REVIEW

Template-directed construction of nanostructure arrays for highly-efficient energy storage and conversion

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Abstract
To ensure the future highly efficient utilization of various sustainable and renewable energy sources, nanostructured electrodes have become more and more important. This review provides a comprehensive summary of recent research progress in template-directed synthesis of nanostructured arrays for highly-efficient energy storage and conversion. We especially focus on nanostructure arrays based on porous anodic aluminum oxide (AAO) template and colloidal crystal template (CCT), because they possess numerous structural advantages resulting from the highly-ordered and highly-oriented structural features of AAO and CCT, such as nanoscale structural tunability, high regularity and predefined spatial orientation/alignment. All these advantages make AAO and CCT template-directed nanostructure arrays as attractive candidates for highly-efficient energy storage and conversion. This review starts with a brief introduction on template-directed construction of nanostructure arrays, including the fabrication and structural features of both the templates (AAO and CCT) and the corresponding as-achieved nanostructure arrays. Then, the advantages, the progress and the challenges of AAO and CCT template-directed nanostructure arrays for the construction of highly-efficient electrochemical energy storage and solar energy conversion devices are summarized, respectively, followed by present status and the prospects for future research.

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Introduction

The development of highly-efficient energy storage and conversion systems is critical for addressing the crucial problems of climate change, limited availability of fossil fuels and environmental pollutions, and it also plays a key role in efficient utilization of sustainable and renewable energy (such as solar and wind energy). Currently, the research about energy storage and conversion is mainly focused on electrochemical energy storage devices (especially, supercapacitors and batteries) and solar energy conversion devices (mainly, photovoltaics and solar water splitting cells). Aiming at pursuing improved efficiency for these energy storage and conversion devices, many efforts have been devoted to the applications of nanostructured materials because of their unusual physical and chemical properties endowed by the nanoscale dimensions [1-11]. It is well accepted that nanostructures with high structural regularity and tunability are desirable for constructing energy devices with optimized performance. Moreover, realizing large-scale arrays of self-standing nanostructures with well spatial orientation and arrangement is another key point to further improve the performance of energy devices. Particularly, the spatial orientation/arrangement of arrayed nanostructures and the corresponding interactions between the neighboring nano-units have large influences on the overall device performance [12]. It is well known that spatially oriented nanostructures with well alignment will not only decrease the barriers of ion transport in electrochemical energy storage devices [12-15], but also improve light absorption resulting from anti-reflection, photonic crystal effect, surface plasmon resonance, etc. in solar energy conversion devices [4]. Over the last decade, numerous examples have sufficiently evidenced the advantages of large-scale well-aligned nanostructure arrays applied for energy-related devices [4-10].

Template-directed construction just offers a convenient and versatile approach to produce nanostructure arrays with the above-mentioned distinguished advantages for energy-related device applications (Figure 1) [16-18]. First, template-directed method could be used to produce nanostructure arrays of many materials in large scale because of its easiness and maneuverability, which is important for practical applications of nanostructures in energy devices. Second, template-directed nanostructure arrays have controllable morphological features in nanoscale dimensions, including shape, size, inter-space, etc. The flexible structural controllability is highly beneficial for the performance optimization of energy-related devices. Third, the spatial orientation and arrangement of template-directed nanostructure arrays is predefined according to the spatial structure of fixed template, and such structure can be retained to form a self-standing array on a substrate even after the template removal. The self-standing nanostructure arrays with certain spatial orientation and alignment are promising building blocks for energy storage and conversion [4,12-15]. By tuning the spatial orientation and alignment of these nanostructure arrays, the performance of energy devices can be further improved. Fourth, template-directed approach is an efficient way to fabricate
nanostructure arrays with high regularity. Specifically, highly-ordered nanostructure arrays can be easily achieved on the basis of some highly-ordered templates (such as porous anodic aluminum oxide template, colloidal crystal template, etc.), which provide opportunities for some exotic optical properties including anti-reflection, photonic bandgaps, surface plasmon resonance and so on. Just because of these advantages described above, template-directed method has great potentials for constructing arrayed nanostructures towards highly-efficient energy storage and conversion, mainly including supercapacitors, batteries, photovoltaic devices and solar water splitting devices as shown in Figure 1.

To date, some literatures have summarized template-directed synthesis of nanostructured materials and their applications. However, with the rapid development of fabrication technology and device integration, a systematic review regarding the progress of template-directed nanostructure arrays for energy storage and conversion is significant but still lacking. In this review, we will summarize the recent progress of template-directed method for constructing nanostructure arrays towards highly-efficient energy-related device applications, mainly for electrochemical energy storage (supercapacitors, batteries) and solar energy conversion (photovoltaic devices and solar water splitting cells). This review will begin with a brief introduction on template-directed construction of nanostructure arrays, including the template types, the applied techniques and the achieved nanostructure arrays. Herein, we especially focus on two kinds of most widely-used templates, porous anodic aluminum oxide (AAO) template and colloidal crystal template (CCT), to illuminate the advantages of template-directed nanostructures with controllable morphology feature, high structural regularity and predefined spatial orientation/arrangement. Thereafter, the superiorities, the progress and the challenges of AAO and CCT template-directed nanostructure arrays for highly-efficient electrochemical energy storage and solar energy conversion applications will be present in details, followed by present status and prospects for future research direction in this field.

Template-directed construction of nanostructure arrays

Generally, template-directed construction of nanostructure arrays includes the following steps: preparing template; physically or chemically synthesizing nanostructures by utilizing template; and removing template (if necessary) [18]. In principle, any substance with nanoscale features, including natural and artificial nanostructured materials, can be used as template for construction of nanostructures. And theoretically, nearly all types of materials (e.g., metals, semiconductors and polymers) could be constructed into nanostructures through template-directed strategies by applying different techniques, such as electrochemical deposition (ECD), atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), sol-gel process, and reactive ion etching (RIE) process, etc. The great advantage of template-directed synthesis strategy is the achievement of nanostructure arrays in large scale with well-defined shape, precisely-controlled size and predefined spatial orientation/arrangement, which are all guided by the template. The size and shape can be effectively tuned by simply changing the nature of the template because of the topologic transformation. Moreover, the spatial orientation and arrangement of the as-obtained nanostructure arrays is predefined by the spatial structure of template, and it could be maintained on a substrate even without the support of template. By taking advantages of the highly-ordered and highly-oriented structural features stemming from self-organization process, both AAO and CCT have been extensively investigated for several decades as nanostructuring templates to fabricate highly-ordered and highly-oriented nanostructure arrays [18-24]. Therefore, we choose AAO and CCT as examples to illuminate the distinct advantages of template-directed nanostructures with controllable morphology features and predefined spatial orientation/arrangement for energy storage and conversion.

Porous anodic aluminum oxide template

Porous AAO has already been used as a template for fabricating nanostructures since Masuda et al. developed a two-step anodization process to fabricate porous AAO with highly ordered pore structure [25]. Porous AAO has a self-ordered, honeycomb-like and highly-oriented pore structure with tunable pore diameter, pore density, pore length and interpore distance, which is obtained by anodizing aluminum foil under proper conditions (potential, acid and temperature) [20,24-25]. The pore diameter and pore density of porous AAO can be finely tuned in a wide range by changing anodization conditions (potential and acid) and further wet-chemical pore-widening process: pore diameter=10–400 nm and pore density=10^8–10^10 pores cm^-2. Determined by the anodization time, the pore length could be greatly tuned from several tens of nanometers to several tens of micrometers and even thicker. Due to the regular and tunable structure features, porous AAOs have been intensively investigated as templates for synthesizing ordered nanostructure arrays of metals [26-28], semiconductors [29-31], carbon [17,32-34], polymers [35,36] and organic materials [37-39] mainly in the forms of zero-dimensional (0D) nanoparticle or one-dimensional (1D) nanowire/nanotube. Besides, three-dimensional (3D) nanopore arrays of metals and polymers have also been fabricated based on AAO template by using a
two-step replication process, which such 3D nanopore arrays have exactly the same structure with AAO template [25,40-43]. As shown in Figure 2, there are basically four kinds of nanostructure arrays that can be fabricated by utilizing porous AAO as a template: (i) nanoparticle, (ii) nanowire, (iii) nanotube, and (iv) nanopore. Based on these four kinds of nanostructures, complicated and hybrid nanostructure arrays like multi-components, core-shell or multi-segmented nanoparticle, nanowire, nanotube or nanopore arrays have been conveniently realized with AAO template by optimizing the parameters of the nanostructures fabricating process [44-46]. All these nanostructure arrays guided by AAO template also possess controllable structural parameters, highly-ordered array structure and highly-oriented structure configuration.

As known, porous AAO fabricating through self-organization process has a poly-domain structure, where the pore arrangement is in short-range order but in long-range disorder. Therefore, the template-directed nanostructure arrays based on self-ordered AAO also have a poly-domain structure configuration. Then, perfectly-ordered AAO templates with uniform pore size and long-range ordered pore arrangement are emerged. Masuda et al. first reported the fabrication of perfectly-ordered AAO by anodizing the surface pre-patternning aluminum foil [47]. After that, perfectly-ordered AAO with triangular, rectangular and hexagonal pore arrangement has been achieved and the techniques for the fabrication of perfectly-ordered AAO have been well developed in recent years [48-50]. Different from self-ordered AAO, the pore arrangement and the inter pore distance of perfectly-ordered AAO only depend on the initial surface patterns on Al foil generated by nano-imprinting process. But like self-ordered AAOS, the pore diameter and length could be further widely tuned by changing the wet-chemical pore widening time and the anodization time, respectively. Therefore, by utilizing perfectly-ordered AAO as the template, highly-oriented and perfectly-ordered nanostructure arrays (nanoparticle, nanowire, nanotube, and nanopillar, etc.) have been synthesized and have exhibited great potentials for different device applications [24,51].

Ultra-thin alumina membrane (UTAM), referring to AAO with the thickness from several tens to several hundreds of nanometers, is one kind of the surface nanopatterning templates [20]. Depending on the connection type with substrate, the UTAMs are divided into two types: attached UTAM and connected UTAM. For attached UTAM, the UTAM is electrostatically attached onto flat substrate through a polymer-assisted transferring process. For connected UTAM, the UTAM is directly fabricated onto the substrate through anodizing a thin aluminum layer pre-deposited on the substrate. Both attached UTAM and connected UTAM have been utilized as templates for fabricating ordered nanostructure arrays on substrate. Attached UTAMs are usually used as shadow mask of either deposition or etching process for the fabrication of well-ordered nanoparticle, nanorod, and nanohole arrays, respectively, on almost any smooth substrate [52-55]. The size and shape of these nanostructure arrays can be well engineered by tuning the pore diameter and length of attached UTAM as well as the conditions of fabrication process [20,56-59]. Moreover, the obtained nanoparticle arrays can not only be directly applied for functional device applications, e.g., memory devices, surface enhanced Raman scattering (SERS) and surface plasmon resonance (SPR) applications [57,58], but also act as catalyst of CVD, vapor-liquid-solid (VLS) and etching process for creating nanowire or nanopillar arrays on the substrate [60,61]. In the case of connected UTAM, it is usually used to directly grow free-standing nanorod arrays of metals and semiconductors on ITO-glass and other conducting substrates for different device applications [62-64].

Colloidal crystal template

Colloidal spheres (typically, polystyrene spheres, PS) with uniform diameter ranging from several micrometers to several tens of nanometers can self-assemble into 2D and 3D ordered arrays under appropriate conditions. Both the 2D and 3D colloidal sphere ordered arrays have been widely utilized as colloidal crystal template (CCT) to fabricate highly-ordered and highly-oriented nanostructure arrays [19,23,65-67]. The 2D CCTs are a monolayer of monodispersed colloidal spheres arranged as a hexagonal close-packed or non-close packed pattern on substrate. It is usually used as surface nanopatterning template for fabricating different surface nanopatterns on the substrate, such as nanodot, nanocrescent, nanoring, nanocolumn, nanobowl, etc., and these surface patterns can be directly used for different applications, e.g., SERS, SPR, photocatalyst and thermochromic applications [65,68-74]. The size and shape of as-obtained surface patterns mainly depend on the diameter of colloidal sphere, as well as the fabrication technique. By pretreatment of the 2D CCTs with thermal annealing or plasma etching, the diameter and inter-space of 2D CCTs could be finely tuned, resulting in widely tunable size and shape of the following obtained surface nanopatterns. Furthermore, like the surface nanopatterns prepared by UTAM technique, these surface nanopatterns could also be utilized as catalyst for synthesizing 1D nanostructure arrays though etching process or CVD method [66]. Additionally, there also have some reports about the direct fabrication of nanowire arrays with 2D CCTs as template [73-75]. Compared with 2D CCTs, the 3D CCTs are more attractive for the construction of 3D nanostructure arrays towards device applications, especially for energy devices. The 3D CCTs are multilayer colloidal spheres packed into predominantly face-centered cubic (fcc) arrays on the substrate. It has been intensively investigated owing to their practical applications as colloidal photonic crystals or as templates for fabricating 3D ordered macroporous (3DOM) structures (shell inverse opal and volume inverse opal, as shown in Figure 2). The 3DOM structures are of great interest for numerous applications, both for the unique optical properties related to their photonic crystal structures (especially for photovoltaic energy conversion devices) and for their bicontinuous nanostructures (especially for electrochemical energy storage devices), i.e., a continuous nanostructured skeleton with large interfacial area and a three-dimensionally interconnected pore system with low tortuosity [67]. More details about CCTs for the fabrication of different nanostructures can refer to several recent reviews [65-67].

Template-directed nanostructure arrays for energy storage

Electrochemical energy storage system is one of the most dominant energy storage systems, mainly consisting of...
supercapacitor and battery (especially lithium-ion batteries). In supercapacitor and battery, the energy storage process includes: (i) ion transport in electrolyte and electrode, (ii) electrochemical reactions in electrode, and (iii) electron transport between electrode and current collector. As well known, the performance of electrochemical energy storage devices is largely affected by the transport of electrons and ions [1,12-13]. Due to the convenience and versatility of template-directed method and the promising structural features of template-directed nanostructure arrays, template-directed method has been widely used for the construction of nanostructure arrays for electrochemical energy storage. Especially, AAO and CCT template-directed nanostructure arrays have well-tunable structural features, large surface area and predefined orientation/alignment, and thus are highly expected in achieving high performance. In details, the AAO and CCT template-directed nanostructure arrays not only provide large and accessible electrode/electrolyte interface and shorter electronic transport path leading to a higher power performance under fast charge/discharge rate [1,76,77], but also and more importantly, the spatially oriented and aligned structure facilitates fast ion diffusion and easy electrolyte access to electrode surface. In this section, we will introduce nanostructure arrays prepared based on AAO and CCT templates for highly-efficient electrochemical energy storage devices. We will give detailed overview about the advantages and the challenges of AAO and CCT template-directed nanostructure arrays in the respect of highly-efficient electrochemical energy storage. To better understand these topics, all potential candidates of template-directed nanostructure arrays are classified according to the structural features.

1D nanostructure arrays based on AAO template

The 1D nanostructure (i.e. nanowire and nanotube) arrays are typical architectures obtained from AAO template. They possess attractive structural features for electrochemical energy storage: well-defined 1D morphology, highly-oriented and aligned array structure, high density, controllable size and interspace, etc. Herein, AAO template-directed nanowire arrays are taken as an example to illuminate the advantages in supercapacitors and batteries. As shown in Figure 3a, when nanowire arrays of active materials are grown on conductive substrate (served as current collectors in supercapacitors and batteries) with AAO as the template, each individual nanowire not only serves as the active materials with large surface area to contribute to the capacitance/capacity but also provides straight pathway for electron transport, which will benefit to the enhancement of the specific capacitance/capacity and the rate capability [78-81]. Moreover, since each individual nanowire directly connects to the current collectors, there is no need for extra binders or conductive additives to construct devices. Meanwhile, the interspace of neighboring nanowires could facilitate the electrolyte penetration during fast charge-discharge process, which will help to improve the rate capability. Especially for lithium-ion batteries, the interwire space of neighboring nanowires could accommodate the volume expansion during the insertion and removal of lithium ions (Li\(^{+}\)) resulting in improving cycle life [79].

Owing to the strong versatility of AAO template-directed method, many kinds of electrode materials are fabricated as nanowire or nanotube arrays for electrochemical energy storage through different technique (Figure 3b-e), such as manganese dioxide (MnO\(_2\)) nanowire and nanotube arrays by sol-gel process or ECD (Figure 3b and c) [82,83], polyaniline (PANI) nanowire arrays by ECD [84], cobalt oxide (CoO\(_x\)) nanotube arrays by ECD [85], vanadium oxide (V\(_2\)O\(_5\)) nanotube arrays by ALD [86], nickel-tin (Ni~Sn) nanowire arrays by co-electrochemical deposition [87,88], nickel oxide (NiO) nanotube arrays by ECD and further annealing process [89], nickel hydroxide (Ni(OH)\(_2\)) by ECD [90], and carbon nanotube and nanofiber arrays by CVD or carbonization (Figure 3e) [91,92], etc. This universal methodology provides abundant material basis as developing highly efficient electrodes for electrochemical energy storage. MnO\(_2\) is considered as one of the most promising electrode materials for supercapacitors due to its high theoretical capacitance (1370 F g\(^{-1}\)), low-cost and environmental benignity [93,94]. The MnO\(_2\) nanowire (Figure 3b) and nanotube arrays (Figure 3c) based on AAO-directed method have been realized as electrodes for supercapacitors and exhibits much better supercapacitor performance than that of MnO\(_2\) film or MnO\(_2\) nanostructures in powdery form [82,83,95]. However, the theoretical capacitance of MnO\(_2\) has rarely been achieved mainly due to its poor electrical conductivity (10\(^{-5}\)–10\(^{-6}\) S cm\(^{-1}\)), which is the bottleneck for its high-power applications in electrochemical energy storage [83,96]. Not only MnO\(_2\), the other transition metal oxides for electrochemical energy storage have the similar difficulties. To improve the electrical conductivity and to realize high specific capacitance for electrochemical energy storage, considerable efforts have been made on the fabrication of hybrid nanostructures based on the development of fabrication methodology. MnO\(_2\) has been combined with highly conductive materials such as carbon nanomaterials, metal nanostructures and conductive polymers [97-99]. Liu and co-workers have synthesized MnO\(_2\)/poly(3,4-ethylenedioxythiophene) (PEDOT) coaxial nanowire arrays through a one-step co-electrochemical deposition process using AAO template (Figure 4) [100,101]. The MnO\(_2\) core is utilized for its high energy density, while the PEDOT shell is applied for its high conductivity (Figure 4b). Although such hybrid structure has improved specific capacitance and rate capability comparing with pure MnO\(_2\) nanowires and PEDOT nanowires (Figure 4e), the specific capacitance (210 F g\(^{-1}\)) is still far from the theoretical value (1370 F g\(^{-1}\)). The possible reason might be the very limited electrode (MnO\(_2\))-electrolyte interface due to the compact PEDOT shell to prevent the electrolyte accessing to MnO\(_2\) core.

Considering the importance of interface between active materials and electrolyte, another kind of AAO template-directed core-shell 1D nanostructure arrays is designed as the electrode for electrochemical energy storage, where conductive materials are first prepared into nanowire or nanotube arrays as nanostructured current collector by utilizing AAO template, thereafter active materials are uniformly coated onto these conductive nanowire/nanotube arrays to form core-shell structures. Compared with the above-mentioned MnO\(_2\@\)PEDOT coaxial structure, such core-shell 1D nanostructure arrays have large electrode/electrolyte interface to improve charge storage as well as...
large electrode-current collector interface to enhance electron transport and collection, and thus should be more efficient to achieve high performance of electrochemical energy storage. As the proof of concept, Taberna et al. have prepared copper (Cu) nanorod arrays as current collectors based on AAO template, followed by coating with iron oxide (Fe3O4) as active materials for lithium-ion batteries (Figure 5a) [102]. Utilizing such Cu@Fe3O4 core–shell nanorod arrays as electrode, the power density of lithium-ion batteries has six times improvement over planar electrodes while maintaining the same total discharging time and excellent rate capability (Figure 5b). Thereafter, through AAO-directed fabrication, various nanowire and nanotube arrays of conductive materials have been further produced as nanostructured current collectors for electrochemical energy storage, such as nickel (Ni) nanowire arrays [103,104], aluminum (Al) nanowire arrays [105,106], PEDOT nanowire arrays [107], gold (Au) nanowire and nanocone arrays [108,109], tin oxide (SnO2) nanowire and nanotube arrays [110,111], titanium nitride (TiN) nanotube arrays [112], and platinum (Pt) nanotube arrays [113], etc. All these nanostructured current collectors have efficiently enabled the improved electrochemical performance of the loaded electroactive materials towards high capacitance/capacity and high rate capability. Another good example of the effects how core-shell 1D nanostructure arrays facilitate both good electrical and ionic conductivity can be seen in the case of MnO2 coated Pt nanotube arrays [113]. Highly-ordered and highly-oriented Pt nanotube arrays have been prepared as current collectors for supercapacitors using AAO template-assisted ALD process. In the MnO2 coated Pt nanotube core–shell structure arrays (Figure 5c), the Pt nanotube core provides good electrical conductivity and large interface between current collector and active materials, and the highly-ordered and highly-oriented structure of MnO2 coated Pt nanotube arrays offer fast ion transport pathway. Finally, the supercapacitor electrode exhibits high specific capacitance (810 F g⁻¹ at a scan rate of 5 mV s⁻¹), excellent rate capability (68% capacitance retention from 2 to 100 A g⁻¹) and excellent cycling stability (as shown in Figure 5d, negligible capacitance loss is observed after 8000 cycles of random charge-discharge with current density ranging from 2 to 100 A g⁻¹). Furthermore, based on free-standing SnO2 nanotube arrays prepared by AAO-assisted ALD process as current collector, Grote and co-workers have synthesized polypyrrole (PPy) coated SnO2 nanotube arrays and MnO2 coated SnO2 nanotube arrays to function as negative and positive electrode, respectively, for the assembling of asymmetric supercapacitor devices (Figure 5e) [111].
The asymmetric supercapacitor device has enlarged operating potential window up to 1.7 V and exhibits a high specific energy of 27.2 W h kg\(^{-1}\) and a high specific power 24.8 kW kg\(^{-1}\), attributing to the core-shell nanotube arrays structure and the asymmetric electrode configuration.

According to the charge storage mechanism of supercapacitors and batteries, larger surface area will benefit to achieve larger electrode-electrolyte interface towards higher energy storage performance. The charge storage performance of both supercapacitors and lithium-ion batteries based on nanowire or nanotube arrays could be potentially enhanced by increasing the length of nanowire or nanotube due to the larger surface area. However, AAO template-directed nanowire and nanotube with high aspect ratio tend to agglomerate together with the formation of clusters after removing AAO template (Figs. 3 and 4a). As a result, the agglomeration will greatly decrease the effective specific surface area and increase the ion-transport barriers at the same time, both of which will impose adverse effects on supercapacitor and battery performance. Advanced fabrication methodology offers novel techniques to further suppress these problems. As well known, the conventional AAO templates with highly-oriented nanopore channels are fabricated by anodizing high-purity (99.999%) Al foil. However, when anodizing low-purity (<99.99%) Al foil, Molchan et al. find that side-holes densely distribute on the wall of the vertical nanochannels of AAO template to form 3D interconnected AAO template [114]. According to this result, Wang et al. have utilized such kind of AAO templates to build up 3D interconnected titanium dioxide (TiO\(_2\)) coated Ni nanowire network for lithium-ion batteries (Figure 6a) [115]. Due to the formation of multiple interconnections in 3D nanowire network after Ni electrochemical deposition, agglomeration of nanowires has been eliminated, and correspondingly the lithium-ion batteries with such electrode have much higher capacity than that of straight TiO\(_2@\)Ni nanowire arrays with the same length (Figure 6b). However, such electrode structure still has some limitations towards highly-efficient electrochemical energy storage. The irregular pore structure in this 3D interconnected nanowire network will introduce bigger ion transport barriers than that of oriented pores in conventional nanowire arrays, leading to negative effect on the rate capability during fast charge-discharge process. On the other hand, different from AAO template obtained from two-step anodization process of high-purity Al

Figure 4  (a) SEM image of MnO\(_2@\)PEDOT coaxial nanowires prepared by one-step co-electrodeposition method. (b) TEM image of a single coaxial nanowire. (c) and (d) EDS maps of S and Mn from the boxed area in (b). (e) Specific capacitance of MnO\(_2\) nanowires (closed blue square), PEDOT nanowires (open purple dots), MnO\(_2\) thin film (open green square) and MnO\(_2@\)PEDOT coaxial nanowires (closed red dots) as a function of current density. Reproduced with permission from Ref. [100]. Copyright 2008 American Chemical Society.
foil, the 3D interconnected AAO template has poor structural controllability due to the chaotic distribution of impurities in low-purity Al foil, which subsequently results in the irregular and poorly controllable structural parameters, such as diameter, length and interwire distance of the obtained nanowires. As demonstrated by Liu et al. for nanowire array as electrodes [97], these parameters indeed play critical role on the final device performance of electrochemical energy storage. The wire diameter determines the surface area, the volume and the weight of current collectors, while the interwire distance determines the valuable volume for loading of electrode materials, the space needed for electrolyte, and also the space to accommodate the volume expansion during the insertion and removal of lithium ions. With regard to a highly-efficient current collector, the wire diameter and interwire distance of AAO template-directed nanowire arrays should be maintained as a balance. Hence, optimization of the structural parameters of AAO template-directed oriented nanowire arrays, including length, diameter, and interwire distance, as current collectors for highly efficient electrochemical energy storage still represents a significant challenge.

3D nanostructure arrays based on AAO template

Besides being a template for fabricating 1D nanostructure arrays, AAO itself is also a promising scaffold for active materials towards electrochemical energy storage because of one of the distinguished structural features of AAO, the vertically aligned nanopore arrays, which could facilitate rapid electrolyte transport. Very recently, Liu et al. report an all-in-one nanopore
battery array by utilizing the vertical nanopore channels of AAO template (Figure 7) [116]. In this all-in-one battery, an array of nanotubular electrodes and a liquid electrolyte is confined within nanopores of AAO template. Integrated current collectors (ruthenium, Ru) and active storage material (V2O5) are conformally fabricated at two ends of AAO nanopore arrays to form nanotubular electrode by controlled-conformality ALD to limit the deposition depth of both Ru and V2O5 (Figure 7). This controlled-conformality ALD process allows the anode-cathode electrical isolation with precisely controlled distance by taking advantage of the long AAO nanopores (50 μm). With prelithiated V2O5 at one end as anode and pristine V2O5 at the other end as cathode, parallel asymmetric nanobattery arrays with an areal density of 2/109 cm2/C0 is achieved. Owing to the highly-oriented vertical nanopore channels of AAO template, the integrated nanotubular electrode design facilitates fast ion and electron transport to achieve with excellent capacity retention (~50% at the 150 C rate, relative to 1 C). The nanotubular array battery exhibits ~80 mAh g−1 at 150 C (24 s charge-discharge time) with more than 80% of initial capacity retained after 1000 cycles at 5 to 25 C.

Another possibility to utilize the structural advantages of porous AAO for electrochemical energy storage is to replicate the nanoporous structure of AAO using conductive materials, because AAO couldn’t be directly used as current collector due to the insulator nature of alumina. Recently, AAO-like metallic nanopore arrays with exactly the same structure as AAO template have been realized to serve as nanostructured current collectors for supercapacitors (Figure 8a and b) [117]. The AAO-like metallic nanopore arrays are prepared by a two-step replication process from AAO. Like AAOs, it has highly oriented vertical nanopore channels. In fact, the structure of nanopore arrays is the negative structure of AAO template-directed nanowire arrays, with the same structural parameters (including unit density, diameter, and length), nanopore arrays have the equivalent specific surface area as that of nanowire arrays. However, nanopore arrays are actually a porous film unlike nanowire arrays, thus the nanopore arrays should not have any agglomeration and collapse like high-aspect-ratio nanowire arrays. When such nanopore arrays are used as a nanostructured electrode, large specific surface area and highly oriented pore structure can be achieved simultaneously. Meanwhile, when applying AAO-like metallic nanopore arrays as current collectors, the large and conductive specific surface area can ensure high capacitance, while the highly oriented and stable nanoporous structure can facilitate ion transport. Owing to the promising structural features, such AAO-like metallic nanopore arrays could overcome the drawbacks (agglomeration and collapse) while maintaining all the structural advantages.

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advantages (large specific surface area and good ion transport) of 1D nanostructure arrays for the achievement of high-performance supercapacitor. As mentioned before, it has to make a balance between wire diameter and interwire distance when applying AAO template-directed nanowire arrays as current collector for supercapacitors [97]. Increasing the wire diameter will result in a larger specific surface area and also could avoid agglomeration of the nanowires because of the resulting lower aspect ratio, but will lead to a smaller interwire distance at the same time. The smaller interwire distance means reduced volume for loading active materials and electrolyte. After deposition of active materials, a

Figure 7  (a) Schematic illustration of parallel nanopore battery array based on AAO template (left) and cross-section schematic view of a single-pore battery (right); rate performance (b), long cycle life with high current density (c) and charge and discharge curves at the second and 1000th cycles (d) of parallel nanopore battery array. Reproduced with permission from Ref. [116]. Copyright 2014, Nature Publishing Group.

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randomly porous structure will easily form due to the smaller interwire distance when increasing the amount of active materials. When the mass loading of MnO$_2$ increases from 80 to 240 $\mu$g cm$^{-2}$, the highly-oriented Ni nanowire arrays are replaced by a randomly porous structure [117]. Such randomly porous structure generates a large ion-transport resistance, and thus resulting in poor rate capability. On the contrary, AAO-like metallic nanopores with larger diameters can offer not only larger conductive specific surface area but also a larger space for the coating of active materials, which is helpful for increasing the mass loading of active materials per unit substrate area. For Ni nanopore with the same diameter as that of Ni nanowire, when the mass loading of MnO$_2$ reaches as high as 400 $\mu$g cm$^{-2}$, the hybrid structure maintains the highly-oriented nanoporous structure as the original Ni nanopore arrays with the remaining pore diameter of about 150 nm (Figure 8c). Hence, such a highly oriented nanoporous structure can promote the transport of electrolyte ions to improve the rate capability of supercapacitors [117].

3DOM structure based on CCT

Not only AAO template-directed 1D and 3D nanostructure arrays, 3DOM structure based on CCT is also considered as scaffold for active materials in supercapacitors [118-120]. The 3DOM structure has a three-dimensionally interconnected pore system with large interfacial area and low tortuosity. The ordered interconnected pore network of 3DOM could benefit electrolyte infiltration to achieve higher ionic conductivity throughout the pores, resulting in high rate capabilities of supercapacitors. In the case of manganese-manganese oxide (Mn-MnO$_2$) 3DOM core-shell electrodes [119], the Mn 3DOM structure is first prepared with monodisperse PS spheres as template via ECD method, and then is anodized in 3 M KCl aqueous solution to form Mn-MnO$_2$ 3DOM core-shell structures. In this Mn-MnO$_2$ 3DOM core-shell electrode, the Mn 3DOM structure provides an electron pathway for charge storage and discharge because of its great electrical conductivity, which is helpful to overcome the key limitation of MnO$_2$. Cyclic voltammetric method shows that the as-prepared Mn-MnO$_2$ 3DOM core-shell electrode has high specific capacitance (1200 F g$^{-1}$, which is very close to the theoretical capacitance of MnO$_2$) and demonstrates that Mn-MnO$_2$ 3DOM core-shell electrode yields greatly improved capacitance performance, at all scan rates 2-4 times than that of a MnO$_2$ electrode. Furthermore, the less scan rate dependence of capacitance and the negligible current-resistance drop indicates the high ionic and electrical conductivity of the Mn-MnO$_2$ 3DOM core-shell electrode [119]. Moreover, the 3DOM structure is also a very useful electrode structure for lithium-ion batteries, especially for the improvement of rate capability. In general, the rate capability of lithium-ion batteries is limited by the transport of Li$^+$ ions across the interfaces between the electrolyte and the electrode and through the electrode materials. The 3DOM structure has been widely regarded to meet this challenge [121-134], because of its various advantages: (i) large surface area and volume to coat more active materials; (ii) well-interconnected pore network to facilitate the transportation and infiltration of electrolyte; (iii) thin wall and porous structure to reduce the electronic and ionic pathways; and (iv) uniform and periodic

Figure 8  SEM images of top view (a) and cross-sectional view (b) of AAO-like Ni nanopore arrays. (c) SEM image of MnO$_2$ coated AAO-like Ni nanopore arrays with MnO$_2$ mass loading of 400 $\mu$g cm$^{-2}$; (d) CV curves of MnO$_2$ coated AAO-like Ni nanopore arrays at different scan rates. Reproduced with permission from Ref. [117]. Copyright 2014 Wiley-VCH Verlag GmbH & Co.
pores ordered in three dimensions to facilitate electrolyte transport. Especially the feature (iii) and (iv) of 3DOM structure are very promising to facilitate Li\(^+\) ions and electrons transport for improving rate capability of lithium-ion batteries. Zhang et al. have prepared Ni 3DOM structure as nanostructured current collector by electrochemical deposition using self-assemble multilayer PS template (Figure 9a and b) [121]. Then MnO\(_2\) are homogeneously deposited on Ni 3DOM current collector as active materials (Figure 9c). The hybrid structures exhibit ultrafast, supercapacitor-like charge and discharge rate capability while maintaining battery-like storage capacities. Such superior performance are attributed to the unique structural features of Ni 3DOM electrode structure, which provide efficient pathways for ion and electron transport as well as very short solid-state diffusion lengths. At the same time, Zhang et al. also point out the importance of the very narrow interconnects between the spherical voids in original 3DOM structure formed by the contact points of the colloidal spheres in the template [121]. When the original 3DOM structure is directly used as a current collector, the narrow interconnects will be rapidly blocked during active material deposition process, finally preventing conformal coating of active material into the depths of the 3DOM structure. Moreover, the resulting ion transport pathway will become discontinuous. Therefore, they further apply electrochemical polishing process to enlarge the interconnect window size between adjacent pores of the original Ni 3DOM structure, leading the overall porosity of Ni 3DOM structure to increase from 74% to 94% (Figure 9a and b). This optimizing 3DOM structure finally contributes to the rapid ion and electron transport, allowing the lithium-ion batteries to be charged to 90% capacity in only 2 min (Figure 9d).

**Template-directed nanostructure arrays for energy conversion**

Besides energy storage, template-directed nanostructure arrays are also attractive for energy conversion, especially for conversion of solar energy, which is the cleanest and...
most abundant available renewable energy source. So far photovoltaics and solar water splitting cells are two major kinds of solar energy conversion devices. Principally, the energy conversion process in these devices involves (i) light absorption, (ii) charge generation and separation, and (iii) charge transport. The light absorption characteristics in the solar spectrum are the basic factor to determine the overall conversion efficiency of solar energy conversion. Studies have shown the fact that nanostructure arrays could largely improve light absorption towards highly-efficient solar energy conversion [135-142]. For example, the nanostructure arrays can spatially redistribute the light intensity and efficiently scatter light in the device resulting in enhanced light absorption [141-143], and thus will enable high quantum efficiencies for solar energy conversion. Moreover, such nanostructure arrays could facilitate carrier collection via orthogonalizing the direction of light propagation and carrier collection [141,144]. In this section, the advantages and progress of AAO and CCT template-directed spatially oriented nanostructure arrays for solar energy conversion applications will be summarized.

### 0D nanostructure arrays based on AAO template

Recently, AAO template-directed 0D nanostructure arrays have been investigated for solar energy conversion, because some 0D metal nanostructure can serve as surface plasmonic structure to improve the light absorption [145-148]. As shown in Figure 10a, surface plasmonic structures can provide three possibilities to improve the light absorption: (i) light scattering using particle plasmons; (ii) light concentration using particle plasmons; and (iii) light trapping using surface plasmon polaritons [147]. Due to the strong dependence of the wavelength at which the local surface plasmon can be excited on the nanostructure, it is principally possible to design plasmonic devices that can harvest photons over the entire solar spectrum. Therefore, the application of

![Figure 10](image.png)

**Figure 10** (a) Three kinds of plasmonic light-trapping geometry to enhance solar light absorption; Reproduced with permission from Ref. [147]. Copyright 2010, Nature Publishing Group. (b) SEM images of Au nanodot arrays with diameter of 50 nm on ITO glass substrate; (c) UV-Vis absorption spectra of 50, 63, and 83 nm Au nanodots on ITO glass; (d) current density response of the TiO2-coated Au nanodots (50 nm) arrays according to light on/off at an anode applied potential of 0.397 V (vs RHE); (e) hydrogen production rate and faradaic efficiency of the TiO2-coated Au nanodots (50 nm) arrays with light irradiation after 1 h on stream. Reproduced with permission from Ref. [150]. Copyright 2014 American Chemical Society.
surface plasmonics is highly expected to improve the light absorption towards highly-efficient solar energy conversion. The concept of surface plasmonics for solar energy conversion has been applied into photovoltaics to reduce the thickness of active layer while keeping or improving light absorption, finally leading to not only lower material costs but also improved electrical characteristics [145-148]. Thinner film would enable higher open circuit voltage and reduced carrier recombination since carriers only need travel very short distance before being collected at the junction, and thus will result in improved cell efficiency and higher photocurrent. Moreover, Knight et al. demonstrate that embedding plasmonic nanostructures within a semiconductor could increase the photocurrent efficiency in a plasmonic nanostructure-diode device [149]. Embedding the plasmonic nanostructures into the semiconductor will introduce vertical electron transport from the Schottky barriers into the semiconductor [149]. These results further verify the nanostructure-diode device [149]. Embedding the plasmonic nanostructures within a semiconductor photocurrent. Moreover, Knight et al. demonstrate that embedding plasmonic nanostructures within a semiconductor could increase the photocurrent efficiency in a plasmonic nanostructure-diode device [149].

Kim et al. have reported plasmon-enhanced PEC water splitting cells by embedding highly-regular Au nanodot arrays into TiO$_2$ layer [150]. In their experiment, highly-regular Au nanodot arrays with different diameters are prepared on ITO glass substrate with the help of AAO templates (Figure 10b). As shown in Figure 10c, the UV-vis absorption spectra of the fabricated Au nanodot arrays with diameter of 50, 63, and 83 nm on ITO glass clearly show the plasmon absorption for all Au nanodot arrays, and also a red-shift of plasmon resonance wavelength as the Au nanodot diameter increases from 50 nm to 83 nm. After coated with TiO$_2$, the TiO$_2$-coated Au nanodot (50 nm) electrodes have shown 25 times enhanced photocurrent density (Figure 10d), which attribute to the embedding of the plasmonic nanostructure into the semiconductor [149], and subsequently high photogenerated carrier collection efficiency compared with bare TiO$_2$ layer (Figure 10e). These results further verify the potentials of the utilization of plasmonic structure for improving solar energy conversion efficiency.

1D nanostructure arrays based on AAO template

The 1D nanostructure arrays, especially nanowires and nanopillars, have been studied in details for photovoltaics and solar water splitting cells because their structural features enable minimized optical losses by reducing refraction, enhanced absorption as well as maximized carrier collection efficiency by decoupling the light absorption and carrier collection directions [151,152]. Compared with nanowire/nanopillar arrays synthesized by other methods, AAO template-directed nanowire/nanopillar arrays are highly-ordered and highly-oriented. They have well-tunable and precisely-controlled structural parameters, including shape, size, interspace, and density, which are all guided from the structural features of AAO template. Moreover, highly-ordered and highly-oriented nanowire/nanopillar arrays with perfect order are more promising for solar energy conversion application because of the uniform optical phenomenon. Additionally, the AAO template leads to some special influences on the microstructure of the as-obtained nanostructure arrays in the case of polymer, for example, poly-(3-hexylthiophene) (P3HT).

Kim et al. find that the P3HT chains in nanorods fabricated using AAO template had a partial face-on orientation with respect to the ITO substrate, while an edge-on conformation in bulk film [153]. They speculate that one of the reasons might be the interactions between the hydrophobic P3HT side chains and the pore wall surface of AAO template. They also find that such chain alignment of P3HT nanorods enhances the electrical conductivity up to ten fold compared with planar films, which is further benefit to improve the performance of organic solar cells. Therefore, AAO template-directed highly-ordered (especially, perfectly-ordered) and highly-oriented nanowire/nanopillar arrays have been extensively studied for photovoltaics and solar water splitting cells in recent years [154-157]. A good example is that perfectly-ordered cadmium sulfide (CdS) nanopillar arrays prepared by using ideally ordered AAO template for photovoltaics (Figure 11a) [158]. Highly-oriented and perfectly-ordered CdS nanopillar arrays have been synthesized via the Au nanoparticle catalyzed VLS growth process by utilizing perfectly-ordered AAO template. Thereafter, cadmium telluride (CdTe) thin films are deposited on CdS nanopillars by CVD method to serve as the photo absorption layer. The CdS nanopillars/CdTe thin-films hybrid structure is found to harvest more light. Specifically, different from the generation and separation of electrohole pairs relying on an internal electric field in conventional thin-film photovoltaics, the photoinduced carrier generation is significant in the entire device thickness and the 3D structure facilitates the efficient separation and collection of photocarriers (Figure 11b). Under AM 1.5 G illumination, a typical cell produces high performance: short circuit current density $J_{sc}$ of 21 mA cm$^{-2}$, open circuit voltage $V_{oc}$ of 0.62 V, fill factor FF of 0.43, and efficiency of 6%. Furthermore, Lin et al. develop a unique type of integrated nanopillar-nanowell structure for photovoltaics by integrating nanopillar and nanowell arrays together vertically (Figure 11c) [159]. Such unique hybrid structure is fabricated from AAO template by anodizing nano-imprinted Al foil and following precisely wet-chemical etching. In this hybrid structure, perfectly-ordered nanopillar-nanowell with cylindrical cavities provides efficient geometric confinement for normally incident light, meanwhile nanopillar with small diameter tips improves angular absorption performance by suppressing reflectance, thus this hybrid structure could significantly enhance light absorption over a long wavelength and large incident angle range by finely tuning the structural parameters of the hybrid structure (Figure 11d). Finally, the a-Si (40 nm) covered nanowell/nanopillar arrays hybrid structure with the overall thickness of 2 $\mu$m obtains 89.27% absorption efficiency of day-integrated light. Such thinner absorber with so high absorption efficiency will be greatly beneficial for thin film photovoltaics owing to the shortened minority carrier migration path and improved carrier collection efficiency [141,158,160].

On the other hand, by utilizing connected-UTAM technologies, nanorod arrays of photoresponsive semiconductors can be directly fabricated onto conducting substrate for solar energy conversion (Figure 12). For example, Schierhorn et al. have utilized connected UTAM to fabricate highly aligned cadmium selenide (CdSe) nanorod arrays on ITO-coated glass for photovoltaic applications (Figure 12b and c) [161,162].
They have investigated the influence of the structural parameters of CdSe nanorod arrays on the contribution to photovoltaic activity, and have found that highly ordered CdSe nanorods can remedy the poor conductance of materials comprised of compacted nanocrystals, resulting in better transfer of electrons from the p-n junctions to the external circuit. Furthermore, based on these highly-ordered CdSe nanorod arrays, nanostructured CdSe-PEDOT:PSS inorganic–organic hybrid Schottky solar cells are realized with overall solar conversion efficiencies exceeding 3% and with extremely large short-circuit photocurrents [163]. Besides, Li et al. have fabricated vertically aligned tantalum nitride (Ta3N5) nanorod arrays with the help of connected UTAM as mask (Figure 12d and e). The as-obtained Ta3N5 nanorod arrays are working as photoanodes of a photoelectrochemical (PEC) water splitting cell and achieve high PEC performance with a photocurrent density of 3.8 mA cm⁻² at 1.23 V (vs RHE) under AM 1.5 G simulated sunlight and an incident photon-to-current conversion efficiency (IPCE) of 41.3% at 440 nm [164].

As previously described, AAO template-directed Au nanodot arrays could enhance efficiency of solar energy conversion contributing to the surface plasmonics, Moskowitz’s group finds that Au nanorod arrays are also highly efficient plasmonic structure to improve the light absorption in visible light range [165,166]. They have fabricated high-performance solar water splitting cells and photovoltaics with visible light based on vertically aligned Au nanorod arrays capped with TiO₂. Vertically aligned Au nanorod arrays are first prepared on ITO glass as plasmonic structures by ECD using connected UTAM as template, and then capped with TiO₂ layer to serve as a plasmonic photoanode in the water splitting cell (Figure 13a). Under visible light illuminating, the excited surface plasmons rapidly decay, producing electron–hole pairs with the hot electrons occupying normally empty states in the conduction band of Au above the Fermi energy (Figure 13b) [167,168]. These hot electrons potentially reach the surface of Au nanorod, and some of them directly transfer from Au nanorods to conduction band of TiO₂ layer through Schottky junction established at the interface between Au nanorods and TiO₂ layer, which then carry out hydrogen ion reduction (Figure 13b). The leaving holes on Au nanorods are to oxidize water to oxygen gas. The fuel production efficiency...
of this plasmonic water splitting cell has up to 20-fold higher at visible wavelengths than that at UV wavelengths, indicating 95% of the effective charge carriers deriving from surface plasmon decay to hot electrons (Figure 13c). Furthermore, if both cobalt-based oxygen evolution catalyst and Pt nanoparticles as hydrogen evolution catalyst are introduced into the cell, the overall performance can be further improved [169]. They have realized a more efficient and autonomous solar water splitting device in which essentially all charge carriers involved in the oxidation and reduction steps arise from the hot electrons resulting from the excitation of surface plasmons in Au nanorod arrays [163,169]. In this device, each Au nanorod functions without external wiring, producing $5 \times 10^{13}$ H₂ molecules per cm$^2$ per s under 1 sun illumination (AM 1.5 and 100 mW cm$^{-2}$), with long-term operational stability.

Besides nanowire and nanopillar arrays, some nanophotonic structure arrays also have been developed based on AAO template for solar energy conversion. Normally, self-ordered AAO template has hexagonal pore arrangement as honeycomb structure, which is the most stable structure in nature. With the help of nano-imprinting technique, AAO template with square pore arrangement is developed with applying proper anodization condition. However, different from hexagonally ordered AAO templates, Qiu et al. find that there have voids filling with unanodized aluminum on the Al foil after removing the alumina layer to form Al nanospike arrays (Figure 14a) [170]. They subtly utilize such Al nanospike arrays for efficient PEC water splitting cell. They deposit ultrathin hematite (α-Fe$_2$O$_3$) film on Al nanospike arrays as active material for the construction of PEC water splitting cell (Figure 14b). In this device structure, the nanophotonic structure of nanospike arrays ensures to harvest light efficiently owing to the anti-reflection effect, the ultrathin hematite films serve as active material to produce photocarriers, and the conductive Al nanospike arrays act as efficient carrier collection path. As a result, three times higher current density at 1.23 V (vs RHE) than that of a planar...
Figure 13  (a) Schematic illustration of the structure and working principle of TiO$_2$-capped Au nanorod arrays as plasmonic anode for solar water splitting; (b) energy band diagram of TiO$_2$-capped Au nanorod arrays plasmonic photoanode unit; (c) photocurrent vs time plots for TiO$_2$-capped Au nanorod arrays plasmonic photoanode under UV and visible light, respectively. Reproduced with permission from Ref. [165]. Copyright 2012 American Chemical Society.

Figure 14  (a) SEM and schematic diagram of Al nanospike embedded in squarely order AAO; (b) SEM image of Fe$_2$O$_3$ decorated Al nanospike arrays; (c) $J$-$V$ curves of the Ti-doped hematite photoelectrodes based on the Al nanospike arrays with different pitch size; (d) SEM images of a-Si:H coated 1.5 $\mu$m pitch inverse nanocone arrays; absorption spectra (e) and $J$-$V$ curves (f) of a-Si:H devices based on 1.5 $\mu$m pitch inverse nanocone arrays with different aspect ratios and the flat reference. Reproduced with permission from Ref. [170] and Ref. [171]. Copyright 2014 American Chemical Society.
photoelectrode has been obtained (Figure 14c). Inverted nanocone arrays are another nanophotonic structure from AAO template (Figure 14d). Lin et al. utilize a multi-step anodization-etching of nanoimprinted Al foil to synthesize Al inverted nanocone arrays with different aspect ratios [171]. Thereafter, thin film amorphous silicon is deposited on Al inverted nanocone arrays. The inverted Si nanocone arrays have obviously enhanced light absorption and device performance over the flat reference device omnidirectionally (Figure 14e and f), owing to efficient antireflection of inverted nanocone structure. Furthermore, Tsiu et al. have prepared nanocone arrays replicated form Al inverted nanocone [172]. Both current-voltage characteristics and quantum efficiency measurements confirm that the nanocone arrays can significantly reduce the reflectance to improve the photovoltaics performance.

### 3DOM structure based on CCT

Different from AAO template-directed 0D and 1D nanosstructure arrays to improve light absorption by reducing reflection or through plasmonic effect, CCT template-directed 3DOM structure (inverse opal structure) is of great interest in solar energy conversion because they possess a photonic crystal structure. It is well-known that photonic crystal offers a unique way to manipulate light based on light-matter interactions via periodically organized dielectric structure, which forbids the propagation of light in a certain direction within a certain spectrum regime (called photonic stop-band) [173–177]. The slow-light effect induced by photonic stop-band, which the light in a photonic crystal travels with very slow velocity due to the strong coherent multi-scattering, is able to increase light harvesting, especially around the absorption edge of semiconductors [178]. Several groups have intensively investigated the fabrication of inverse opal structure of photoreponsive semiconductors to improve the light absorption and photoelectric conversion efficiency in photovoltaics and photocatalytic chemical process [179–180]. As known, the wide electronic band gap of photoreponsive semiconductors leads to low utilization efficiency for solar light because of their light absorption spectra are mainly located in UV range, which accounts for only 4% of solar irradiation. In these literatures, the slow-light effect in a photonic crystal has been proved to enhance the interaction of light with photoreponsive semiconductors and to amplify photochemical reactions, and thus increasing the light absorption and energy conversion efficiency. According to the modified Bragg’s law, the photonic stop-band of inverse-opal of semiconductors depends on the pore size [191,192]. The pore size of inverse opal structure fabricated using self-assembling colloidal sphere templates is widely tunable by modifying the diameter of colloidal sphere. Therefore, the photonic stop-band of inverse-opal for different semiconductors can be conventionally realized [193,194]. For example, the photonic stop-band in inverse opal of tungsten oxide (WO₃) could be tuned either into or out of the electronic absorption band gap by changing the pore size of inverse opal (Figure 15) [194]. The electronic band gap of WO₃ is around 2.6 eV, corresponding to a wavelength of around 470 nm. As shown in Figure 15b, when the pore size of WO₃ inverse opal is 260 nm, the photonic stop-band center is at 415 nm and the resulting slow-light is in the vicinity of 440 nm, while for WO₃ inverse opal with pore size of 360 nm, the photonic stop-band center is at 580 nm and the resulting slow-light is in the vicinity of 630 nm [193]. The slow-light wavelength for WO₃ inverse opal with pore size of 260 nm is thus overlapped with the electronic absorption edge of WO₃. Therefore, the slow-light is trapped in the WO₃ matrix by multiple scattering and diffraction, which induces much stronger interaction between light and WO₃ matrix, and thus generating more photoinduced carriers. The more IPCE enhancement in the spectral regime from 410 to 460 nm (Figure 15c) which is consistent with its stronger slow-light absorption range of 420–460 nm further confirms the slow-light effect to improve the light absorption around the absorption edge of WO₃. Finally, with WO₃ inverse opal with pore size of 260 nm as photoanode, the photocurrent density is two-fold of that of a disordered porous WO₃ photoanode (Figure 15d). These results indicate that the light harvesting and photo-to-current conversion efficiency could be remarkably enhanced by utilizing slow-light effect in inverse-opal. The inverse slow light directed from colloidal sphere templates is a three-dimensionally periodic dual-pore structure as shown in Figure 16, which is defined as the macropores surrounded by the final skeletal walls (P1) and another pores (P2) between neighboring macropores [195]. The interconnected pores in macroporous films is considered to be able to improve the mass transport through the film, reduce the length of the macropore channel, and increase the accessible surface area of the thin film. In the previously mentioned works, the influences of P1 on PEC performance have been widely studied. However, the lack of the research about the pores between neighboring P1 is due to the difficulties in synthetic control over the pore size of P2. As shown in Figure 16a, Zhou et al. develop a new strategy by a combination of sandwich solution infiltration and post-heating treatment to obtain inverse-opal structures with controllable P1 and P2 [196,197]. In this strategy, the P1 size is determined by the diameter of PS spheres, and the P2 size is controlled by the contact surface-to-volume ratio which is tuned by changing the post-heating time. Since the morphology and structure mainly depend on the template rather than the type of precursor solution, many materials, including binary materials (Bi₂O₃), ternary materials (BiVO₄, LiV₂O₈ and Bi₃W₁₃O₄₂), and even doped materials (Mo:BiVO₄, Figure 16b), can be easily fabricated into inverse opal structure with desirable dual pore size. Moreover, this method is also valuable to obtain 3DOM structure with larger porosity for electrical energy conversion applications [121]. The performance of PEC water splitting cells based on the obtained Mo:BiVO₄ inverse opal structure demonstrates the strong dependence with the size of P2 [197]. A smaller mesopore size of P2 is beneficial for charge migration both in the bulk and on the surface, producing high photocurrent density (Figure 16c). These results provide a worthy guideline for further design of highly-efficient photoelectrodes with inverse opal architectures.
Hybrid structure of 1D nanostructure arrays and 3DOM

Furthermore, by combining the advantages of nanowire and nanotube for solar energy conversion, such as direct-ed electron transport pathways, reduced carrier diffusion length and diminished charge recombination, with the unique photonic crystal structure of inverse opal, novel nanowire- inverse opal hybrid architecture has been developed. Mihi et al. first demonstrate and realize this concept by transferring TiO2 inverse opal onto zinc oxide (ZnO) nanowire arrays for dye-sensitized solar cells (DSSCs) [198]. However, the enhancement in the efficiency of the DSSCs is not very satisfied, where the efficiency of a model TiO2 DSSC system only slightly increased from 2.3% to 3.2%. The reason might be attributed to the absence of electrical coupling arising from the poor physical contacts between inverse opal of TiO2 and ZnO nanowire arrays. To enhance the electrical coupling, Karuturi et al. have directly synthesized ZnO nanowire arrays onto TiO2 inverse opal to form a bilayer structure to realize both electrical and optical coupling [199]. Owing to the light harvesting enhancement through back reflections and slow light effect in TiO2 inverse opal and the electrical coupling enhancement between ZnO nanowire arrays and TiO2 inverse opal, the PEC performance of the bilayer photoanode has been obviously improved in comparison to that of pure ZnO nanowire arrays as photoanode. Very recently, Zhang et al. have constructed a TiO2 bilayer structure photoanode of TiO2 inverse opal assembled on TiO2 nanorod arrays (Figure 17a) [200]. Moreover, Au nanoparticles are in situ deposited into this TiO2 bilayer structure to function as plasmonic structures. Therefore, such photoanode couples the advantages of nanorod arrays, the slow light effect in inverse opal and the hot electron effect induced by SPR. As shown in Figure 17a, under sunlight illumination, the localized slow photon from the TiO2 inverse opal will increase the SPR absorbance of Au nanoparticles when the slow photon region is tuned to overlap with the SPR region, and thus more energetic hot electrons are generated in the Au nanoparticles through the excitation and decay of SPR and subsequently are transferred to the conduction band of TiO2 either by overcoming the Schottky barriers at the interface between Au nanoparticles and TiO2 or through a tunneling effect. The hybrid photoanode exhibits much higher photocurrent density and gas production efficiency (Figure 17c and d). The photoconversion efficiency of this plasmonic PEC water splitting system has approached 0.71%, which is one of the in Au/TiO2 PEC systems. This work provides a rational strategy for the design of hybrid structure photoelectrodes to enhance PEC water splitting efficiency. Considering the random ZnO nanowire arrays and TiO2 nanorod arrays, the
PEC performance might be further improved by combining inverse opal structure with AAO template-directed perfectly-ordered nanowire or nanorod arrays.

Conclusions and prospective

Over the last few years, great progress has been accomplished in the fabrication of various template-directed nanostructure arrays for energy storage and conversion. Advanced template-directed construction serves as a convenient and versatile methodology to provide more and more novel nanostructure arrays in large scale to meet the multifunctional requirements of practical applications. These nanostructure arrays possess tunable nanoscale features, high regularity, and predefined spatial orientation/arrangement due to the topologic transformation from the easily pre-controlled templates (typically, porous anodic aluminum oxide template and colloidal crystal template). Combining the advantages of nanomaterials and the spatial architecture design, utilization of these nanostructure arrays as electrodes contributes a lot to corresponding breakthroughs in energy storage and conversion, especially in supercapacitors, batteries, photovoltaics and solar water splitting cells.

In the future, to further improve the energy storage and conversion efficiency using nanostructure arrays and finally reach the practical application level, the following research points shall be paid high attentions. First, considerable research remains to be carried out to fully unleash their technological potential for diverse devices. Deep understanding and controlling the relevant kinetic processes could offer more essential guideline for well-directed design of nanostructure arrays as efficient electrodes in various energy-related devices. Second, new and emerging simulation tools, including topology optimization and genetic algorithms, are motivated by the need for further design of electrode architectures. Third, although the template-directed construction is universal in theory, the subset of materials and structures that can be fabricated remains limited. In order to be able to pattern any material with any multidimensional structure as required in large scale, further advances in template-directed construction methodology are necessary for enhanced and multifunctional.

Figure 16  (a) Schematic illustration of the post-heating approach for controlling mesopores and macropore in 3DOM architectures; Reproduced with permission from Ref. [196]. Copyright 2013 Wiley-VCH Verlag GmbH & Co. (b) Typical SEM image of 3DOM Mo:BiVO₄ architecture; (c) comparison of photocurrent density-potential curves (solid line) and dark-current density-potential curves (dashed line) of 3DOM Mo:BiVO₄ photoanode with unordered Mo:BiVO₄ and undoped BiVO₄ photoanodes. Reproduced with permission from Ref. [197]. Copyright 2014 American Chemical Society.

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energy devices in future. Though the relative study is beyond our present review, we are looking forward that more efforts can be harvested in these open questions in the near future.

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Figure 17 (a) Schematic diagram of the mechanism for synergistic action of the slow photon effect of TiO₂ inverse opal and the SPR effect of Au nanoparticles for PEC water splitting with visible light; (b) SEM image of TiO₂ inverse opal assembled on TiO₂ nanorod arrays; (c) linear sweep voltammograms of different photoanodes under dark and simulated sunlight illumination; (d) the evolution of H₂ and O₂ gases of different photoanodes under simulated sunlight illumination. Reproduced with permission from Ref. [200]. Copyright Royal Society of Chemistry 2014.
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Template-directed construction of nanostructure arrays for highly-efficient energy storage and conversion

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