Hollow nanostructures have shown great promise for energy storage, conversion, and production technologies. Significant efforts have been devoted to the design and synthesis of hollow nanostructures with diverse compositional and geometric characteristics in the past decade. However, the correlation between their structure and energy-related performance has not been reviewed thoroughly in the literature. Here, some representative examples of designing hollow nanostructure to effectively solve the problems of energy-related technologies are highlighted, such as lithium-ion batteries, lithium-metal anodes, lithium–sulfur (Li–S) batteries, supercapacitors, dye-sensitized solar cells, electrocatalysis, and photoelectrochemical cells. The great effect of structure engineering on the performance is discussed in depth, which will benefit the better design of hollow nanostructures to fulfill the requirements of specific applications and simultaneously enrich the diversity of the hollow nanostructure family. Finally, future directions of hollow nanostructure design to solve emerging challenges and further improve the performance of energy-related technologies are also provided.

1. Introduction

Hollow nanostructures refer to nanosized materials with well-defined boundaries and interior cavities. Their structural features endow them a low density, high surface-to-volume ratio, short mass- and charge-transport lengths, and high volumetric loading capacity.[1–9] These attractive properties make hollow nanostructures promising candidates for various energy-related technologies, such as lithium-ion batteries (LIBs), lithium-metal anode, lithium–sulfur (Li–S) batteries, supercapacitors (SCs), dye-sensitized solar cells (DSSCs), electrocatalysis, and photoelectrochemical (PEC) cells.[10–17] As Scheme 1 shows, hollow nanostructures used as electrode materials for LIBs and SCs can offer more accessible storage sites and larger electrode/electrolyte contact area, thus a higher specific capacity and shorter mass/charge-transport path. Besides, the interior void space can buffer the destructive volume expansion and alleviate stress/strain produced during cycling, resulting in improved cycling stability.[18–20] As lithium host for lithium-metal anode, they can lower the local lithium deposition current density, inhibit the growth of Li dendrites, stabilize the solid electrolyte interlayer (SEI), and confine the volume expansion of lithium;[21] as sulfur host for Li–S batteries, they can provide large void space for S-loading as well as confine formed soluble polysulfides (PLSs).[22,23] as photoanodes for DSSCs, they can achieve excellent light harvesting by simultaneously enhancing the multiple light diffractions and reflections on shell structures, and also allow a high dye loading and penetration of electrolyte into the hollow space, thus leading to a shorter charge-transport length.[24] As electrocatalysis, hollow nanostructures effectively isolate catalytic species, thus enabling the combination of incompatible catalytic functions and cascade reactions. In addition, selectivity of catalytic reactions can be improved either by controlling the shell pore structure or chemical compatibility.[25] when applied for PEC cells, they can provide more catalytic centers due to their large specific surface area and can achieve more efficient light harvesting due to the shorter charge carrier length and light trapping effect within the inner void space.[26]

Given the above advantages, great efforts have been devoted to the design and synthesis of hollow nanostructures for energy storage, conversion, and production applications. Generally, the synthesis methodology for the fabrication of hollow nanostructures can be divided into two categories: templating method using hard (SiO2, polystyrene (PS) sphere, carbon, etc.) or soft (gas bubbles, vesicles, micelles, etc.) materials as the sacrificed templates, and template-free method adopting Kirkendall effect, Ostwald ripening, ion exchange, selective etching, etc.[27–32]
Abundant simple hollow nanostructures such as single- or double-shelled ones have been fabricated. However, complex hollow nanostructures with multiple shells or cavities, which possess more advantages over their simple counterparts such as higher volumetric energy density, better mechanical and electrochemical stability, and stronger light harvesting, are not easy to achieve. Although some complex hollow nanostructures have been successfully fabricated, for example, multishelled SiO₂ hollow spheres using shell-by-shell assembly[33] or multishelled Cu₂O using vesicle-templating method,[34] these synthetic methods suffered from tedious processes and are limited to particular material. In 2009, the Wang group reported a general and scalable sequential templating approach to fabricate multishelled hollow metal oxide microspheres using solid carbonaceous microspheres (CMSs) as templates to incorporate metal precursors followed by a one-step annealing process. This approach has been successfully applied to prepare a variety of multishelled hollow nanostructures such as ZnO, α-Fe₂O₃, Co₃O₄, SnO₂, Mn₃O₄, TiO₂, NiO, MnO₂, V₂O₅, LiMn₂O₄, TiO₂/Fe₂TiO₅, and CoₓMnᵧO z.[10,13,16,17,20,24,35–41]

In addition, the compositional and geometric characteristics of these complex hollow nanostructures have also been accurately controlled, thus significantly enriching the hollow nanostructure family to serve different energy-related application areas.

In the last decade, several high-quality reviews have summarized the progress of hollow nanostructures in the absence of special focus on the structure–performance correlation.[8,9] This review aims to explore the relationship between their structure and the energy-related application performance. By highlighting some typical examples of designing hollow nanostructure for applications such as LIBs, lithium-metal anode, Li–S batteries, SCs, DSSCs, electrocatalysis, and PEC cells, we present here some in-depth understandings of the decisive role of structure engineering on performance. Additionally, some future
2. Diversity of Hollow Nanostructures

During the past decades, significant progress on the design and synthesis of hollow nanostructures has been achieved, resulting in the formation of various kinds of hollow nanostructures. These hollow structures show great diversity in both compositional and geometric aspects (Scheme 2). Except for inorganic (oxide, sulfide, carbide, nitride, fluoride, etc.) and organic (azithromycin, poly(3,4-ethylenedioxythiophene), polypyrrole, etc.) hollow structures, inorganic/organic hybrid systems that are believed to effectively integrate the fascinating properties of each component have also been successfully achieved. In addition, hollow nanostructures with adjustable and controllable compositions for different shells are also fabricated. Besides the compositional complexity, geometric diversity is another important aspect, which can be achieved by finely optimizing the synthetic methodologies. In addition to familiar spherical and tubular shapes, hollow structures with polyhedral, cubic, prismatic, or bowl-like shapes have also been achieved, exhibiting great promise in both the synthesis and application aspect. Apart from the adjustable morphology, the subunits for engineering the shell are diverse from 0D nanoparticles, 1D nanotubes or nanorods, to 2D nanoflakes, or nanosheets, leading to hierarchical pathways for mass/charge transport. Furthermore, complex structures with multiple shell architectures or internal constructions (multiple chambers or cores) have also been achieved to meet the specific requirements of diverse applications.

3. Synthetic Methodology of Hollow Nanostructures

The synthetic methodologies for hollow nanostructures can be simply classified into two types: templating method (including hard and soft templating methods) and template-free method (including Ostwald ripening, Kirkendall effect, ion exchange, and selective etching).

3.1. Templating Method

3.1.1. Hard Templating Method

Hard templating method is the most common and effective method to prepare hollow nanostructures. Various kinds of hard templates have been adopted, such as SiO2, polystyrene sphere, nickel, anodic aluminum oxide (AAO), carbonaceous microsphere, etc.

Cui and co-workers developed a dual-purpose Ni-templated method for the synthesis of Si microparticle–graphene (SiMP@Gr) yolk–shell structure. First, Ni is conformally coated on Si microparticles, which serves as both the catalyst for graphene growth and the sacrificial layer for providing void space. Next, a benign carburization process is applied to activate the low-temperature graphene growth on Ni-coated SiMP through a dissolution–precipitation mechanism. Last, the Ni template was removed using FeCl3 aqueous solution, providing void space to accommodate the volumetric expansion of SiMP within the graphene cage. In addition, other Si-based hollow nanostructures can also be developed by using SiO2 as templates, such as silicon pomegranate structure and Si nanoparticle-encapsulated continuous hollow carbon tubes.

However, the above method requires predefined micro/nanotemplates and effective coating of the precursors on the surfaces of templates. In 2009, the Wang group reported a general and scalable sequential templating approach to fabricate multishelled hollow metal oxide microspheres, which
uses CMSs as templates to incorporate metal precursors followed by a one-step annealing process (Figure 2a–m). This general method is distinguished from other hard templating methods: the formation of target shells is accompanied by the gradual removal of templates instead of preformation of all the target shells before template removal. When annealed in air, a temperature gradient along the radical direction is formed, making the exterior of carbonaceous microspheres more easily combusted. In addition, the metal ions within the exterior template accumulate, oxidize into metal oxides, and form a rigid shell when a certain “threshold” value reached. Further heating results in the separation of the outer metal oxide shells and inner carbon templates, as well as multiple template removal and metal oxide crystallization process, forming more shells inside and eventually the multishelled hollow structures are achieved.

In addition, by controlling adsorption process (adjusting adsorption temperature, solvent composition, adsorption duration, pH value, precursors, and pretreatment of CMS templates) and heating conditions (heating rate, duration, and atmosphere), various structural parameters of the multishelled hollow structures including the shape, shell number, size, and thickness, as well as the intershell spacing can be well controlled. For example, the intershell space of multishelled ZnO hollow microspheres is enlarged by increasing heating rate (Figure 2n). Moreover, the shell number of multishelled Co3O4 hollow microspheres can be increased by raising the adsorption temperature, the ratio of ethanol to water...
Figure 2. Fabrication of multishelled hollow microsphere using a sequential templating approach. 
a) Scheme of the synthesis of metal oxide multishelled hollow microsphere using a sequential templating approach. TEM images of as-prepared multishelled: b) ZnO, c) α-Fe₂O₃, d) Co₃O₄, e) SnO₂, f) Mn₂O₃, g) TiO₂, h) NiO, i) MnO₂, j) V₂O₅, k) LiMn₂O₄, l) TiO₂/Fe₂TiO₅, and m) (Co₂/3Mn¹/₃)(Co⁵/₆Mn¹/₆)²O₄ hollow microspheres. Scale bar is 200 nm.

b)-n) Control of the intershell spacing of multishelled ZnO hollow microspheres by adjusting heating processes. o) Control of the shell number of multishelled Co₃O₄ hollow microspheres by adjusting the adsorption conditions. p) Control of geometric parameters of V₂O₅ hollow structures. q) Control of the shell number of CoₓMnᵧO₉ by adjusting the molar ratio of Co/Mn.

in precursor solutions, as well as pretreating the CMSs with HCl solution (Figure 2o).\textsuperscript{[20]} Besides, the shell number, shell thickness, and morphology of V$_2$O$_5$ hollow nanostructures were also controlled through adjusting the adsorption conditions of anionic V precursor ions (Figure 2p).\textsuperscript{[30]} In addition with mixed metal oxide hollow structures (for example, Co$_x$Mn$_y$O$_z$), their structural parameters are controlled by simply changing the molar ratio of Co/Mn during the adsorption process, thus realizing the control on the metal oxides crystallization rate and resulted shell parameters (Figure 2q).\textsuperscript{[41]}

3.1.2. Soft Templating Method

Besides hard templates, some soft templates such as gas bubbles, supramolecular micelles, polymer vesicles, and so forth can also be applied to fabricate hollow nanostructures. Targeted shells grow along the interfacial region and hollow nanostructure could be obtained after the removal of the template.\textsuperscript{[28,34,61–67]}

Schüth and co-workers reported the synthesis of hollow polymer spheres (HPS), Pt, or PtCo bimetallic nanoparticles within the hollow carbon spheres (Pt@HCS or PtCo@HCS) by using polymer micelles as soft templates.\textsuperscript{[64]} As Figure 3a shows, P123 (EO20–PO70–EO20) and sodium oleate (SO) form micelles which then converted into uniform emulsions after mixing with acidic solutions. During the hydrothermal process, the polymerization of precursors takes place at the surface of emulsion droplets, leading to the formation of HPS. Besides, when platinum salts added, they were reduced to Pt nanoparticles by formaldehyde and encapsulated by HPS to obtain Pt@HPS which converted into Pt@HCS after pyrolysis under argon atmosphere. Furthermore, PtCo bimetallic nanoparticles within the hollow carbon spheres (Pt@HCS) were also fabricated by

![Figure 3](https://www.advancedsciencenews.com)

Figure 3. Fabrication of hollow nanostructures by soft templating method. a) Scheme for the fabrication of hollow polymer spheres, Pt nanoparticles or PtCo bimetallic nanoparticles within the hollow carbon spheres (Pt@HCS, PtCo@HCS). b) Scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM) images, and elemental mapping of PtCo@HCS. c) Formation of Cu$_2$O hollow structures using the CTAB template. d–g) TEM images of single- (d), double- (e), triple- (f), and quadruple-shelled (g) Cu$_2$O hollow structures. a,b) Reproduced with permission.\textsuperscript{[64]} Copyright 2014, Nature Publishing Group. c–g) Reproduced with permission.\textsuperscript{[34]} Copyright 2007, Wiley-VCH.
introducing the nucleation of cobalt metal on preformed Pt nanocrystals with ion exchange and annealing (Figure 3b). Additionally, other hollow nanostructures (Figure 3c–g), such as multishelled Cu₂O,[34] SiO₂,[66] and double-shelled ferricydrite hollow spheres,[67] were also achieved by adopting cetyltrimethylammonium bromide (CTAB) micelles, vesicles, and twice gas bubble as soft templates.

3.2. Template-Free Method

3.2.1. Kirkendall Effect

The classical Kirkendall effect in metallurgy refers to the dissimilar mutual diffusion rates of two metals, so that void occurs in the zone of the more rapidly diffusing material to compensate for the unequal material flow. Coming to the nanoscaled Kirkendall process, small voids are generated at the interface, enlarged through the surface diffusion of atoms, and finally evolve into a hollow cavity inside the shell.[29,68] Since first demonstrated by the Alivisatos group, Kirkendall effect has been widely used for rationally designing hollow nanostructures of various components, including Cu₂O, Fe₂O₃, ZnO, ZnAl₂O₄, Ce₁₋ₓZrₓO₂, CoS, ZnS, PbS, CuS, CdS, CoSe₂, AgₓSe, Cu₂₋ₓSeₓ, NiₓP or CoₓP, AlN, etc. [69–87] Representatively, Chen et al. reported the synthesis of Pt₃Ni hollow nanoframes using solid PtNi₃ polyhedra as the starting materials through the Kirkendall effect.[83] When oleylamine-capped PtNi₃ polyhedra was dispersed in nonpolar solvents, surface Ni atoms are more easily oxidized and dissolved than Pt atoms, which drives the surface compositional change of PtNi₃ from Ni-rich to Pt-rich, along with the formation and enlargement of void cavity to achieve nanoframes (Figure 4a–e). Besides, other complicated hollow nanostructures can also be obtained with the controlled Kirkendall process, such as Pt@CoO yolk–shell structure,[89] planar bilayer of ZnO-Al₂O₃,[84] single-crystalline NiₓP nanospheres,[86] etc.

3.2.2. Ostwald Ripening

Due to the great difference in interfacial energy between the smaller particles and the larger ones, smaller particles tend to dissolve and redissolve on larger particles during the crystalline growth process,[30] resulting in the further growth of larger particles and disappearance of smaller ones. This process is defined as Ostwald ripening, which has been adopted to synthesize various hollow nanostructures, such as Cu₂O, TiO₂, SnO₂, Fe₂O₃, Ni(OH)₂, Cu₃S, CdMoO₄, ZnWO₄, etc.[88–102] For example, a variety of Cu₂O hollow nanostructures, including shell-in-shell nanoparticle,[88] multiple-shell core–shell, and yolk–shell structures, have been demonstrated by different groups with the tailored Ostwald ripening process (Figure 5a–c).[89]

3.2.3. Ion Exchange

Ion exchange indicates the exchange of ions (either cations or anions) between a solution and a solid particle. It has been widely employed in the fabrication of hollow nanostructures.[9,31] As a successful example, Shen et al. reported the synthesis of ternary nickel cobalt sulfide (NiCo₂S₄) hollow structure through controlled ion exchange during the sulfidation process of nickel cobalt glycerate (NiCo-glycerate) spheres (Figure 6a).[18] At first, sulfide (S²⁻) ions react with metal ions at the surface of NiCo-glycerate and produce NiCo-glycerate@NiCo₂S₄ core–shell structure. Followed diffusion of S²⁻ ions inward and metal cations outward results in the continuous growth of the NiCo₂S₄ shell and formation of well-defined gap between the shell and inner NiCo-glycerate core. As reaction proceeds, the diffusion process slows down in the result of a secondary NiCo₂S₄ shell and enlargement of gap between individual shells, forming yolk–shell or ball-in-ball hollow spheres (Figure 6b,c). Moreover, with a proper control of the precursor system, a series of ion exchange processes were achieved by Xiong and Zeng.[43]
achieving single-, double-, triple-, or even quadruple-shelled Cu$_2$S hollow spheres.

3.2.4. Selective Etching

Selective etching represents the process that selectively removes part of single-component material to create cavity by chemical treatment or calcination. It applies for a large variety of materials, including SiO$_2$, periodic mesoporous organosilica (PMO), Prussian Blue, CoSn(OH)$_6$, ZnSn(OH)$_6$, ZnSnO$_3$, Zn$_2$SnO$_4$/SnO$_2$, etc., with a common feature that they all consist of a "soft" region and a "hard" one. For example, during the Stöber synthetic process, the hydrolysis of tetraethyl orthosilicate proceeds stepwisely to give monomers of different hydrolysis extent, leading to the formation of SiO$_2$ spheres with the condensation of these monomers. As a result, the inner region ("soft region") of SiO$_2$ spheres formed at the early stage has a low crosslinking degree and thus low chemical stability, whereas the outer layer forming "hard region." After some post-treatment process such as incubation, the unstable "soft region" can be stabilized and selectively etched to achieve hollow structures. Chen and co-workers reported the synthesis of multishelled AuNP@SiO$_2$ yolk–shell structures by a repeated SiO$_2$ deposition–incubation–etching method (Figure 7). Additionally, multishelled PMO spheres, CoSn(OH)$_6$, and ZnSn(OH)$_6$ hollow cubes have also been fabricated through selective etching.
4. Hollow Nanostructures for Energy Storage

The attractive structural and compositional features of hollow nanostructures endow them abundant advantageous characteristics, making them great promise in various energy storage technologies.

4.1. Lithium-Ion Batteries

Lithium-ion batteries have played an increasingly important role in portable electronics, hybrid and electric vehicles, and even grid-scale storage. However, with the ever-growing demands of newly emerging electronics and facilities, significant efforts still need to be made on the development of high-energy LIBs.

Metal oxide- or silicon-based electrodes are promising candidates to achieve a much higher capacity compared with the state-of-the-art graphite electrodes. However, a high energy usually accompanies with large volumetric change, which will induce unstable structure and poor cycling stability. Hollow nanostructures with an interior void space buffering the volume expansion and alleviating the structural strains can provide a better cycling stability than their solid bulk counterparts. Besides, other advantages are embraced by hollow nanostructures as electrode materials: 1) the larger specific surface area of hollow nanostructures provides an enlarged electrode-electrolyte contact area and increased accessible reactive sites, thus a larger gravimetric capacity; 2) the hollow structures ensure a shortened diffusion distance for both charges and ions, thus a better rate capability; more interestingly, complex hollow nanostructures demonstrate more advantages than their simple counterparts, such as larger volumetric capacity and better mechanical and electrochemical stabilities. Given these advantages, various kinds of hollow nanostructures have been fabricated as high-performance electrode materials for LIBs, including Co$_3$O$_4$, Fe$_2$O$_3$, Mn$_2$O$_3$, NiO, TiO$_2$, V$_2$O$_5$, Si, SiO$_x$, SnO$_x$, Li$_2$Ti$_2$O$_4$, LiMn$_2$O$_4$, or AB$_2$O$_4$ (A, B = Mn, Co, Fe, Ni, Cu, and Zn).

4.1.1. Metal Oxide–Based Hollow Nanostructured Electrodes

Metal oxides are attractive candidates as electrode materials for LIBs because of their high theoretical capacity and safety characteristics. Wang et al. fabricated single-, double-, triple- and quadruple-shelled Co$_3$O$_4$ hollow microspheres in high yield and purity through a sequential templating method. As anode materials for LIBs, Co$_3$O$_4$ hollow microspheres exhibited high specific capacity and good cycling stability, wherein triple-shelled Co$_3$O$_4$ one showed the highest specific capacity and best cycling performance (1117.3 mA h g$^{-1}$ was achieved at a high current density of 2000 mA g$^{-1}$) (Figure 8a,b), benefited from the optimal volume-occupying rate after lithiation, which guarantees a high volumetric specific capacity and good structure stability simultaneously (Figure 8c). TiO$_2$ is another type of promising anode material for LIBs due to its high thermal and chemical stability and high power density. In addition, multishelled TiO$_2$ hollow nanostructures exhibited significantly improved cycling performance and rate capability over that of the commercial Degussa P25, with 119 mA h g$^{-1}$ achieved at a current rate of 10 C even after 1200 cycles for the triple-shelled (Figure 8d–k).

Except for anodes, hollow nanostructured metal oxides have also shown great promise as cathode materials for LIBs. Vanadium oxide (V$_2$O$_5$) is an attractive cathode material for LIBs because of its high theoretical specific capacity and abundance. Multishelled V$_2$O$_5$ hollow microspheres was fabricated by the Wang group through a novel concept of competitive
anion-adsorption by CMS templates followed with a Trojan catalytic combustion process (Figure 8l–q). As cathode materials for LIBs, the triple-shelled V$_2$O$_5$ hollow microspheres exhibit a record-high initial specific capacity of 447.9 mA·h·g$^{-1}$ at 1000 mA·g$^{-1}$, good cycling stability (0.10% loss per cycle), and excellent rate capability (Figure 8r,s). The excellent performance is profited from the impressive stability and good electrochemical kinetics of the multishelled hollow structures which provide large lithium-storage sites, short diffusion length, effective buffering of volume change, and favorable distribution of the induced stress/strain.

Figure 8. Metal-oxide-based hollow nanostructured electrodes for lithium-ion batteries. a) Cycling stability test of Co$_3$O$_4$ hollow microspheres and commercial nanoparticles. b) Discharge capacity for Co$_3$O$_4$ triple-shelled hollow microspheres and commercial nanoparticles at different current densities. c) Illustration for the structure changes of Co$_3$O$_4$ with different structures during Li$^+$ insertion/extraction processes. TEM images of TiO$_2$ hollow microspheres: d) single-, e) double- f) triple-shelled, and g) double-, h) triple-, and i) quadruple-shelled with closed exterior double shells. j) Cycling performance of TiO$_2$ hollow microspheres at 1 C. k) Cycling performance at various current rates. TEM images of: l) thin single- and m) double-shelled, n) thick triple-shelled, o) thick single-shelled, p) thin triple-shelled, and q) multicavitated V$_2$O$_5$ hollow microspheres. r) Discharge capacity versus cycle number for V$_2$O$_5$ hollow microspheres and nanosheets at 1000 mA·g$^{-1}$. s) Electrochemical impedance spectroscopy (EIS) test for multishelled V$_2$O$_5$ hollow spheres and V$_2$O$_5$ nanosheets ($R_\text{ct}$, charge transfer resistance; CPE1, constant phase element; $Z_w$, Warburg impedance). a–c) Reproduced with permission. [20] Copyright 2013, Wiley-VCH. d–k) Reproduced with permission. [36] Copyright 2014, American Chemical Society. l–s) Reproduced with permission. [13] Copyright 2016, Nature Publishing Group.
4.1.2. Silicon-Based Hollow Nanostructured Electrodes

Besides metal oxides, silicon is another attractive anode material for high-energy LIBs due to its 10-time higher theoretical capacity over commercial graphite anodes. However, the 300% volume expansion of silicon during battery operation severely limits the application of silicon, giving rise to mechanical fracture, interparticle electrical contact loss, unstable SEI, and severe side reactions. Hollow nanostructured silicon with nanoscaled size has proved to effectively alleviate the stress/strain and buffer the volume expansion. As a result, abundant of nanostructured silicon has been developed as anode materials for lithium-ion batteries.\[138]\ In the Cui group alone, there have been 11 generations of nanostructured silicon designed.\[12,19,55,139–147]\ Below, we introduce several typical examples of hollow nanostructured silicon for lithium-ion batteries.

In 2012, to stabilize the electrode–electrolyte interface and prevent repeated SEI formation, Cui and co-workers designed a double-walled Si–Si\(_{0.4}\) hollow nanotube anode (Figure 9a–c).\[19]\ The outside Si\(_{0.4}\) wall allows the easy transport of lithium ions and is mechanically strong enough to restrict the second silicon wall to expand toward the inside void space. Thus, a stable SEI is formed and kept outside during cycling. As anodes for lithium-ion batteries, these double-walled Si–Si\(_{0.4}\) hollow tubes exhibited superior cycling stability with 88% capacity retention after 6000 cycles.

For nanosized silicon, severe side reactions may arise from the excessively large surface area, leading to unsatisfactory areal and volumetric capacity. To address these issues, Cui and co-workers developed a pomegranate-structured silicon secondary particle, each consists of many silicon nanoparticle@carbon yolk–shell particles (Figure 9d,e).\[12]\ The assembly of nanoparticles to microsized secondary particles greatly decreases the

![Figure 9. Silicon-based hollow nanostructured electrodes for lithium-ion batteries. a,b) SEM images of double-walled Si–Si\(_{0.4}\) nanotube (DWSiNT) before (a) and after (b) cycling. c) Capacity of DWSiNT cycled at various rates from 1 C to 20 C. d,e) TEM images of silicon pomegranates before (d) and after (e) lithiation. f) Delithiation capacity for the first 1000 galvanostatic cycles of the silicon pomegranate and other structures. g,h) TEM images of a nonfilling carbon-coated porous silicon microparticle before (g) and after (h) lithiation. i) Delithiation capacity for the first 1000 galvanostatic cycles of the porous silicon microparticle with different coatings. j,k) TEM images of SiMP@Gr structure before (j) and after (k) lithiation. l) Half-cell delithiation capacity of SiMP@Gr with no conductive additives. Bare and amorphous-carbon-coated SiMP are control samples with carbon-black conductive additives. The inset SEM/TEM images are the corresponding schematics of the structures. a–c) Reproduced with permission.\[19]\ Copyright 2012, Nature Publishing Group. d–f) Reproduced with permission.\[12]\ Copyright 2014, Nature Publishing Group. g–i) Reproduced with permission.\[146]\ Copyright 2015, American Chemical Society. j–k) Reproduced with permission.\[56]\ Copyright 2016, Nature Publishing Group.

surface area and increases the tap density. Besides, the internal void space can sufficiently buffer the volume expansion, while carbon shell limits most SEI formation to the outer surface and stabilizes it during cycling. As a result, superior cyclability (97% capacity retention after 1000 cycles), high Coulombic efficiency (CE) (99.87%), and large volumetric capacity (1270 mA h cm\(^{-3}\)) were achieved simultaneously (Figure 9f). In addition, a non-filling carbon-coated porous silicon microparticle (nC-pSiMP) consisting of interconnected primary silicon nanoparticles, and only its outer surface was coated with carbon, was also developed (Figure 9g,h).\(^{[146]}\) exhibiting a high areal capacity of 3 mA h cm\(^{-2}\) (Figure 9i).

Although great improvements have been achieved by the above works, the Coulombic efficiency is still unsatisfactory which is due to irreversible trapping of Li by the dendrites bonding of an amorphous carbon coating. Cui and co-workers introduced a graphene encapsulated silicon microparticle yolk–shell structure to further improve the Coulombic efficiency as well as the energy density (Figure 9j,k).\(^{[56]}\) The mechanically strong graphene enables a stable solid electrolyte interface, while the gap between graphene cage and silicon core accommodates volume expansion. As a result, the graphene-encapsulated Si microparticle exhibits a high initial Coulombic efficiency of 93.2% and stable cycling (Figure 9l). In addition, hollow nanostructured silicon interconnected with highly adhesive binder as integrated anode for lithium-ion batteries has also shown impressive cycling stability as demonstrated by Guo and co-workers.\(^{[148]}\)

### 4.2. Lithium-Metal Anodes

Lithium metal is the ultimate choice for the anode of a lithium battery because of its superb theoretical capacity (3860 mA h g\(^{-1}\) or 2061 mA h cm\(^{-3}\)), lowest electrochemical potential (−3.04 V vs the standard hydrogen electrode (SHE)), and its indispensability for Li–S and Li–air systems.\(^{[149–151]}\) However, many challenges still remain to be addressed, such as the dendrite formation and growth, unstable SEI, severe side reactions, and infinite relative volume change. Hollow nanostructures have shown to be good candidates to solve these problems: 1) hollow nanostructured lithium electrode can realize low local current density, thus inhibiting lithium dendrite growth; 2) as lithium hosts or coating layers, they can provide a stable interface between the electrode and electrolyte, thus stabilizing SEI and reducing side reactions; and 3) as lithium hosts, they can limit the lithium expansion within the host, thus improving cycling stability.\(^{[152–155]}\)

Cui and co-workers pioneered the concept of nanoscale interfacial engineering to stabilize SEI by coating a monolayer of interconnected amorphous hollow carbon nanospheres on the lithium-metal anode (Figure 10a–c).\(^{[14]}\) During deposition, Li ions pass through the carbon shell and deposit underneath, thus dendrites can be mechanically suppressed up to a current density of 1 mA cm\(^{-2}\). Moreover, the SEI are limited to the top of the carbon shell and moved together with it during cycling without fracturing. As a result, the Coulombic efficiency improves to ≈99% for more than 150 cycles, which is significantly better than the unmodified samples (Figure 10d).

Besides, the Cui group found that Au with a definite Li solubility exhibited a lower nucleation barrier than other substrates, which could guide the preferential deposition of Li on Au. Thus, a structure of Au nanoparticles embedded in carbon hollow sphere structure for was designed by the Cui group for lithium-metal anodes (Figure 10e,f).\(^{[21]}\) During deposition, the lithium metal is found to preferentially and mainly grow inside the hollow carbon spheres without any lithium dendrite growth. The mechanically stable carbon spheres insures a stable SEI formation. Such selective deposition and stable encapsulation of lithium metal eliminate dendrite formation and enable improved cycling stability. Even in corrosive alkyl carbonate electrolytes, this structured lithium electrode shows a high Coulombic efficiency of 98% for more than 300 cycles (Figure 10f).

Although great progress has been achieved for hollow nanostructured lithium-metal anodes, issues such as the decreased initial Coulombic efficiency and low energy density of the whole battery due to the introduced nanostructured host need to be addressed. New forms of well-designed structures, especially the composite structures are expected to be developed in the future to further improve the Coulombic efficiency, energy density, and safety of lithium-metal anodes.

### 4.3. Lithium–Sulfur Batteries

Lithium–sulfur batteries, owning to its high theoretical energy density of 2600 W h kg\(^{-1}\) or 2800 W h L\(^{-1}\), natural abundance and nontoxicity of sulfur, have been widely recognized as promising candidates for next-generation batteries.\(^{[151–160]}\) Despite the overwhelming advantages, large-scale commercial use is so far postponed by some key challenges: i) the insulating nature of sulfur and its discharge products, leads to the poor material utilization and low actual specific capacity; ii) the dissolution of polysulfides induces shuttle effect, causing material loss, bad stability and low Coulombic efficiency; and iii) the 80% volume expansion during lithiations results in the damage of electrode structure.\(^{[22,155,161]}\) In recent years, extensive efforts have been devoted to the engineering of various sulfur hosts to improve the conductivity, abate the dissolution and enhance the stability of sulfur electrodes. Among various sulfur hosts, hollow nanostructures demonstrate some unique advantages.\(^{[162,163]}\) 1) the large internal void space not only provides high sulfur loading but also accommodates the volume expansion during lithiation; 2) the conductive shells improve the conductivity and effectively confine the soluble polysulfides.

Hollow carbon materials have been widely developed as sulfur hosts because of their good electrical conductivity, light weight and large pore volume.\(^{[15,23,164–168]}\) Cui and co-workers designed a hollow carbon nanofiber-encapsulated sulfur electrode structure for effective trapping of polysulfides.\(^{[58]}\) Anodic aluminum oxide templates were used not only to guide the growth of carbon nanofiber, but also confine sulfur infusion into the hollow fibers (Figure 11a). The high aspect ratio of the carbon nanofibers is ideally for trapping polysulfides, and the thin carbon wall facilitates lithium-ion transport. Besides, these nanofibers provide a large specific surface area for high sulfur-loading amount and prevent pulverization of electrode materials during cycling. As a result, a high specific capacity of...
about 730 mA h g\(^{-1}\) was observed at C/5 rate (1 C = 1675 mA g\(^{-1}\)) after 150 cycles (Figure 11b,c). The Guan group developed a tube-in-tube carbon nanostructure with multiwalled carbon nanotubes (MWNTs) embedded within hollow carbon nanotubes and used for trapping sulfur (S-TTCN) (Figure 11d).

The obtained S-TTCN achieved impressive rate capability with 550 mA h g\(^{-1}\) still delivered even at a rate of 6 A g\(^{-1}\) (Figure 11e,f). This is benefited from the good electrical conductivity and porous carbon layers which can effectively inhibit the dissolution of lithium polysulfides. In addition, the Cui group found that the detachment of Li\(_x\)S from the carbon surface is a key factor causing the capacity decay over cycling,

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**Figure 10.** The application of hollow nanostructures for lithium-metal anodes. a) Schematic for the design of a hollow carbon nanosphere coated on the Cu substrate to stabilize SEI layer. b) Cross-sectional SEM image of the hollow carbon nanospheres. c) Deposited Li elevates the hollow carbon nanosphere layer due to weak binding between the carbon layer and the Cu substrate. d) Comparison of cycling stabilities of the Cu electrode coated with hollow carbon nanospheres (solid symbols) and the bare Cu electrode (hollow symbols) at 0.5 or 1.0 mA cm\(^{-2}\). e) Schematic of Li-metal nanocapsule design with Au NPs loaded inside hollow carbon spheres. f) Coulombic efficiency of different electrodes when cycled in alkyl carbonate electrolyte. a–d) Reproduced with permission.© 2014, Nature Publishing Group. e,f) Reproduced with permission.© 2016, Nature Publishing Group.
Except for carbon host, conductive polymer or metal oxide additives including Al₂O₃, La₂O₃, Mg₀.₆Cu₀.₄O, and Mg₀.₆Ni₀.₄O have also been proved to effectively hinder polysulfides dissolution through chemical adsorption.⁴¹⁷⁰⁻⁴¹⁷⁴ The Cui group reported a 3D hydrogen reduced TiO₂–sulfur inverse opal structure to achieve both sulfur physical encapsulation and polysulfides chemical binding simultaneously.⁵⁹ Sulfur can infuse into the TiO₂ void space through the openings at the top surface, while the strong binding interaction between hydrogen reduced TiO₂ with polysulfides effectively prevent the polysulfides from dissolution (Figure 11i). With such TiO₂–sulfur yolk–shell structure, a reversible capacity of ≈890 mA h g⁻¹ remained after 200 cycles of charge/discharge at a C/5 rate (Figure 11j,k). Despite the impressive progress, further improvement of performance can be obtained by optimizing the host-sulfur species interaction and the content of the host, as well as better understanding of the reaction mechanism during the process of Li–S batteries.

4.4. Supercapacitors

Electrochemical capacitors, also named supercapacitors, which can bridge the big gap of energy density and power density between batteries and conventional capacitors, have witnessed significant advancement and great potential in many application areas.¹⁷⁵⁻¹⁸¹ In recent years, tremendous efforts have been
focused on the improvement of the energy density and cycling
stability of supercapacitors, without sacrificing their power den-
sities. Compared to solid bulk materials, hollow nanostructured
materials have been proved to be more suitable electrode mate-
rals for supercapacitors given the following advantages[8,182,183]:
1) hollow nanostructure can provide more accessible reactive
sites, resulting in a larger energy density; 2) the porous shells
enhance the accessibility of the electrolyte to the active surface,
thus shortening transport length for both ions and charges,
resulting in a higher power density; and 3) more importantly,
for complex hollow nanostructures with multiple shells, the
exterior shell protects the interior shells from electrochemical
dissolution as well as mechanical damage, resulting in a better
cycling stability.

The Cui group reported a bamboo-like graphitic carbon
nanofiber with a well-balanced macro-, meso-, and micro-
porosity as electrode materials for flexible all-solid-state
supercapacitors (Figure 12a–c), it exhibited excellent mechan-
ical flexibility and extraordinarily high stability with ≈100% of
the initial capacitance retained after 5000 cycles.[184]

Compared to carbon materials, metal oxides, especially
those with multiple redox states can afford a much higher
capacitance and have demonstrated great promise as elec-
trode materials for supercapacitors. The Zhu group prepared
hollow fusiform RuO2·xH2O through a hard template method
(Figure 12d).[185] These well-defined hollow RuO2·xH2O struc-
ture exhibited a typical pseudocapacitive behavior as electrode
material for supercapacitor with an obvious rectangular-like
shape observed from the CV curve (Figure 12e). Moreover, the
long-term cycling stability is also very impressive with 823 F g⁻¹
remained after 1000 cycles (Figure 12f).

Although RuO2 exhibits prominent capacitive properties,
its high cost and environmentally hazardous property limit its
practical application. Transition metal oxides such as MnO2,
are cheaper and environmentally friendly and have drawn wide
interest as electrode materials for supercapacitors. The Li group
fabricated urchin-like MnO2 hollow spheres through a soft-
template method (Figure 12g).[186] Among three types of MnO2
structures, urchin-like hollow spheres exhibited the highest
specific capacitance and best rate capability (Figure 12 h, i), it

![Figure 12. The application of hollow nanostructures for supercapacitors. a) TEM images of bamboo-like carbon nanofibers. b) Current voltage (CV) profiles of the carbon nanofiber electrode between 10 and 100 mV s⁻¹. c) Cycling stability of a carbon electrode at 10 A g⁻¹. d) TEM image of hollow fusiform RuO2·xH2O. e) Cyclic voltammogram measured at different scan rates. f) Cycling performance of RuO2·xH2O electrode. g) TEM image of urchin-like MnO2 hollow nanospheres. h) Cyclic voltammogram curve of different structured MnO2, scanned at 5 mV s⁻¹. i) Specific capacitance at different current densities. a–c) Reproduced with permission.[184] Copyright 2015, American Chemical Society. d–f) Reproduced with permission.[185] Copyright 2013, Royal Society of Chemistry. g–i) Reproduced with permission.[186] Copyright 2013, Royal Society of Chemistry.](image-url)
is ascribed to the hollow urchin-like structure which not only contributes to the large specific surface area but also serves as electrolyte reservoir thus enabling the inside of the MnO$_2$ accessible to the electrolyte and increasing the utilization of active materials.

Besides, other hollow nanostructures such as hollow carbon sphere, Mn$_3$O$_4$, Co$_3$O$_4$, MnO$_2$, NiO, CoS, NiS, MnO$_2$/TiN, Ni(OH)$_2$, NiCo$_2$O$_4$, NiCo$_2$S$_4$, etc., have also been explored as high-performance electrodes for supercapacitors.$^{18,38,125,187–195}$ With a comprehensive and deep understanding of the relationship between the structure and function, smarter hollow nanostructure–based supercapacitors will be developed to further improve the performance.

4.5. Dye-Sensitized Solar Cells

Dye-sensitized solar cells have been demonstrated as one of the most promising photovoltaic devices to offer green, sustainable, renewable and large-scale energy generation.$^{196–205}$ Although great improvement has progressed rapidly for DSSCs, there are still some challenges to address, of which charge recombination and poor light harvesting efficiency are the main ones.$^{7,206,207}$ Hollow nanostructures as photoanodes for DSSCs can effectively relieve these problems. The shell structures simultaneously increase the diffractions and the reflections, thus leading to a better light harvesting efficiency; the penetration of electrolyte into the hollow space shortens the charges transport length and inhibits the charge recombination. Especially, complex hollow nanostructure can possess a better light harvesting efficiency over their simple counterparts, due to the multiple diffractions and reflections on the multiple shells or chambers. In addition, their larger volumetric surface area can provide a higher dye loading amount.$^{208,209}$

Given that, large amounts of hollow nanostructures have been designed as photoanodes for DSSCs, such as TiO$_2$, ZnO, SnO$_2$, Au@TiO$_2$, TiO$_2$/SnO$_2$, ZnO/SnO$_2$, etc.$^{16,24,209–216}$ The Wang group successfully synthesized multishelled ZnO hollow microspheres with controlled shell number and inter-shell spacings as photoanodes for DSSCs (Figure 13a).$^{16}$ They found that the light scattering ability of hollow microspheres increases with the increase of shell number, and a close double shell in the exterior can make further improvement. As a result, quadruple-shelled ZnO hollow microspheres with close double shells in the exterior achieved a high efficiency of 5.6% (Figure 13b–d). Besides ZnO, quintuple-shelled SnO$_2$ hollow microspheres with closed exterior double shells (5S–SnO$_2$–HMS–CDS) are also designed and used as photoanodes or scattering layer for DSSCs, exhibiting high conversion efficiency of 7.18% or 9.53% benefiting from the larger bandgap and faster charge carriers mobility of SnO$_2$ (Figure 13e,f).$^{24}$

In addition, other hybrid hollow nanostructures have also been designed as photoanodes for DSSCs to improve the conversion efficiency, including Au@TiO$_2$ core–shell hollow submicrospheres,$^{214}$ hybrid TiO$_2$/ZnO hollow particles,$^{210}$ TiO$_2$-coated multilayered SnO$_2$ hollow microspheres,$^{212}$

Figure 13. The application of hollow nanostructures for dye-sensitized solar cells. a) TEM images (scale bars are 300 nm), b) $J$–$V$ curves of DSSCs, c) corresponding UV–vis diffuse reflectance spectra, and d) schematic showing the multiple reflection of light by ZnO hollow microspheres: i) single-shelled, ii) double-shelled, iii) triple-shelled, iv) quadruple-shelled, v) double-shelled (with close double shells outside), vi) triple-shelled (with close double shells outside and smaller hollow core), and vii) quadruple-shelled (with close double shells outside and double-shelled hollow core). e) TEM images of quintuple-shelled SnO$_2$ hollow microspheres. f) $J$–$V$ curves of the photoanodes composed of 6 µm 5S–SnO$_2$–HMS (top) and 10 µm P25 layer (bottom). a–d) Reproduced with permission.$^{16}$ Copyright 2012, Wiley-VCH. e,f) Reproduced with permission.$^{24}$ Copyright 2014, Wiley-VCH.
etc. Despite the achievements, the efficiency still needs to be further improved for practical application through more fine manipulation on the compositional and geometric parameters of the structures.

4.6. Electrocatalysis

Energy and environment crisis has triggered urgent demand for renewable and green energy conversion technologies, such as water splitting and fuel cells. A major challenge in these sustainable energy conversion technologies is the development of highly efficient and robust electrocatalysis to catalyze involved electrochemical reactions, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), methanol oxidation reaction (MOR), etc.\textsuperscript{[227,230,231,232]} Hollow nanostructured electrocatalysis has drawn worldwide interest, given the following key advantages:\textsuperscript{[219]} 1) Different catalytic functionality or species can be placed in sequentially localized compartments, which not only enables the combination of incompatible catalytic functions within the same material but also enables cascade reactions; 2) selectivity of catalytic reactions can be improved either by controlling the shell pore structure to sieve molecules or by controlling the shell chemical compatibility to adjust molecule diffusion; 3) the large specific surface area improves catalyst loading amount and increases contact area between catalysts and reactants; and 4) the thin shell facilitates mass transport.

The Sun group reported a microwave-assisted synthetic route to obtain hollow cobalt sulfide nanoprisms (MW-CoS) (Figure 14a).\textsuperscript{[226]} Notably, MW-CoS exhibited a better catalytic HER activity than ST-CoS prepared though traditional solvothermal method: the overpotentials required to drive the same cathodic current densities are much smaller and the Tafel slope is also lower than that of ST-CoS (Figure 14b). Moreover, the slope of the linear relationship between current density and scan rate for MW-CoS is larger than that of ST-CoS, suggesting that MW-CoS is more effective in enlarging the catalytically active surface area which agrees well with its larger specific surface area and higher total pore volume measured by the BET method. In addition, other hollow nanostructured electrocatalysts including Mo\textsubscript{0.9}C,\textsuperscript{[221]} WC,\textsuperscript{[222]} IrNi\textsubscript{N},\textsuperscript{[223]} Ni\textsubscript{2}P,\textsuperscript{[224]} Co\textsubscript{0}P,\textsuperscript{[225]} CoMoS\textsubscript{3},\textsuperscript{[226]} etc., have also been reported to improve hydrogen evolution reaction activity.

Despite the highly improved HER activity, large-scale H\textsubscript{2} production could be hindered by the sluggish oxygen evolution reaction at the anode. The Yan group fabricated α-Ni(OH)\textsubscript{2} hollow microspheres assembled by nanosheets (Figure 14f), which afforded the largest oxygen-evolving current among all the studied catalysts and reached a current density of 10 mA cm\textsuperscript{−2} at a small overpotential of 0.331 V (Figure 14g).\textsuperscript{[227]} The Tafel slope of α-Ni(OH)\textsubscript{2} hollow sphere is a mere \textasciitilde42 mV decade\textsuperscript{−1}, which is much smaller than that of all other catalysts studied including RuO\textsubscript{2} (Figure 14h), demonstrating its more efficient kinetics of water oxidation.

Besides HER and OER, hollow nanostructures have also demonstrated significant improvement in electro-catalyzing kinetics of water oxidation. The Wang group reported a synthesis of N-doped carbon nanotube frameworks (NCNTFs) derived from metal–organic frameworks.\textsuperscript{[215]} Remarkably, the NCNTF sample exhibits higher ORR activity than the commercial Pt/C electrocatalyst in terms of half-wave potential (\(E_{1/2}\): 0.87 V vs 0.84 V in Figure 14j). The smaller Tafel slope of NCNTFs than that of Pt/C further confirms the better ORR activity of the NCNTFs. Furthermore, the NCNTFs electrode showed superior stability to the Pt/C electrode: about 96% of the original current density is retained for the NCNTFs electrode, whereas only 71% left for the Pt/C electrode (Figure 14k).

In fuel cells, platinum is one of the most efficient electrolys. However, it is expensive and source-limited. A feasible approach is to alloy platinum with nonprecious metals and design hollow nanostructures thus fully expose the platinum activity. The Lou group report the synthesis of PtCu\textsubscript{3} nanocage (Figure 14l) as attractive electrocatalyst for methanol oxidation reaction.\textsuperscript{[228]} The specific electrochemical active surface area (ECSA) of PtCu\textsubscript{3} is three times that of PtCu\textsubscript{4} solid nanoparticles (Figure 14m). Besides, the methanol oxidation current density of PtCu\textsubscript{3} nanocages (14.1 mA cm\textsuperscript{−2}) is higher than both that of PtCu\textsubscript{4} nanoparticles (8.4 mA cm\textsuperscript{−2}) and the commercial Pt electrocatalyst (12.8 mA cm\textsuperscript{−2}). The enhanced MOR performance could be attributed to the unique hollow nanostructure and possible synergetic effect of Pt and Cu components. In addition, other Pt-based hollow nanostructures including PtAg/C,\textsuperscript{[229]} PtNi,\textsuperscript{[230]} and PtCu\textsuperscript{231} have also demonstrated superior electrocatalysis performance.

4.7. Photoelectrochemical Cells

Photoelectrochemical cells integrate photocatalysis with electrocatalysis, where photoabsorption excites the generation of electron–hole pairs while the applied potential facilitates the separation of photoinduced carriers. As another type of photovoltaic devices, photoelectrochemical cells can convert solar light into storable chemical energy, and have been applied for water splitting, wastewater treatment and CO\textsubscript{2} reduction.\textsuperscript{[232–236]} Engineering of solids as hollow nanostructures can provide intrinsic advantages to realize highly efficient PEC cells, such as high specific surface area which provides more catalytic centers, porous shell structure which facilitates mass transport and more efficient light harvesting due to the shorter charge carrier length and light trapping effect within the inner void space.\textsuperscript{[219]} As a result, various hollow nanostructures such as Sn-doped Hollow Alpha-Fe\textsubscript{2}O\textsubscript{3}, urchin-like TiO\textsubscript{2}, TiO\textsubscript{2} inverse opal embedded with ZnO nanowires and sensitized with CdS quantum dots, hollow microspheres consisting of TiO\textsubscript{0.9}O\textsubscript{2} and graphene nanosheets, CuO–TiO\textsubscript{2},N\textsubscript{2} hollow nanocubes, Bi\textsubscript{2}WO\textsubscript{6} hollow microspheres, etc., have been demonstrated for efficient PEC cells.\textsuperscript{[237–241]}

Cheng and co-workers fabricated urchin-like TiO\textsubscript{2} which is assembled with a 4 μm hollow TiO\textsubscript{2} spheres core and radial TiO\textsubscript{2} nanorod shell (Figure 15a).\textsuperscript{[239]} When applied as photo-anode for PEC water splitting, urchin-like TiO\textsubscript{2} electrode exhibited a superior performance, achieving a highest photocurrent of \(0.9 \text{ mA cm}^{-2}\), which is about 4.5 times larger than that of TiO\textsubscript{2} microsphere photoanode (Figure 15b). Besides, urchin-like TiO\textsubscript{2} electrode showed a much better photoswitching
performance with fast response and recovery times (Figure 15c). Compared to bare TiO$_2$, TiO$_2$-based composites have proved to be better candidates for PEC water splitting. The Fan group designed 3D-ordered nanobushes consisting of dense networks of ZnO nanowires embedded within TiO$_2$ inverse opal nanostructures (Figure 15d).
CdS quantum dots, these nanobushes demonstrated a great promise for PEC hydrogen generation: achieved an impressive photocurrent density of 6.2 mA cm$^{-2}$ (Figure 15e), as well as fast photo response and good photostability (Figure 15f).

In addition to water splitting, PEC cells for CO$_2$ reduction stands out with the potential to simultaneously address the energy and environmental concerns. Schaak and co-workers prepared hollow CuO nanocubes decorated with nanoparticles of titanium oxynitride (TiO$_2$-$N_x$) using Cu$_3$N as a sacrificial template (Figure 15g).\cite{239} UV–vis diffuse reflectance spectra show that the CuO–TiO$_2$-$N_x$ hollow nanocubes absorb more in the 350–500 nm range than the CuO control, which suggests that the TiO$_2$-$N_x$ component contributes to the absorbance below 500 nm (Figure 15h,i). As a result, the methane production rate for the CuO–TiO$_2$-$N_x$ nanocubes is 41.3 ppm g$^{-1}$ h$^{-1}$, which was 1.5 and 2.5 times higher than for CuO@TiO$_2$ core–shell nanostructure and commercial Degussa P25 reference materials, respectively. The superior PEC performance of CuO–TiO$_2$-$N_x$ nanocubes is ascribed to the advantageous heterojunctions alongside a hollow nanostructure, which exposes both joint phases to reactants and improves light harvesting.
5. Summary and Outlook

We have highlighted the progress of designing hollow nanostructure to effectively address the challenges of energy storage, conversion, and production technologies. By exploring the correlation between hollow nanostructures and their energy-related performances, some in-depth understandings about the effect of structure engineering on performance are presented here, which enable the better design of hollow nanostructures to fulfill the requirements of specific application and simultaneously enrich the diversity of hollow nanostructure family. We believe future efforts should be devoted to the following aspects to further boost this field.

For the design and synthesis of hollow nanostructures, first, the tedious synthesis procedures with limited yield should be replaced with more facile and scalable methods. In addition, factors such as industrial scalability, environmental feasibility, and the cost should also be considered when developing new synthetic methodologies. Second, the in-depth understanding of the basic material science and chemical reaction mechanism involved in the fabrication process, which is key to the precise control of hollow nanostructures, are expected to be achieved in the future. Third, except for oxides or sulfides, the breadth of hollow nanostructured materials should be improved to other important materials such as carbides, nitrides, fluorides, phosphides, selenides, etc. Lastly, the further development on diverse structures is expected to widen the application areas. Complex hollow materials with Janus structures or heterogeneous counterparts with different compositions in different shells are ideal candidates for cascade reactions. Hollow structures with more shells or interior chambers are anticipated to enhance the merits of hollow nanostructures and potentially improve the performance.

For the application part, the detailed and accurate explanation to the improvement of energy storage performance by adopting hollow nanostructures is, to some extent, insufficient and lack of strong evidences. This could be progressively improved by in situ observation of the material transformation behaviors at the atomic level with the assistance of theoretical calculation and advanced characterization techniques. Additionally, one should note that the situations of hollow nanostructures in different applications would be very different. Therefore, the precise design of hollow nanostructures for specific application is required. Specifically, the void-to-solid volume ratio in the hollow structures should be carefully optimized to ensure enough void space to buffer the volume expansion of silicon, metal oxide, lithium metal, sulfur, or other electrode materials, meanwhile maximize their volumetric energy density. Moreover, the ratio of hollow nanostructured host in the overall electrode should also be optimized to achieve high energy density without sacrificing other merits. In addition, the large specific surface area of hollow nanostructures for LIBs, SCs, or lithium-metal anodes can also be double-edged sword: on the one hand it can increase reactive sites and/or decrease local Li-deposition current; on the other hand, it can introduce severe side reactions and induce low Coulombic efficiency. Therefore, great effort should be devoted to the surface modification of hollow nanostructures to selectively inhibit the side reactions while maintaining the desired reactive sites. Inversely, with regard to DSSCs, PEC cells and Li–S batteries, it is generally favorable to improve the specific surface area of hollow nanostructured photoanodes or sulfur host, thus enhancing the loading capacity for DSSCs and PEC cells, and promoting entrapping of polysulfides for Li–S batteries. Besides, the design of hollow nanostructures combined with materials of different light-absorption ability is also worth explored to further enhance the light harvesting for DSSCs and PEC cells. With regard to electrocatalysis, the higher concentration of structural defects in hollow nanostructures may modify the electronic structure of electrocatalysis and optimize the binding of intermediates, thus enhancing the electrocatalysis performance. Finally, to make hollow nanostructures evolve from proof-of-concept studies and reach practical application, their porosity should be finely optimized to ensure a sufficient mechanical sturdiness to resist the compression (e.g., calendering process during the electrode fabrication) or shear forces (e.g., fluidized-bed reactors).

Given the continuous efforts devoted to this field, we are confident that the future design of hollow nanostructures can solve the emerging challenges, further improve the performance, and accelerate large-scale energy storage applications.

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Conflict of Interest

The authors declare no conflict of interest.

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