 atmosphere. Wang et al [29] studied the influence of preparation parameters on the growth of CuO films, for which no CuO nanowires were formed when voltage was too high or too low. This is ascribed to the fact that low voltage is not enough to trigger the following reaction: Cu → Cu^{2+} + 2e^{-}; on the contrary, too high voltage increases the tendency toward intermediate precipitation.

Up to date, besides the 1D CuO nanostructures, CuO of varying nanostructures have also been created. For instance, Luo et al, fabricated a novel graphene-like CuO nanofilms on the copper foam by an in situ anodization [105]. The synthetic experiment was performed in an electrochemical cell using copper foam as the working electrode and Pt sheet as counter electrode. 3 M KOH aqueous solution containing 0.07 M cetyltrimethylammonium bromide (CTAB) was selected as the electrolyte which was deaerated by a dry N2 stream. Subsequently, a constant current density of 1 mA cm^{-2} was applied to the copper foam for 20 min to prepared pale-blue Cu(OH)2 films which were dehydrated (150 °C) and annealed (200 °C) under argon flow to obtain CuO nanofilms (figure 11). Significantly, as shown in figure 11(d), as such CuO nanofilms supported on the copper foam can be employed as freestanding, binder-free photocatalyst for degradation of organic dye pollutant.

4.8.1. Cu2O/CuO
Cu2O, as a quintessential p-type semiconductor, has been attracted enormous attention. It is worthwhile to note that both reduction (Cu2O to Cu) and oxidation (Cu2O to CuO) can be achieved simultaneously in anodized Cu2O/CuO nanocomposite for playing their cooperativity [110]. For example, as shown in figure 12, Cu2O–CuO composite thin film can be prepared by an integrated anodization-thermal treatment method, in which mixed solution consisting of EG, potassium hydroxide (0.75 wt%), deionized water (3.0 wt%) and
sodium fluoride (0.20–0.35 wt%) was utilized as the electrolyte, Cu foil as working electrode, and platinum plate as counter electrode. Note that CuO nanowire protective layer was fabricated by annealing the anodized Cu2O foil at different temperature ranging from 250 °C to 450 °C giving rise to Cu2O–CuO composite film. Moreover, it was significant to unravel that the CuO nanowire protective layer capped on the outer layer of Cu2O–CuO composite thin film is beneficial for decreasing the photocorrosion of Cu2O and thus improving PEC stability of Cu2O photoelectrode by passivating its redox activities (figure 12(d)). In general, pure Cu2O can be prepared at low anodization voltage as shown in reaction (4). At a higher applied voltage, reaction (5) occurs and both the reactions take place simultaneously under moderate conditions

\[
\begin{align*}
\text{Cu} - e^- & \rightarrow \text{Cu}^+ , \\
2\text{Cu}^+ + 2\text{OH}^- & \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}, \\
\text{Cu} - 2e^- & \rightarrow \text{Cu}^{2+} , \\
\text{Cu}^{2+} + 2\text{OH}^- & \rightarrow \text{CuO} + \text{H}_2\text{O} .
\end{align*}
\]

(4)

(5)

In another typical work, He and co-workers [111] demonstrated the fabrication of leaf-like CuO–Cu2O nanostructure on the copper foam by anodization and it exhibits 3D connect and quasi-connect structure, which provides abundant redox active sites,shortens ion diffusion pathway and improves the electrolyte penetrating efficiency. Another merit of anodization in fabricating Cu-based nanostructures is that heterogeneous oxide growth on the same substrate can be efficiently achieved by changing the appropriate oxidation conditions rather than introducing other reagents, which is difficult to achieve by other methods.

4.9. NiO

Similar to Cu2O, Nickel oxide (NiO) is among the forefront p-type oxide semiconductor, which is particularly attractive for photocatalytic applications owing to its environmentally benign nature and low cost [113]. However, NiO films could not be prepared by conventional anodization method because dissolution rate of NiO in acidic and fluoride-containing electrolytes was much faster than the growth rate of NiO itself [112]. To solve this problem, Teoh et al [112] demonstrated an efficacious alkaline anodization approach to synthesize NiO film, in which mixed solution containing potassium hydroxide (KOH, 0.5 wt%), 5 wt% deionized water and glycerol (94.5 wt%) was utilized as the electrolyte in a two-electrode electrochemical cell at 60 V potential. As manifested in figures 13(a)–(c), such-anodized NiO films are characteristic of highly macroporous structure due to rapid dissolution of oxide layer during the anodization process. Significantly, these NiO films demonstrate extremely stable photocurrent during PEC water splitting lasting to 20 h in comparison with commercial NiO counterpart (figure 13). Noteworthily, alkaline anodization approach provides an alternative method for conventional anodized materials that are incompatible with conventional acidic and fluoride electrolytes.
Similarly, Wang et al [114] first demonstrated electrochemical construction of Ni-based films by anodization of Ni foil in fluorine acid electrolyte which consists of NH$_4$F (0.5 wt%) and H$_3$PO$_4$ (85 wt%) at constant potential (3.5 V, 5 min) followed by annealing in air (400 °C, 20 min). Compared with state-of-the-art Ni-based catalysts, anodized NiO outperforms most of Ni-based catalysts.

As described above, a large variety of 1D transition metal oxides prepared by electrochemical anodization technique have been specifically elucidated. For clarifying the booming developments in this field, figure 14 summarizes the developments of 1D semiconductors for photocatalysis and photoelectrocatalysis over the past five years, from which it is apparent that representative materials are mainly concentrated on TiO$_2$, ZnO, WO$_3$ and Fe$_2$O$_3$. However, note that predominant materials such as wide-band-gap TiO$_2$ and ZnO are inexpensive and stable but they cannot harvest light in the visible region. Moreover, although narrow-band-gap semiconductors such as CuO can take full advantage of visible light, they suffer from unfavorable instability and high cost. On the other hand, charge recombination is another critical factor that limits the solar energy conversion efficiency of photocatalysts and photoelectrodes. In this regard, development of inexpensive, stable and highly efficient photocatalysts/photoelectrodes with favorable bandgap is of paramount importance to the commercialization of photocatalysis for substantial solar energy conversion in the near future.

5. Strategies for modifying anodized 1D semiconductors

5.1. Transition metal element doping

1D semiconductor nanostructures that are highly ordered and vertically oriented have been considered to be ideal candidates for photocatalytic applications such as photocatalytic water splitting to produce H$_2$ and mineralization of organic pollutants due to their unique structural merits including high specific surface area and short charge transport length along the vertical direction [43]. Nonetheless, developments of 1D
semiconductors prepared by anodizing metal foil/or foam have been retarded owing to relatively large bandgap ($E_g$) of semiconductors, which remarkably limits its light absorption range especially in the visible spectrum region. To solve this dilemma, it is highly desirable to extend the light response range of anodized metal oxide arrays, which is of paramount importance to boost the photocatalytic and PEC performances of anodized 1D nanomaterials. To this end, various strategies have been explored to reinforce the light absorption capability of anodized 1D semiconductors and simultaneously, to prolong the lifetime of photogenerated electron–hole charge carriers. Among which, transition metal element doping has been established as an efficacious route to mediate the electronic structures of anodized 1D semiconductors for narrowing the bandgap energy.

Additional energy level would form within the band gap of anodized metal oxides arrays when metal ions were incorporated into the semiconductor lattice, which may greatly influence the photogenerated charge carriers transfer [116]. Conclusively, substantially improved photocatalytic performances can be achieved owing to the metal ions doping to facilitate charge carrier transport, for which reduction energy level of the doped

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**Figure 13.** Top-view FESEM images of nanoporous NiO anodized at 60 V for (a) 0.5, (b) 2, (c) 12 h, (d) amperometric photocurrents response of different NiO electrodes under simulated solar light (300 W) irradiation at a bias of $-0.25$ V versus RHE. (Reproduced with permission from [112]. Copyright 2014, American Chemical Society.)

**Figure 14.** Overview of the number of papers published on (a) 'M$_x$O$_y$ and photocat' and (b) 'M$_x$O$_y$ and photoelectrocatalysis' (M = transition metal) as a function of years, as searched in Web of Science on 25 January 2019.
metal ions should be lower than the conduction band (CB) of the semiconductor and the oxidation energy level of the doped metal ions should be less positive than the VB of the semiconductor. With respect to the construction of metal ions-doped 1D semiconductors, it is essential to develop efficacious approach to introduce metal ions into the lattice of 1D semiconductors without changing vertically oriented architecture. For instance, Ni-doped TNTAs can be prepared by anodizing Ti–Ni alloys in combination with annealing treatment \[117\]. In another work, W-doped Ta2O5 NTs were fabricated by anodizing TaW alloys with different tungsten content in conjunction with a suitable high-temperature ammonia treatment. It was significant to unravel that W doping can decrease the bandgap of Ta3N5 from 2 down to 1.75 eV and markedly enhance the PEC water splitting performance of Ta3N5NTs \[115\]. Alternatively, in situ doping of alkali metal (Li+, Na+, K+, Rb+, and Cs+) in Nb2O5 was also demonstrated by modified anodization of Nb foil at high frequency and negative-to-positive pulsed voltage, for which the optimally doped Nb2O5 NTs show twofold enhancement in PEC water splitting efficiencies compared with undoped counterpart, owing to improved charge separation and transfer \[118\].

5.2. Non-metal element doping
Another efficient way to extend the photoresponse of anodized 1D semiconductors is non-metal element doping, most of which are mainly centered on carbon \[120\], nitrogen \[121\], sulfur \[122\], and phosphorus doping \[123\], which result in remarkably enhanced visible-light-driven photocatalytic performances. For example, tungsten trioxide (WO3) prepared by anodization of W foil was doped with N via NH4OH treatment at high temperature \(450^\circ\)C \[124\]. Incorporation of N into WO3 reduces the bandgap from 2.9 to 2.2 eV, thereby lowering the onset potential and increasing the photocurrent density at fixed potential for oxygen evolution reaction under visible light illumination. In another work, N-Doped Ta oxide NTs were fabricated by anodization of Ta foil in an aqueous H2SO4 + HF solution forming Ta oxide NTs, followed by high-temperature transformation of Ta oxide to TaOxNy in an ammonia atmosphere \[125\]. The N-doped TaOxNy NTs have been demonstrated to be the most efficient photocatalyst under visible light irradiation among various non-metal-element-doped photocatalysts, which is mainly ascribed to the fact that p states of nitrogen places just above the VB maximum of most metal oxides, thereby contributing to the bandgap narrowing without substantial increase of charge recombination \[116\]. Alternatively, sulfur doping has also been evidenced to facilitate similar bandgap narrowing; nonetheless, it is worth noting that ionic radius of sulfur was too large to be easily introduced into the lattice of anodized metal oxides. For example, an Ar/H2 plasma-assisted S doping

**Figure 15.** Cross-sectional FESEM images of (a) pure tantalum and (b) 0.5% W alloyed Ta2O5 NTs with top-view FESEM images in the insets. (c) PEC results of co-catalyst loaded undoped and W-doped Ta3N5 NTs with corresponding photographs in the insets. (d) LSV (2 mV s\(^{-1}\)) results of pure tantalum, 0.5%W and 5% W alloyed Ta3N5 NTs under chopped simulated solar light irradiation (AM 1.5 G) in 1 M KOH aqueous solution \(\text{pH} = 13.7\). (Reproduced with permission from \[115\]. Copyright 2015, Elsevier.)
strategy was developed to modify rutile TiO$_2$ (R–TiO$_2$–S), by which an ultrathin amorphous surface layer (ca. 3 nm) was induced and it considerably improved the light absorption capability of TiO$_2$ (figure 16) [119].

5.3. Nobel metal deposition
Modification of anodized 1D semiconductors with noble metal NPs has been established to be an efficient approach to significantly enhance the photocatalytic and PEC performances of anodized metal oxide NTs [127, 128]. Deposition of metal NPs on the metal oxide NTs is beneficial for retarding the recombination of photoexcited electron–hole pairs, in which metal NPs can serve as ‘electron reservoirs’ to capture photoelectrons, which allows efficient electron transfer from the CB of semiconductor (TiO$_2$) to metal NPs, giving rise to prolonged lifetime of charge carriers [116]. For example, coupling TiO$_2$ with metal NPs is able to facilitate the Fermi level of metal/TiO$_2$ lower than the CB of TiO$_2$, which allows efficient electron transfer from the CB of TiO$_2$ to metal NPs [129, 130]. Meantime, formation of Schottky barrier between TiO$_2$ and metal NPs blocks the back-transfer of electrons, resulting in efficient separation of charge carriers. In another typical work, as shown in figure 17, a facile and green layer-by-layer (LBL) assembly strategy was developed by us to fabricate highly ordered metal/TNTA heterostructures, i.e. M/TNTAs (M = Au, Ag, Pt) heterostructures based on pronounced electrostatic interaction [131]. It was found that these metal (Au, Ag, Pt) NPs can serve as electron traps to boost separation of photoinduced electrons and holes leading to markedly enhanced photoactivities. Apart from LBL assembly approach, other synthetic strategy was developed to achieve decoration of Au NPs on the anodized tungsten–oxide (Au/WO$_x$) nanostructures [132].

Besides, plasmon-induced solar energy conversion was also proposed as a promising route to improve the photoactivities of anodized 1D semiconductors [133, 134]. There are some reports on the plasmonic effect of metal NPs in the field of photocatalysis. For example, Ag/α-Fe$_2$O$_3$/TiO$_2$ NTs heterostructures were fabricated by an electrochemical anodization method assisted by pulse sonication [135]. In such a ternary heterostructure, a new SPR-induced photocatalytic mechanism was presented for the remarkably enhanced photoactivity of Ag/α-Fe$_2$O$_3$/TiO$_2$ NTs, in which Ag ingredient imparts its plasmonic and electron-donating properties owing to the unique plasmonic effect, followed by transfer of photoelectrons from Ag NPs to the CB of α-Fe$_2$O$_3$/TiO$_2$, thereby resulting in pronouncedly enhanced photoactivities of ternary nanostructure.

Figure 16. HRTEM images of (a) R–TiO$_2$ and (b) R–TiO$_2$–S with corresponding elemental mapping results (c)–(c)$_3$. (d) UV–vis absorption spectra of different TiO$_2$ samples. (Reproduced with permission from [119]. John Wiley & Sons. ©2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
5.4. Construction of p–n heterojunctions

A central challenge still remains in reducing the quick recombination rate of photogenerated electron–hole pairs over anodized metal oxides. Although structural modulation of metal oxides to nanotubular structure may open a convenient avenue to improve the photocatalytic efficiency, it in essence cannot tackle the central issue of photocatalysis [137]. Therefore, considerable endeavors have been devoted to reinforcing the photoactivities of anodized metal oxides by constructing p–n heterojunctions. As performed by Teng’s group [136], n-type Ta$_3$N$_5$ and p-type Co ion were combined to construct build-in electric field in the interfacial region of p–n heterojunction (figure 18(a)), which benefits separation of charge carriers by accelerating the poor surface catalytic dynamics. More specifically, Ta$_3$N$_5$ were fabricated by anodization of Ta foil and then annealed in a NH$_3$ atmosphere producing Ta$_3$N$_5$ film with n-type conductivity. Furthermore, loading Co ions during and after anodization produces a Ta$_3$N$_5$–Co film consisting of p- and n-type Ta$_3$N$_5$ domains. Significantly, Ta$_3$N$_5$–Co photoanode exhibited considerable improved PEC water splitting performance under simulated solar light irradiation compared with bare Ta$_3$N$_5$, which is attributed to the synergistic interaction between p-type Co ions and n-type Ta$_3$N$_5$ that is beneficial for solar harvesting, charge separation, hence resulting in remarkably improved photocathode activities (figures 18(c), (d)).

6. Photocatalytic and PEC applications of anodized 1D semiconductors

6.1. Environmental remediation

Non-selective photocatalysis has been extensively explored owing to its great significance to environmental remediation [139], by which contaminants are completely mineralized to less toxic inorganic compounds, such as water, carbon dioxide, and salts. Spatially ordered anodized 1D metal oxides can serve as efficient photocatalysts in non-selective degradation of organic pollutants for environmental amelioration on account of their superior electron mobility, high adsorption capacity and large specific surface area [138, 140, 141]. For example, as demonstrated by Zheng’s group [138], CuWO$_4$@Cu$_2$O film was prepared on the copper mesh by a one-step anodization method. Moreover, it was disclosed that anodized CuWO$_4$@Cu$_2$O composite thin film demonstrated remarkably enhanced photocatalytic performance toward degradation of organic dye pollutant under visible light irradiation (figure 19). The underlying reason accounting for the substantially enhanced photoactivity of CuWO$_4$@Cu$_2$O nanocomposites is attributed to the suitable type II band alignment between CuWO$_4$ and Cu$_2$O, thus boosting the separation of charge carriers and light-harvesting efficiency [142].
Figure 18. (a) HRTEM image, (b) UV–vis absorption spectra, (c) LSV results (10 mV s\(^{-1}\)), (d) Electrochemical EIS results of Ta\(_2\)N\(_5\) and Ta\(_2\)N\(_5\):Co films under simulated solar light irradiation (AM 1.5 G, 100 mW cm\(^{-2}\)). (Reproduced with permission from [136]. Copyright 2014, The Royal Society of Chemistry.)

Figure 19. (a)–(d) FESEM image of anodized CuWO\(_4\)@Cu\(_2\)O film on the copper mesh with corresponding photograph and cauliflower model in the insets of (a) and (d). (e) Photoactivities of different samples under visible light irradiation along with the (f) change of UV–absorption spectra during the photodegradation of MB over CuWO\(_4\)@Cu\(_2\)O film. (Reprinted with the permission from [138]. Copyright 2017, Elsevier.)
6.2. Hydrogen production
With the increasing concern over the global energy crisis, solar-driven photocatalysis utilizing 1D semiconductors to generate clean chemical fuels such as photocatalytic hydrogen production has been deemed as a promising route to meet the increasing worldwide demands for clean energy [116]. Some typical works on photocatalytic hydrogen production over anodized 1D semiconductors have been extensively reported [143–145]. For instance, hierarchical anodized Ta2O5 NTs functionalized with NiO NPs (NiO/Ta2O5 NTs) was prepared by Teixeira’s group [143]. It was significant to reveal that NiO/Ta2O5 NTs nanocomposite exhibited much more enhanced H2 production rate (figure 20) in comparison with pure Ta2O5 NTs under the same conditions, which results from the synergetic effect of improved separation of electron–hole pairs, increased catalytic active sites and enhanced light absorption afforded by NiO NPs as well as unique hierarchical structure.

6.3. CO2 photoreduction
Solar-energy-driven conversion of CO2 to hydrocarbon fuels can generate chemical fuels to meet increasing energy demand and reduce CO2 emission for mitigating greenhouse effect. Thus far, diverse 1D nanostructures have been fabricated for photoreduction of CO2 to chemical fuels [147–149]. Among which, PEC CO2 reduction technique has been regarded as an efficient and promising route to harness solar energy since it is economically feasible and environmentally benign. Among diverse semiconductors, spatially ordered 1D nanostructures are especially suitable for PEC CO2 reduction on account of their unique structural merits [148, 150–152]. For instance, Song and co-workers fabricated Si photoelectrode with nanoporous Au mesh as co-catalyst by electrochemical anodization for highly selective and efficient PEC CO2 reduction under simulated solar light irradiation [146]. In this work, the authors evidenced that such anodized Si photoelectrode exhibited highly efficient selective CO2 reduction performance to CO in aqueous solution. Figure 21(a) shows the PEC current density–potential (j–V) curves of Si photoelectrodes with and without reduced anodic (RA) treatment in CO2 saturated 0.2 M KHCO3 under simulated solar light irradiation, from which it is apparent that Si photoelectrodes with nanoporous Au mesh exhibit a saturation photocurrent density of ca. −10 mA cm−2 far
surpassing bare Si photoelectrode. Comparison of Faradaic efficiency (FE) for CO production (figure 21(b)) among different samples highlights the superior PEC CO2 reduction performance of RA-treated Au mesh structured Si photoelectrode. Specifically, most of the photocurrent is consumed for H2 generation at potential above −0.10 V and CO FE gradually increases to 41% at −0.44 V for untreated Si photoelectrode with Au mesh. In contrast, treated Si photoelectrode with Au mesh dramatically improves the selectivity of CO with FE of 77% at −0.10 V.

6.4. PEC water splitting

With increasing concern over global energy crisis caused by the massive use of conventional fossil fuels, artificial photosynthesis aiming to produce valuable chemical fuels based on solar energy has been attracting enormous attention in the past few decades. Particularly, PEC water splitting has been deemed as a ‘Holy Grail’ of modern science [5, 154]. Aligned porosity, good crystallinity, and oriented nature of nanotube or nanoporous structure make anodized 1D semiconductors ideal candidates for PEC water splitting [153, 155, 156]. For instance, more recently, as displayed in figure 22, hierarchical Fe2O3 nanostructures with multidimensional nano/micro-architectures were constructed by electrochemical anodization of Fe foams (AFF) were directly used as photoanodes for PEC water splitting [153]. The results indicated that thus-anodized AFF shows substantially enhanced PEC water splitting performances reaching to substantially high photocurrent density of 2.29 mA cm⁻² (1.23 V versus RHE) along with favorable FE under simulated solar light irradiation (AM 1.5 G).

7. Outlooks and perspectives

In summary, in this review article, we have systematically summarized the recent progress on electrochemically anodized 1D semiconductors except conventional TiO2 NTs for multifunctional photocatalytic and PEC applications. In the first part, definition, classification, and developments of electrochemical anodization technique were comprehensively elucidated and rationally summarized. Subsequently, principle of the electrochemical anodization technique together with the predominant influencing factors that dictate the
structure of anodized metal oxides arrays were concisely introduced. In the following section, great attention was paid to summarizing the various mainstream categories of anodized metal oxides arrays which were utilized for multifarious photocatalytic and PEC applications. Furthermore, modification strategies frequently utilized to improve the photocatalytic and PEC performances of anodized metal oxides arrays were further presented with a view to boost light absorption of anodized metal oxides and reinforce the separation of photoinduced charge carriers.

Despite the impressive advancement made in the past few years, there are still some challenges that can put forward the development of electrochemical anodization technique. Firstly, although some theoretical models have been presented in previous works, comprehensive elucidation on the fundamental principle of anodization process at the nanoscale level is still far from satisfactory and the intrinsic relationship between structure/photoactivity and anodizing conditions have not yet been clearly clarified. We believe more instructive information on the anodization technique especially the specific anodization dynamics would be uncovered with booming developments of sophisticated analytical tools such as in situ synchrotron, in situ TEM, Raman and XPS. Secondly, although various metal (e.g. Ti, Fe, W, Ta, Zr, Hf, Cu, etc) foils have been utilized as anodizing substrates for fabricating self-aligned metal oxides arrays in previous works, there is still a wide range of scope to explore new types of anodic materials. For example, more alloyed metal foils can be fabricated by sophisticated production process in the near future and this would remarkably enrich the types of anodized metal oxides [157]. Finally, it should be noted that applications of anodized 1D semiconductors currently being investigated are predominantly confined to conventional photocatalytic reactions such as photocatalytic degradation of various organic pollutants and photocatalytic hydrogen generation. Thus far, directly utilizing anodized 1D metal oxides for plasmonic photocatalysis, PEC CO2 reduction, photocatalytic or PEC ammonia reduction and photocatalytic overall water splitting has not yet been reported and they are closely associated with future development direction of photocatalysis and photoelectrocatalysis in the next decade.

We strongly envisage that new category of anodized metal oxides will definitely bring more degree of freedom for rationally designing diverse high-efficiency photocatalysts or photoelectrodes. Consequently, electrochemical anodization technique represents the future direction for developments of sustainable technologies and energy resources, which is of paramount importance for achieving substantial solar energy conversion.

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