

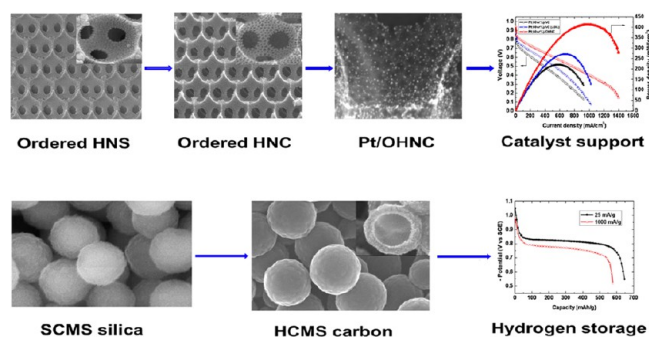
Hierarchical Nanostructured Carbons with Meso–Macroporosity: Design, Characterization, and Applications

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CONSPECTUS



Nanostructured porous carbon materials have diverse applications including sorbents, catalyst supports for fuel cells, electrode materials for capacitors, and hydrogen storage systems. When these materials have hierarchical porosity, interconnected pores of different dimensions, their potential application is increased. Hierarchical nanostructured carbons (HNCs) that contain 3D-interconnected macroporous/mesoporous and mesoporous/microporous structures have enhanced properties compared with single-sized porous carbon materials, because they have improved mass transport through the macropores/mesopores and enhanced selectivity and increased specific surface area on the level of fine pore systems through mesopores/micropores. The HNCs with macro/mesoporosity are of particular interest because chemists can tailor specific applications through controllable synthesis of HNCs with designed nanostructures.

An efficient and commonly used technique for creating HNCs is “nanocasting”, a technique that first involves the creation of a sacrificial silica template with hierarchical porous nanostructure and then the impregnation of the silica template with an appropriate carbon source. This is followed by carbonization of the filled carbon precursor, and subsequent removal of the silica template. The resulting HNC is an inverse replica of its parent hierarchical nanostructured silica (HNS). Through such nanocasting, scientists can create different HNC frameworks with tailored pore structures and narrow pore size distribution. Generally, HNSs with specific structure and 3D-interconnected porosity are needed to fabricate HNCs using the nanocasting strategy. However, how can we fabricate a HNS framework with tailored structure and hierarchical porosity of meso–macropores?

This Account reports on our recent work in the development of novel HNCs and their interesting applications. We have explored a series of strategies to address the challenges in synthesis of HNSs and HNCs. Through careful control of experimental parameters, we found we could readily create new HNSs and HNCs with tailored structure and hierarchical porosity. In this Account, we describe the applications of the HNCs in low-temperature fuel cells, in Li ion batteries, in quantum-dot-sensitized solar cells (QDSSCs) and as hydrogen storage materials. Fuel cell and QDSSC polarization performance data reveal that both the ordered HNC and spherical HNC with uniform macro- and mesoporosity demonstrate superior catalyst support effect and considerably enhanced photovoltaic performance due to their incredible structural characteristics. For hydrogen and lithium storage applications, primary experimental results show that spherical HNCs with uniform macroporous core/mesoporous shell and ordered HNC are highly beneficial in terms of a high hydrogen (or Li) uptake, good rate capability and excellent cycling retainability. These data suggest that the innovative HNCs with tailored nanostructure may find promising applications in the rapid and efficient storage of hydrogen (or Li).

Introduction

Nanostructured porous carbon materials are attracting much interest due to their potential applications as sorbents,¹ for separation and filtration,² as photonic crystals,³ as catalyst supports for low-temperature fuel cells,⁴ as electrode materials for electrochemical capacitors,⁵ in lithium ion batteries,⁶ in solar cells,⁷ as hydrogen storage systems,⁸ and as sensors and in other emerging nanotechnologies. Novel synthesis methods have been developed to prepare porous carbon materials with designed morphology, porosities, and architectures, especially carbon frameworks with hierarchical porosity, namely, mesopores in combination with macropores or micropores. Due to their unique structural features compared with those of single-pore carbon materials, such as macropores connected with mesopores, the design of hierarchical nanostructured carbons (HNCs) with tailored macropores/mesopores has developed into an important research area.

A very effective and most commonly used technique for creating HNCs is “nanocasting”, a technique that involves first the creation of a sacrificial hierarchical nanostructured silica (HNS) template, followed by the impregnation of the HNS template with an appropriate carbon source, then carbonization of the filled carbon precursor, and subsequent removal of the template. The resulting carbon is an inverse replica HNC of its parent HNS. Mainly ordered mesoporous carbons (OMCs) and disordered HNCs with macro/mesoporosity have been reported through this technique.⁹ However, the pore size of OMCs is difficult to control and usually less than 5 nm,¹⁰ which is greatly different from their parent ordered mesoporous silicas whose pore size can be readily tuned through varying the temperature, altering the chain length of the surfactants and molecular weight of the block copolymers,¹¹ or adding organic swelling agents.¹² Single-sized OMCs with small mesopores have found many limitations in some specific applications where rapid mass transport is required. On the other hand, hierarchical meso- and macroporous carbons can be also prepared through a soft template approach using the spinodal decomposition of a mesophase pitch carbon precursor and organic polymers.¹³ However, in this case, disordered meso- and macropores with different pore sizes ranging from a few nanometers to several micrometers were obtained, resulting in relatively lower surface area unlike HNCs with uniform pore size and high surface area of current topic in this Account, which are generated from nanocasting of sacrificial hard HNSs.

Major challenges for fabrication of ordered HNCs (OHNCs) with both 3D-interconnected macroporous and mesoporous structures lie in complexity and difficulty of creation of interconnected meso–macroporous HNSs with long-range order. To date, several strategies have been developed to prepare ordered and interconnected meso–macroporous HNSs mainly through the combination of colloidal crystal as macrotemplate and inorganic precursors and surfactant (or copolymer) as mesotemplate.^{14–20} Silica monoliths with hierarchical porosity have been also prepared mainly using dual template approaches and similarly templated to produce carbon monoliths, which exactly replicate the pore hierarchy of the monolith template.²¹ Recently, ordered carbon aerogels (OCA) were developed in which colloidal crystals of polystyrene (PS) spheres were used as templates.^{22,23} Ordered arrays of PS spheres were infused with a resorcinol–formaldehyde (RF) sol–gel solution. Periodic macroporous RF aerogels were obtained after supercritical drying with liquid carbon dioxide. These materials can be carbonized under N₂ to afford the corresponding macroporous OCAs. More recently, Cheng prepared HNCs by using silica microspheres as hard template and F127 as soft template.²⁴ Our previous work on synthesis of OHNCs with both interconnected macroporous and mesoporous structures²⁵ may provide some significant and key information on how to fabricate ordered meso–macroporous HNSs, which are the basic prerequisite for fabrication of OHNCs through nanocasting. Although some strategies have been developed to prepare ordered macro–mesoporous HNSs,^{14–16} the procedures involved in these strategies are rather complex and time-consuming. Our recent work on the synthesis of ordered bimodal porous silica by a facile sol–gel approach greatly simplifies the procedure and is supposed to provide further insights into easy synthesis of ordered macro–mesoporous HNSs and OHNCs.²⁶ Apart from macro–mesoporous OHNCs, spherical HNCs with fantastic specific nanostructures such as hollow macroporous core/mesoporous shell have been developed through nanocasting technique.²⁷ Although they are cataloged as mesoporous HNCs, their hollow macroporous cores actually play key roles for fast mass transport⁵ just like the macropores in OHNCs, which differ considerably from the other mesoporous HNCs. Furthermore, the hollow macroporous cores, which are connected and open to the outer mesoporous shell can serve as an electrolyte reservoir, facilitating mass transport and enabling hollow core–mesoporous shell carbons (HCMSCs) to perform better than other HNCs.²⁸ For the similarity in the roles of macropores and great

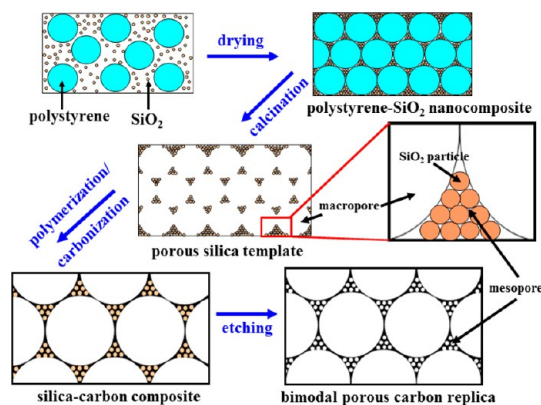


FIGURE 1. Schematic illustration for the synthesis of OHNC.²⁵ Adapted with permission from ref 25. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

potential applications generated by their specific hierarchical nanostructures, the HCMSCs are also presented in this Account.

Due to their unique structural characteristics, particularly 3D-interconnected nanostructures with hierarchical porosity, providing not only large specific surface area for high catalytic activity but also highly developed hierarchical macro/mesoporosity for fast mass transport, the HNC materials have demonstrated considerably improved performance wherever employed in fuel cells,⁴ solar cells,⁷ and hydrogen⁸ and Li⁶ storage applications.

Fabricating HNCs with Ordered Macro/Mesoporous Array

1. Fabrication of OHNC through Nanocasting Using OHNS as Template. This synthesis strategy involves two main steps: (i) synthesis of OHNSs through self-assembly of PS spheres with colloidal dispersion of small silica particles followed by pyrolysis to remove PS array and (ii) synthesis of OHNCs through nanocasting of the OHNS template. A representative schematic diagram for this synthesis strategy is illustrated in Figure 1 and outlined in detail in the following paragraphs.

For a typical synthesis of an OHNS, monodisperse PS spheres were first mixed with a colloidal dispersion of much smaller silica particles. Silica is one of the most commonly used materials to fabricate colloidal crystals. Furthermore, the surfaces of the silica spheres are usually terminated with silanol groups ($-\text{Si}-\text{OH}$), enabling covalent grafting of versatile functional groups such as $-\text{NH}_2$, $-\text{SH}$, $-\text{COOH}$, $-\text{NCO}$, and $-\text{CHO}$, which can be introduced into the surface layer of polymer spheres such as PS.²⁹ Upon gradual drying of the mixture, the PS spheres self-assemble into an ordered lattice

where the mesosized smaller silica particles are forced to pack closely at the interstices between the PS spheres, which leads to the generation of particulate silica gels around the ordered PS lattice. Next, the resulting composite was slowly heated to 773 K under air to remove the PS colloids and to sinter the silica nanoparticles, which resulted in an OHNS composed of particulate silica gels in the wall of the ordered macropore array. Such calcination also plays an important role of reinforcing the silica framework structure through solid connections at their contact points by slightly sintering the neighboring silica particles. Interestingly, the voids between the sintered silica particles in the resulting OHNS also provide fully interconnected mesopores. The size distribution of the small silica particles is the key parameter in creating 3D long-range order. If the size distribution of the small silica particles is too big, a much lower amount of silica particles than required can be forced into the interstices between the PS spheres, and they cannot pack closely in the confined space. In addition, ordered assembly between PS spheres and silica particles cannot be maintained often due to wide size distribution of silica particles. Particularly, when the PS spheres are removed, it might be difficult for the as-produced porous silica template to possess a long range order, which may suffer from a collapse of the nanostructure due to insufficient mechanical strength. Particularly, it becomes more difficult for the derived carbon replica to possess a 3D long-range order after the removal of the silica template because of the similar but more severe problem from the structural strength.

An OHNC could be synthesized using the OHNS as sacrificial template and divinylbenzene (DVB)²⁵ or furfuryl alcohol (FFA)⁴ as carbon precursor. The OHNS was dried at 343 K for 4 h prior to impregnation with the carbon precursor. During impregnation, the precursor was adsorbed into the mesopore voids between silica particles of the OHNS due to capillary effect. The OHNC was obtained after carbonization of the carbon precursor and subsequent dissolution of the OHNS framework in the resulting carbon–OHNS composite. The removal of the mesosized silica particles in the OHNS resulted in corresponding mesopores embedded in the carbon wall in addition to the macropores generated by removal of the PS particles. As revealed by the SEM images shown in Figure 2, the resulting macropores reflect the highly ordered hexagonal array of the sacrificial PS particles. The size of the large macropores can be manipulated by controlling the diameter of the PS spheres, while the size of the small mesopores and the overall specific surface area are determined by the silica nanoparticles (NPs).

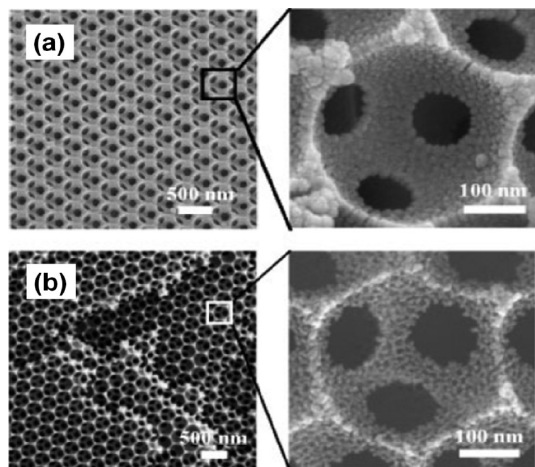


FIGURE 2. Typical SEM images for OHNS (a) and OHNC (b).²⁵ Adapted with permission from ref 25. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

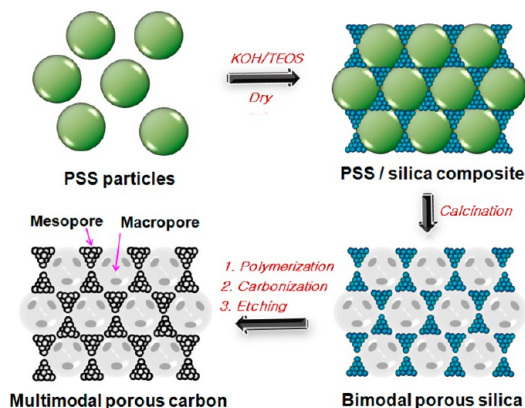


FIGURE 3. Schematic illustration for simpler synthesis of OHNS and OHNC.²⁶ Reproduced with permission from ref 26. Copyright 2010 Elsevier Ltd.

2. Simpler Fabrication Strategy for OHNSs and OHNCs.

Recently, our group has developed a more direct and simpler strategy for fabricating OHNSs through a facile sol–gel approach, as shown in Figure 3. Monodisperse silica NPs are produced in situ in a mixed solution of silica precursor (i.e., tetraethyl orthosilicate (TEOS)) in the presence of uniform poly(styrene sulfonate) (PSS) particles. Thus, extra processes of preparing silica NPs separately and controlling self-assembly between the PS and silica particles reported in our previous methodology²⁵ are avoided, which greatly simplifies the procedures for OHNS synthesis. This new strategy is supposed to provide further insights into easy synthesis of OHNSs and OHNCs.²⁶ The synthesis of the OHNS was performed using dispersed PSS spheres as template and TEOS as silica precursor. KOH was used as a catalyst for the in situ sol–gel generation of silica NPs. Details for

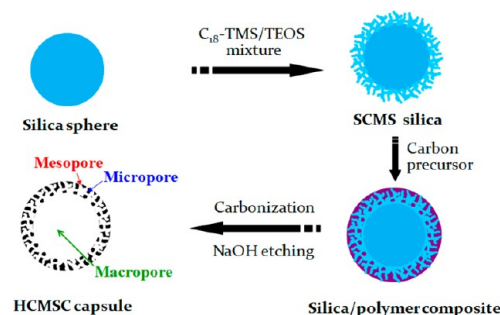


FIGURE 4. Schematic illustration for synthesis of SCMS silica and HCMSC. Reproduced from ref 8. Copyright 2008 American Chemical Society.

synthesis of the OHNS and the OHNC are documented in our previous work.²⁶ The images in Figure SI 1 (Supporting Information) reveal similar nanostructures for the OHNS and OHNC to that previously reported,²⁵ proving the success of the simpler synthesis strategy.

Fabricating HNCs with Hollow Macroporous Core/Mesoporous Shell Nanoarchitecture

HCMSC is another kind of important porous carbon material with unique hierarchical macro/mesoporosity. The first spherical HCMSC with macroporous core was produced by our research group using submicrometer-size spherical solid core–mesoporous shell (SCMS) silica as a template.²⁷ HCMSC with a different core shape (nonspherical) has also been synthesized through the nanocasting technique.¹

1. Synthesis of HCMSC Using SCMS Silica as Template.

First spherical carbon capsules with HCMSC structures were synthesized by using SCMS spheres as templates,²⁷ as illustrated in the schematic diagram shown in Figure 4. The uniform silica spheres as a starting material can be produced in various sizes by controlling the amount of TEOS added into the aqueous ammonia according to Stöber method. A typical synthesis route for SCMS silica is as follows. A mixed solution containing TEOS and octadecyl-trimethoxysilane ($C_{18}TMS$) with a molar ratio of TEOS to $C_{18}TMS$ of 3–5 was added into the colloidal solution containing the silica spheres and further reacted for 1 h. The resulting octadecyl group incorporated silica shell/solid core nanocomposite was retrieved by centrifugation, dried at room temperature and further calcined at 823 K to produce the final pure SCMS silica material (Kaiser approach). The SCMS silica can be produced in various sizes and various shell thicknesses by using the solid silica spheres with various sizes and adjusting the molar ratio of $C_{18}TMS$ to TEOS, respectively.⁸ Mesosize and microsize thickness silica walls can be generated in the

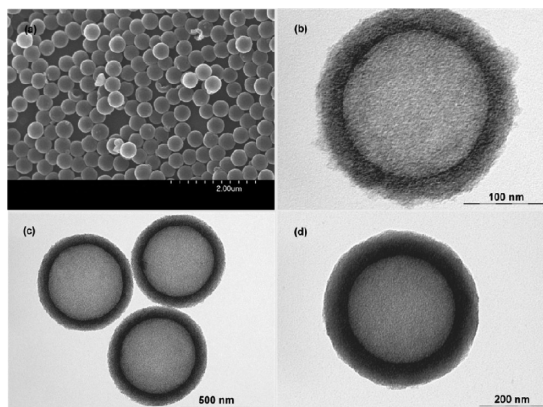


FIGURE 5. SEM (a) and TEM images for HCMSCs: $C_{180/40}$ (b), $C_{340/40}$ (c), and $C_{340/70}$ (d). Panels b–d reproduced from ref 8. Copyright 2008 American Chemical Society.

shell of the SCMS silica from the interaction of C_{18} TMS and TEOS, which are the primary sources of meso- and micropores of the replicated HCMSC. In general, a higher ratio of C_{18} TMS to TEOS tends to increase the mesopore size and to decrease the silica wall thickness in the shell of the SCMS silica, thus to some extent increasing the micropore volume in the corresponding HCMSC.⁸

Carbon precursor is incorporated into the mesoporous channels separated by silica walls in the shell of the SCMS silica. After carbonization of polymerized carbon precursor and removal of SCMS silica, HCMSCs with a macroporous hollow core in combination with a meso-/microporous shell can be produced with various surface characteristics (surface area, pore volume, meso- and microporosity). As revealed by the SEM image shown in Figure 5a, HCMSC capsules are generated as uniform individual discrete particles. TEM images shown in Figure 5b–d reveal various core size and shell thickness for HCMSCs.

A typical nitrogen adsorption–desorption isotherm shown in Figure SI 2 (Supporting Information) can be classified as type-IV typical of mesoporous material with clear capillary condensation step for the HCMSC $_{180/40}$. In addition to the mesopores, a large quantity of micropores formed during the carbonization of carbon precursor and in part from the microsize thickness silica walls in the silica/carbon composite were also found in the shell of the HCMSC as indicated in a significant increase of adsorbed nitrogen at low pressure range, suggesting a hierarchical nanostructure of macropores (macroscopic hollow core) in combination with mesopores and micropores in the mesoporous shell.

2. Facile Synthesis of HCMSC through Co-condensation Reactions. The strong interest in nanostructured functional materials has motivated the scalable production of high-

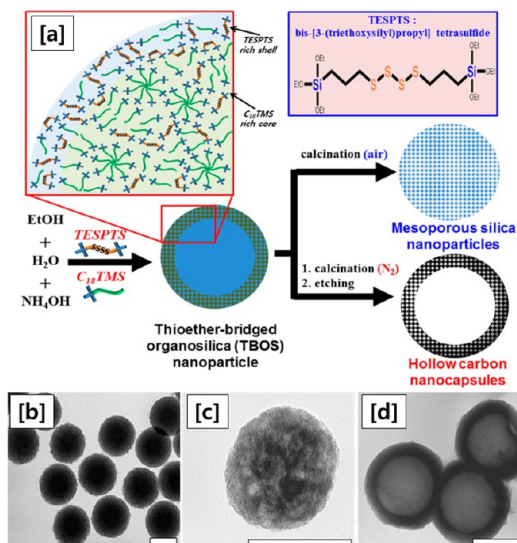


FIGURE 6. Schematic illustration of C_{18} TMS-TESPTS organosilica and its topological transformations (a), TEM images of as-prepared C_{18} TMS-TESPTS organosilica (b), after calcination in air (c), and in N_2 followed by silica etching (d). The scale bars represent 100 nm. Panels b–d reproduced from ref 28. Copyright 2012 American Chemical Society.

quality mesoporous silicas and carbonaceous materials. Although many approaches have been explored for this goal, it is highly desired and still remains a challenge to develop a straightforward strategy for simple and cost-effective fabrication of nanostructured functional materials. Very recently, we have successfully demonstrated a simple sol–gel preparation of bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPTS)-based organosilica nanostructured materials and their topological transformations, through which porous spherical silica or carbon and hollow silica or carbon capsule have been synthesized.²⁸ As presented in the schematic diagram shown in Figure 6, TESPTS-based materials were prepared through a base-catalyzed sol–gel process using C_{18} TMS as a structure mediator along with TESPTS mainly as a framework precursor as well as a structure-directing agent.

For a typical synthesis, a mixed solution containing TESPTS and C_{18} TMS was added into a stirred cosolvent solution including DI water, ethanol, and aqueous ammonia. The hydrophobic octadecyl chains of the C_{18} TMS first form micelle-like self-assembly structures with hydrophilic trihydroxysilyl groups as heads. A reactive core is then expanded by the base-catalyzed co-condensation of C_{18} TMS or TESPTS over the C_{18} TMS self-assembly structure. The resulting as-synthesized particle is an inorganic–organic hybrid core–shell-like structure with a silica-rich aggregate derived from co-condensation of hydrophilic trihydroxysilyl groups of C_{18} TMS and TESPTS as core composition and with an

organic-rich coassembly structure between $-(\text{CH}_2)_3-\text{S}_4-(\text{CH}_2)_3-$ of TESPTS and octadecyl chains of C_{18}TMS as shell framework. TESPTS can contribute a carbon source as well as a silica source. Thus, calcination in N_2 and subsequent silica etching generate hollow carbon capsules with mesoporous shells, while air calcination produces porous silica spheres from the silica-rich core. The conversion of the organic moiety to carbon is likely to be facilitated by the sulfide group of TESPTS, which could considerably increase the carbon yield via dehydration and sulfonation reactions, facilitating the cross-linking process of alkyl groups and helping the aromatization process.

The TESPTS-based organosilica composites contain both silica and carbon sources in the framework and thus provide a more direct route to nanostructured silica and carbon with a reduced number of synthesis steps compared with the previous hard template method. In particular, this is the first example of direct scalable synthesis of uniform hollow silica and carbon capsules with high levels of mesoporosity in the shell. Thus, the current organosilica route offers a straightforward strategy for simple and cost-effective scalable fabrication of novel nanostructured functional materials.

Applications

Due to their large specific surface area and unique hierarchical nanostructures, OHNC and HCMSC materials have found diverse emerging applications. In this section, selected applications of the OHNC and HCMSC materials are highlighted.

1. Catalyst Support in Fuel Cells. Low-temperature fuel cells, particularly proton exchange membrane fuel cells (PEMFCs), have been of great interest as future energy sources for applications such as low- or zero-emission electric vehicles, distributed home power generators, and power sources for portable electronics. However, the commercial viability of PEMFC technology has been hindered by several challenges mainly including poor kinetics of the oxygen reduction reaction (ORR) and high cost of noble metal (i.e., Pt) catalysts. One effective approach to decrease the cost and enhance catalytic activity of catalysts is preparation of metal catalyst NPs with high dispersion on their supports.

Carbon black Vulcan XC-72 (VC) has been widely used as a catalyst support in PEMFCs due to its relatively large surface area and excellent chemical stability.³⁰ However, the carbon black VC contains a significant amount of micropores (ca. 47% of total pores), some of which are too small (less than 1 nm in diameter) to be accessible to the electrolyte polymer, resulting in the entrapped Pt NPs not contributing to

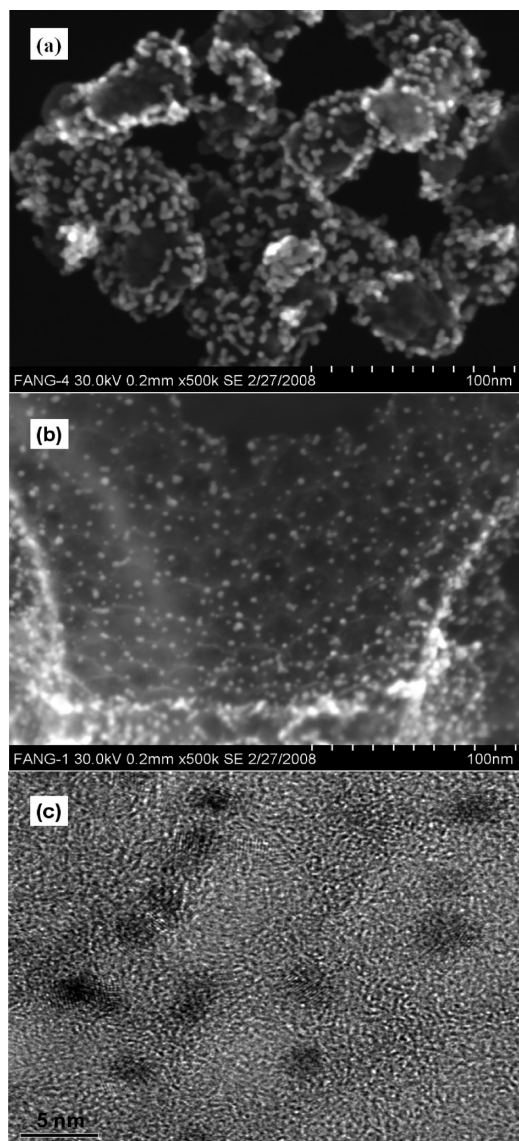


FIGURE 7. High-resolution SEM images for Pt(60 wt %)/VC (a) and Pt(60 wt %)/OHNC (b) and HRTEM image for Pt(60 wt %)/OHNC (c). Reproduced from ref 4. Copyright 2009 American Chemical Society.

the electrode reactions due to the absence of the triple-phase boundaries (i.e., gas–electrolyte–electrode). Some novel nanostructured carbon materials have recently been investigated as possible catalyst supports for PEMFCs, including carbon nanotubes (CNTs) and carbon nanofibers (CNFs). Although the CNT-supported Pt electrode showed approximately 20% higher power density than the VC-supported one, realistic application of CNTs has been hindered by several difficulties associated with their processes involving synthesis, purification, dispersion, and surface activation. CNF-supported Pt (20 wt %) only exhibited a slightly improved electrocatalytic performance than the VC-supported one.³¹

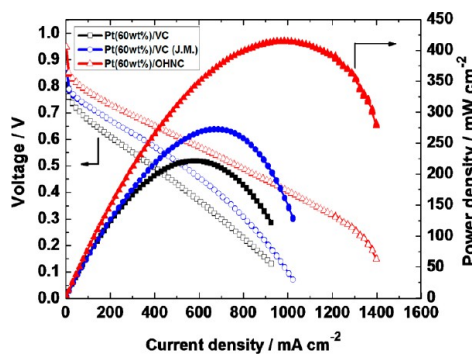


FIGURE 8. Polarization and power density plots at 60 °C for PEMFCs using VC- or OHNC-supported Pt (60 wt %) cathode catalysts. Reproduced from ref 4. Copyright 2009 American Chemical Society.

In our previous study, OHNC was explored for the first time to support high loading of Pt NPs as a cathode catalyst in PEMFCs.⁴ As shown in Figure 7, for the VC-supported Pt (60 wt %) catalyst, Pt NPs have particle sizes of ca. 4.2–5.6 nm, and some Pt NPs have gathered together to form agglomerates with larger particle size. In contrast, Pt NPs are basically deposited separately and homogeneously on the wall of mesopores and on the outer surface of the OHNC support with smaller particle size. The HR-TEM image reveals that most Pt NPs in the Pt (60 wt %)/OHNC have a size of ca. 3.0 nm. As a result, the OHNC-supported Pt cathode catalyst possesses higher electrocatalytic activity toward ORR, as evident in Figure 8 and in Figure SI 3 (Supporting Information). Much higher power density achieved by the OHNC-supported Pt catalyst is attributable to the unique hierarchical pore structure of the OHNC. First, larger surface area and mesopore volume enable the Pt NPs to deposit more uniformly on the surface of the OHNC with much smaller particle size, resulting in much higher electrochemical active surface area. Second, the interconnecting ordered larger macropores in combination with mesopores form an open network, providing a fast pathway to the active sites (i.e., location of Pt NPs), through which the reactants and the products can be readily transported to and away from the active sites, avoiding mass transport limitations. In particular, the mesopore channels with large pore volume open to the macropores are ideal sites for active Pt NPs, boosting the catalytic reaction and reagent diffusion. In contrast, the smaller surface area of the VC with varying pore sizes makes the dispersion of Pt NPs less uniform with much larger particle sizes, and the randomly distributed pores with broad PSD (from micropores to macropores) and poor pore connectivity in the VC make the mass transport far from efficient. In addition, the OHNC-supported Pt catalyst also possesses

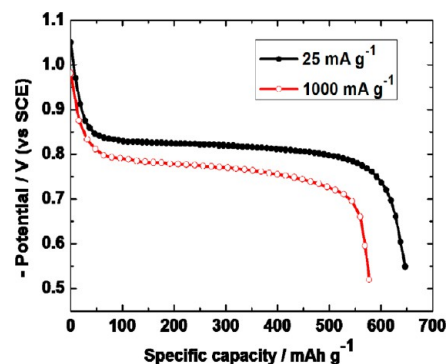


FIGURE 9. The first galvanostatic discharge curves at 25 and 1000 mA g⁻¹ for HCMSC_{180/40} electrode in 6.0 M KOH. Reproduced from ref 8. Copyright 2008 American Chemical Society.

comparable electrochemical stability to the VC-supported one (Table SI 1 and Figure SI 4, Supporting Information).

2. Hydrogen Storage Application. Hydrogen is the most abundant element in the universe. A safe, effective, and cheap hydrogen storage system is crucial for hydrogen fuel cells or hydrogen-driven combustion engines. Typical methods of storing hydrogen include compressed gas, liquefied hydrogen, chemisorptions in the form of metal hydrides,³² ammonia borane,³³ or physisorption using high surface adsorbents such as carbon and microporous metal–organic frameworks (MOFs).³⁴ Although AB₅-type alloys (i.e., LaNi₅) have been widely used in commercial hydrogen storage systems, their reversible gravimetric storage densities are low (ca. 300 mA · h g⁻¹).³² Ammonia borane is a particularly interesting hydrogen storage material due to an inherently large gravimetric and volumetric hydrogen density. However, relatively low thermal stability and high preparation cost have been major concerns. Use of MOFs requires a combination of small pores, which enable a lower pressure for hydrogen storage, and a larger specific surface area for a high storage capacity. Unfortunately, presently existing MOFs with the highest surface area possess relatively large pores, and the frameworks with very small cavities show a low specific surface area. In recent years, upon investigation of the storage capacity of the same microporous material by electrochemistry and under hydrogen pressure of 70 bar at 0 °C, uptakes of ca. 2 wt % and 0.4 wt % have been found, respectively,³⁵ suggesting electrochemical hydrogen storage has been proven as an elegant and more efficient approach at ambient pressure and temperature.

In our previous study, spherical HNCs and HCMSCs with various core sizes or shell thicknesses have been explored for electrochemical hydrogen storage.⁸ Compared with an OMC material with a BET surface area of ca. 1883 m² g⁻¹, the

HCMSC_{180/40} with much smaller surface area (i.e., 1314 m² g⁻¹) demonstrated a hydrogen storage capacity of 586 mA·h g⁻¹ (corresponding to 2.17 wt %) at a discharge rate of 25 mA g⁻¹, which is larger than that (ca. 527 mA·h g⁻¹) reported for the OMC, strongly implying the structural benefits from the HCMSC, which has a hierarchical macro-/meso-/microporosity compared with the OMC with meso-/microporosity. Furthermore, as evident in Figure 9, the hydrogen uptake (i.e., 521 mA·h g⁻¹) of the HCMSC_{180/40} at 1000 mA g⁻¹ is slightly smaller than that achieved at 25 mA g⁻¹, delivering the adsorbed hydrogen quickly at high discharge rate. Interestingly, this value (i.e., 521 mA·h g⁻¹) is much larger than that (i.e., 380 mA·h g⁻¹) of purified MWCNTs at 100 mA g⁻¹. Compared with other nanostructured porous materials, the superb hydrogen storage capability of the HCMSC is mainly attributable to its unique nanoarchitecture. The macroporous hollow core in the HCMSC can be used as an electrolyte solution buffering reservoir to minimize the diffusion distance to the interior surface of the mesoporous shell, while the mesoporous channels in the shell open to the macroporous core form fast mass transport networks around the micropores in the shell, which provide sites for diffusion and adsorption of hydrogen. With this hierarchical nanostructure design, three electrochemical processes (i.e., buffering electrolyte species in the macroporous core, transporting electrolyte species through the mesoporous shell, and facilitating adsorption of hydrogen species in the micropores) involved in electrochemical hydrogen storage can take place very quickly and efficiently even at high charging-discharging rate.

Recent works on advanced CAs demonstrated interesting and inspiring results about hydrogen storage. It was reported that the amount of surface excess hydrogen adsorbed on activated CA at 77 K and ca. 3.5 MPa varies linearly with BET surface area up to 2500 m²/g,²³ and the gravimetric uptake is ca. 1 wt % H₂ per 500 m²/g of surface area.³⁶ Based on this prediction, our HNC with a surface area of ca. 2400 m²/g³⁷ is expected to have a hydrogen storage of ca. 4.8 wt %. In addition, incorporation of transition metals (i.e., Ni) or alkali metals (i.e., Li) has been reported to greatly improve hydrogen storage capacity of carbon materials.³⁸ Therefore, hydrogen storage capacity of HNCs can be expected to increase further after the doping of Ni/Li.

In addition to low-temperature fuel cells and hydrogen storage, the HNCs developed in this Account have already found other fantastic applications such as in Li ion batteries,^{6,37} dye-sensitized or quantum dot sensitized solar cell (QDSSC),⁷ and electrochemical capacitors.⁵ More

detailed information about Li ion battery and QDSSC applications can be found in the Supporting Information.

Summary and Outlook

Hierarchical nanostructured porous materials have attracted much attention due to their important roles in the systematic study of structure–property relationship and their technological promise in applications. Also, well-defined multimodal pore architectures favor the elucidation of fundamental aspects of sorption theory such as diffusion and hysteresis. OHNC and HCMSC are two novel representative HNC materials that possess adjustable and well-defined macropores and tunable and interconnected mesopores. The studies discussed in this Account have demonstrated the versatility of colloidal templates to selectively design different types of HNCs and their promising applications. Despite considerable efforts recently to devise routes to hierarchical porous structures, HNCs with controllable meso/macroporosities are still in a relatively early stage of technical development. A number of challenges still remain before these materials will find viable practical applications. The main challenge lies in the limited diversity of the template materials mainly including silica and PS. Novel template materials with tailored shapes and functions should be pursued, which may lead to the creation of a series of distinctive properties to the carbon replica. Some recent works have focused on this issue. Biomimetic materials have been reported as inspiration for the design of materials with hierarchical nanostructures.³⁹ Anodic aluminum oxide (AAO) membrane is another typical example. Novel HNC materials, that is, mesoporous carbon nanofiber materials, have been created by using AAO membrane as template, which has already found promising application in QDSSC.⁷ In addition, in order to optimize the performance of a material for a specific application, it is desirable to combine different levels of porosity into one material framework. In applications such as catalysis in fuel cells, where the diffusion of molecules through the pore structure is vital for optimum performance, a highly ramified network of macro-/mesopores is desired. While for the storage applications such as H₂ or Li storage, large specific surface area is an additional plus. The combination of large surface area and mesopore volume and hierarchical macro–meso/microporosity has endowed HNCs with superb structural characteristics for a diversity of emerging applications, such as in gas adsorption, fuel cells, DSSCs and QDSSCs, H₂ storage, Li ion batteries, electrochemical capacitors. In addition, HNCs are expected to have other novel applications such as metal-free electrocatalysts

for ORR in alkaline media and highly efficient electrode materials for desalination of seawater and brackish water from saline aquifers. We believe that the growing interest in HNCs will certainly fuel the excitement and stimulate research in this field and more applications will be explored in the future. In addition, a great deal of novel hierarchical nanostructured materials with different compositions such as metal, metal oxide, silica, and polymer, will be developed through the same or similar nanocasting technologies to one that has been applied to the fabrication of HNCs.⁴⁰

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Supporting Information. SEM images for OHNS and OHNC, surface structural parameters for OHNC and HCMSCs, ORR plots, chronoamperometric curves, adsorption isotherms for the HCMSC, Li storage capacities for OHNC, photovoltaic performance for various materials, and some applications. This information is available free of charge via the Internet at <http://pubs.acs.org>.

BIOGRAPHICAL INFORMATION

Baizeng Fang received his Ph.D. degree in Materials Science from University of Science and Technology, Beijing, China, in 1997. He worked as a postdoctoral fellow (PDF) at ECN Holland in 1998, JSPS research Fellow and guest researcher in 2000–2004 at IRI, Japan, PDF in 2004–2005 at AIST, Japan, and Lise Meitner Scientist, FWF, Austria, in 2005–2006. He joined Prof. Jong-Sung Yu's group as a PDF at Hannam University, Korea, in 2006–2008 and as a research professor at Korea University, Korea, since 2008. His research interests include development of novel nanostructured materials for applications in fuel cells, hydrogen storage, solar cells, electrochemical capacitors, secondary batteries (i.e., Li-ion batteries, redox flow batteries), metal–air fuel cells, catalysis, and electrochemistry.

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FOOTNOTES

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REFERENCES

- Ji, Q.-M.; Yoon, S.-B.; Hill, J.; Vinu, A.; Yu, J.-S.; Ariga, K. Layer-by-Layer Films of Dual-Pore Carbon Capsules with Designable Selectivity of Gas Adsorption. *J. Am. Chem. Soc.* **2009**, *131*, 4220–4221.
- Sarrade, S.; Rios, G.; Carles, M. Supercritical CO₂ Extraction Coupled with Nanofiltration Separation: Applications to Natural Products. *Sep. Purif. Technol.* **1998**, *14*, 19–25.
- Tetreault, N.; Miguez, H.; Ozin, G. Silicon Inverse Opal — A Platform for Photonic Bandgap Research. *Adv. Mater.* **2004**, *16*, 1471–1476.
- Fang, B.-Z.; Kim, J.-H.; Kim, M.-S.; Yu, J.-S. Ordered Hierarchical Nanostructured Carbon as a Highly Efficient Cathode Catalyst Support in Proton Exchange Membrane Fuel Cell. *Chem. Mater.* **2009**, *21*, 789–796.
- Fang, B.-Z.; Kim, J.-H.; Kim, M.-S.; Bonakdarpour, A.; Lam, A.; Wilkinson, D.; Yu, J.-S. Simple Fabrication of Hollow Core Carbon Spheres with Hierarchical Nanoarchitecture for Ultrahigh Electrical Charge Storage. *J. Mater. Chem.* **2012**, *22*, 19031–19038.
- Fang, B.-Z.; Kim, M.-S.; Kim, J.-H.; Lim, S.-M.; Yu, J.-S. Ordered Multimodal Porous Carbon with Hierarchical Nanostructure for High Li Storage Capacity and Good Cycling Performance. *J. Mater. Chem.* **2010**, *20*, 10253–10259.
- Fang, B.-Z.; Kim, M.-W.; Fan, S.-Q.; Kim, J.-H.; Wilkinson, D.; Ko, J.-J.; Yu, J.-S. Facile Synthesis of Open Mesoporous Carbon Nanofibers with Tailored Hierarchical Nanostructure as a Highly Efficient Counter Electrode in CdSe Quantum-dot Sensitized Solar Cells. *J. Mater. Chem.* **2011**, *21*, 8742–8748.
- Fang, B.-Z.; Kim, J.-H.; Kim, M.-S.; Yu, J.-S. Controllable Synthesis of Hierarchical Nanostructured Hollow Core/Mesopore Shell Carbon for Electrochemical Hydrogen Storage. *Langmuir* **2008**, *24*, 12068–12072.
- Taguchi, A.; Smatt, J.; Lindén, M. Carbon Monoliths Possessing a Hierarchical, Fully Interconnected Porosity. *Adv. Mater.* **2003**, *15*, 1209–1211.
- Lee, J.-S.; Joo, S.-H.; Ryoo, R. Synthesis of Mesoporous Silicas of Controlled Pore Wall Thickness and Their Replication to Ordered Nanoporous Carbons with Various Pore Diameters. *J. Am. Chem. Soc.* **2002**, *124*, 1156–1157.
- Zhao, D.-Y.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G.-H.; Chmelka, B.-F.; Stucky, G.-D. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Å Pores. *Science* **1998**, *279*, 548–552.
- Kresge, C.; Leonowicz, M.; Roth, W.; Vartuli, J.; Beck, J. Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism. *Nature* **1992**, *359*, 710–712.
- Adelhelm, P.; Hu, Y.-S.; Chuenchom, L.; Antonietti, M.; Smarsly, B. M.; Maier, J. Generation of Hierarchical Meso- and Macroporous Carbon from Mesophase Pitch by Spinodal Decomposition using Polymer Templates. *Adv. Mater.* **2007**, *19*, 4012–4017.
- Holland, B.; Abrams, L.; Stein, A. Dual Templating of Macroporous Silicates with Zeolitic Microporous Frameworks. *J. Am. Chem. Soc.* **1999**, *121*, 4308–4309.

- 15 Antonietti, M.; Berton, B.; Göltner, C.; Hentze, H. Synthesis of Mesoporous Silica with Large Pores and Bimodal Pore Size Distribution by Templating of Polymer Lattices. *Adv. Mater.* **1998**, *10*, 154–159.
- 16 Lebeau, B.; Fowler, C.; Mann, S.; Farcet, C.; Charleux, B.; Sanchez, C. Synthesis of Hierarchically Ordered Dye-Functionalised Mesoporous Silica with Macroporous Architecture by Dual Templating. *J. Mater. Chem.* **2000**, *10*, 2105–2108.
- 17 Iskandar, F.; Mikrajuddin; Okuyama, K. Controllability of Pore Size and Porosity on Self-Organized Porous Silica Particles. *Nano Lett.* **2002**, *2*, 389–392.
- 18 Gates, B.; Qin, D.; Xia, Y.-N. Assembly of Nanoparticles into Opaline Structures over Large Areas. *Adv. Mater.* **1999**, *11*, 466–468.
- 19 Yin, Y.-D.; Lu, Y.; Gates, B.; Xia, Y.-N. Template-Assisted Self-Assembly: A Practical Route to Complex Aggregates of Monodispersed Colloids with Well-Defined Sizes, Shapes, and Structures. *J. Am. Chem. Soc.* **2001**, *123*, 8718–8729.
- 20 Yuan, Z.-Y.; Su, B.-L. Insights into Hierarchically Meso–Macroporous Structured Materials. *J. Mater. Chem.* **2006**, *16*, 663–677.
- 21 Taguchi, A.; Smatt, J. H.; Linden, M. Carbon Monoliths Possessing a Hierarchical, Fully Interconnected Porosity. *Adv. Mater.* **2003**, *15*, 1209–1211.
- 22 Baumann, T.; Satcher, J. Template-Directed Synthesis of Periodic Macroporous Organic and Carbon Aerogels. *J. Non-Cryst. Solids* **2004**, *350*, 120–125.
- 23 Biener, J.; Stadermann, M.; Suss, M.; Worsley, M.; Biener, M.; Rose, K.; Baumann, T. Advanced Carbon Aerogels for Energy Applications. *Energy Environ. Sci.* **2011**, *4*, 656–667.
- 24 Cheng, Q.-L.; Xia, Y.-M.; Pavlinek, V.; Yan, Y.-F.; Li, C.-Z.; Saha, P. Effects of Macropore Size on Structural and Electrochemical Properties of Hierarchical Porous Carbons. *J. Mater. Sci.* **2012**, *47*, 6444–6450.
- 25 Chai, G.-S.; Shin, I.-S.; Yu, J.-S. Synthesis of Ordered, Uniform Macroporous Carbon with Mesoporous Wall Templated by Aggregates of Polystyrene Spheres and Silica Particles for Use as Catalyst supports in Direct Methanol Fuel Cells. *Adv. Mater.* **2004**, *16*, 2057–2061.
- 26 Kim, J.-H.; Fang, B.-Z.; Kim, M.-S.; Yoon, S.-B.; Bae, T.-S.; Ranade, D.; Yu, J.-S. Facile Synthesis of Bimodal Porous Silica and Multimodal Porous Carbon as an Anode Catalyst Support in Polymer Exchange Membrane Fuel Cell. *Electrochim. Acta* **2010**, *55*, 7628–7633.
- 27 Yoon, S.-B.; Sohn, K.-N.; Kim, J.-Y.; Shin, C.-H.; Yu, J.-S.; Hyeon, T.-H. Fabrication of Carbon Capsules with Hollow Macroporous Core/Mesoporous Shell Structures. *Adv. Mater.* **2002**, *14*, 19–21.
- 28 Kim, J.-H.; Fang, B.-Z.; Song, M.-Y.; Yu, J.-S. Topological Transformation of Thioether-Bridged Organosilicas into Nanostructured Functional Materials. *Chem. Mater.* **2012**, *24*, 2256–2264.
- 29 Lu, L.-H.; Eychmüller, A. Ordered Macroporous Bimetallic Nanostructures: Design, Characterization, and Applications. *Acc. Chem. Res.* **2008**, *41*, 244–253.
- 30 Fang, B.-Z.; Chaudhari, N.-K.; Kim, M.-S.; Kim, J.-H.; Yu, J.-S. Homogeneous Deposition of Platinum Nanoparticles on Carbon Black for Proton Exchange Membrane Fuel Cell Application. *J. Am. Chem. Soc.* **2009**, *131*, 15330–15338.
- 31 Yuan, F.-L.; Ryu, H. The Synthesis, Characterization, and Performance of Carbon Nanotubes and Carbon Nanofibres with Controlled Size and Morphology as a Catalyst Support Material for a Polymer Electrolyte Membrane Fuel Cell. *Nanotechnology* **2004**, *15*, s596–s602.
- 32 Cohen, R.; Wemick, J. Hydrogen Storage Materials: Properties and Possibilities. *Science* **1981**, *214*, 1081–1087.
- 33 Lin, Y.; Mao, W.; Mao, H.-K. Storage of Molecular Hydrogen in an Ammonia Borane Compound at High Pressure. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 8113–8116.
- 34 Rosi, N.; Eckert, J.; Eddaoudi, M.; Vodak, D.; Kim, J.; O’Keeffe, M.; Yaghi, O. Hydrogen Storage in Microporous Metal–Organic Frameworks. *Science* **2003**, *300*, 1127–1129.
- 35 Jurewicz, K.; Frackowiak, E.; Béguin, F. Enhancement of Reversible Hydrogen Capacity into Activated Carbon through Water Electrolysis. *Electrochim. Solid State Lett.* **2001**, *4*, A27–A29.
- 36 Panella, B.; Hirscher, M.; Roth, S. Hydrogen Adsorption in Different Carbon Nanostructures. *Carbon* **2005**, *43*, 2209–2214.
- 37 Kim, M.-S.; Fang, B.-Z.; Kim, J.-H.; Yang, D.; Kim, Y.-K.; Bae, T.-S.; Yu, J.-S. Ultra-high Li Storage Capacity Demonstrated by Hollow Carbon Capsules with Hierarchical Nanoarchitecture. *J. Mater. Chem.* **2011**, *21*, 19362–19367.
- 38 Ataca, C.; Akturk, E.; Ciraci, S.; Ustunel, H. High-Capacity Hydrogen Storage by Metallized Graphene. *Appl. Phys. Lett.* **2008**, *93*, No. 043123.
- 39 Peng, W.-H.; Zhu, S.-M.; Wang, W.-L.; Zhang, W.; Gu, J.-J.; Hu, X.-B.; Zhang, D.; Chen, Z.-X. 3D Network Magnetophotonic Crystals Fabricated on Morpho Butterfly Wing Templates. *Adv. Funct. Mater.* **2012**, *22*, 2072–2080.
- 40 Kim, J.-Y.; Yoon, S.-B.; Yu, J.-S. Template Synthesis of a New Mesoporous Silica from Highly Ordered Mesoporous Carbon Molecular Sieves. *Chem. Mater.* **2003**, *15*, 1932–1934.