



Carbon Nanomaterials With Hollow Structures: A Mini-Review

Fan Liu^{1†}, Yu Cheng^{1,2†}, Junchao Tan^{1*}, Jiantong Li³, Haoyan Cheng⁴, Hao Hu⁴, Chunya Du¹, Shuang Zhao¹, Yan Yan^{1*} and Mingkai Liu^{1*}

¹ Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou, China, ² Hubei Key Laboratory of Polymer Materials, Ministry-of-Education Key Laboratory for the Green Preparation and Application of Functional Materials, School of Materials Science & Engineering, Hubei University, Wuhan, China, ³ Henan Engineering Laboratory of Flame-Retardant and Functional Materials, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, China, ⁴ Collaborative Innovation Center of Nonferrous Metals, School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang, China

OPEN ACCESS

Edited by:

Xiaomin Li,
Fudan University, China

Reviewed by:

Xing-Long Wu,
Northeast Normal University, China
Zhongrong Shen,
Chinese Academy of Sciences, China

*Correspondence:

Mingkai Liu
liumingkai@jsnu.edu.cn
Junchao Tan
tanchaozxf@126.com
Yan Yan
yanyan@jsnu.edu.cn

[†]These authors have contributed
equally to this work

Specialty section:

This article was submitted to
Nanoscience,
a section of the journal
Frontiers in Chemistry

Received: 16 February 2021

Accepted: 23 February 2021

Published: 30 March 2021

Citation:

Liu F, Cheng Y, Tan J, Li J, Cheng H,
Hu H, Du C, Zhao S, Yan Y and Liu M
(2021) Carbon Nanomaterials With
Hollow Structures: A Mini-Review.
Front. Chem. 9:668336.
doi: 10.3389/fchem.2021.668336

Carbon nanomaterials with high electrical conductivity, good chemical, and mechanical stability have attracted increasing attentions and shown wide applications in recent years. In particular, hollow carbon nanomaterials, which possess ultrahigh specific surface area, large surface-to-volume ratios, and controllable pore size distribution, will benefit to provide abundant active sites, and mass loading vacancy, accelerate electron/ion transfer as well as contribute to the specific density of energy storage systems. In this mini-review, we summarize the recent progresses of hollow carbon nanomaterials by focusing on the synthesis approaches and corresponding nanostructures, including template-free and hard-template carbon hollow structures, metal organic framework-based hollow carbon structures, bowl-like and cage-like structures, as well as hollow fibers. The design and synthesis strategies of these hollow carbon nanomaterials have been systematically discussed. Finally, the emerging challenges and future prospective for developing advanced hollow carbon structures were outlined.

Keywords: carbon materials, nanostructures, hollow morphology, synthesis strategies, structural information

INTRODUCTION

Carbon, one of the most important elements in nature, has been utilized in human civilization for more than 3,000 years (Hu et al., 2010). In the past decades, three significant breakthroughs mark that carbon based materials have entered the nano era: (1) In 1985, C60 namely fullerene was exploited by Kroto et al. (1985); (2) Iijima (1991) reported carbon nanotube in 1991; (3) In 2004, graphene was developed by Novoselov et al. (2004). Since then, carbon nanomaterials have become a hotspot, hence, various novel nanostructures and synthesis approaches have been developed (Wang Q. et al., 2017; Li et al., 2018; Zhang P. et al., 2018; Liu M. et al., 2019; Sun et al., 2019a; Zhan et al., 2019; Shen et al., 2020; Yan et al., 2020; Yang et al., 2020).

Recently, carbon-based nanomaterials have been widely developed and been used in many fields such as energy storage and conversion, photocatalysis, electrocatalysis, gas, and water treatment systems and biomedicine (Liu et al., 2017a,b, 2018; Yang et al., 2018; Liu Y. Q. et al., 2019; Sun et al., 2019b,c; Zhang and Lou, 2019; Guo et al., 2020; Wu C. et al., 2020; Yuan et al., 2020a,c,d). Among various carbon nanomaterials, hollow carbon nanostructures (HCNs) (Figure 1) have attracted considerable interests due to their high thermal stability, strong electron transport ability, large specific surface area, plentiful exposed active sites, and flexible shape and

structure (Wen et al., 2007; Guo et al., 2019; Chen et al., 2020; Gao et al., 2020; Wang et al., 2020; Yuan et al., 2020b). A large number of studies have shown that HCNs exhibit excellent performance for energy, catalysis, electronics, biomedical, and so on in terms of their unique hollow structures.

In this mini-review, we summarize the recent advances of HCNs by focusing on the synthesis approaches and corresponding nanostructures, including hollow carbon spheres based on template-free and hard-template methods, metal organic framework-derived HCNs, bowl-like, cage-like, and fiber-shaped HCNs. The emerging challenges and future prospective for developing advanced hollow carbon structures were also outlined. We believe that this mini-review could offer some new insights and inspire extensive interests to accelerate and explore the innovations of HCNs.

HOLLOW CARBON BASED ON TEMPLATE-FREE APPROACH

Template-free method, which also termed self-template method, is regarded as a facile and one-step strategy for the synthesis of HCNs. Usually, template-free method involves Kirkendall effect, Ostwald ripening, ion exchange, and selective etching (Zhang and Lou, 2019).

In 2001, Wang et al. first reported a facile hydrothermal route to prepare monodispersed hard carbon spherules. Sugar was selected as precursor, and hydrothermal treated for 5 h at 190°C, and followed by a carbonizing process, the carbon spheres were obtained (Wang et al., 2001). The as-prepared carbon sphere exhibited a specific surface area of 400 m²/g and lithium storage capacity up to 430 mAh/g, which undoubtedly opened the door for practical application of carbon materials in energy storage. After that, X. Sun and Y. Li studied the mechanism of preparing carbon spheres from glucose by hydrothermal method, and further developed a general synthesis strategy of hybrid, hollow, or porous carbon spheres (Sun and Li, 2004). To date, hydrothermal or solvothermal carbonization method has been developed into a classical strategy, by which numerous hollow carbon spheres were successfully synthesized (Han et al., 2011; Liang et al., 2015; Chen et al., 2018; Wang et al., 2019).

In recent years, a great many of new strategies have been developed. For instance, a facile one-step carbonization process to prepare hollow carbon spheres with different sizes from 100 to 400 nm, was presented by Natarajan and co-workers. Polypropylene (PP) and polyethylene (PE), which recovered from spent lithium-ion batteries, were heated at 800°C for 2 h. After cooling and washing with benzene, the product with specific surface area and total pore volume of 402 m²/g and 0.30 cm³/g was obtained (Figure 2A) (Natarajan et al., 2019). In addition, Sun and co-authors synthesized N-doped hollow carbon spheres by stepwise polymerizing and carbonizing procedure. Industrialized monomers, pyromellitic dianhydride (PMDA) and 4, 4-oxydianiline (ODA), were used as raw materials, and stepwise polymerized at ambient temperature, the obtained homopolymer self-assembled into poly (amic acid) (PAA) vesicles. After carbonizing at

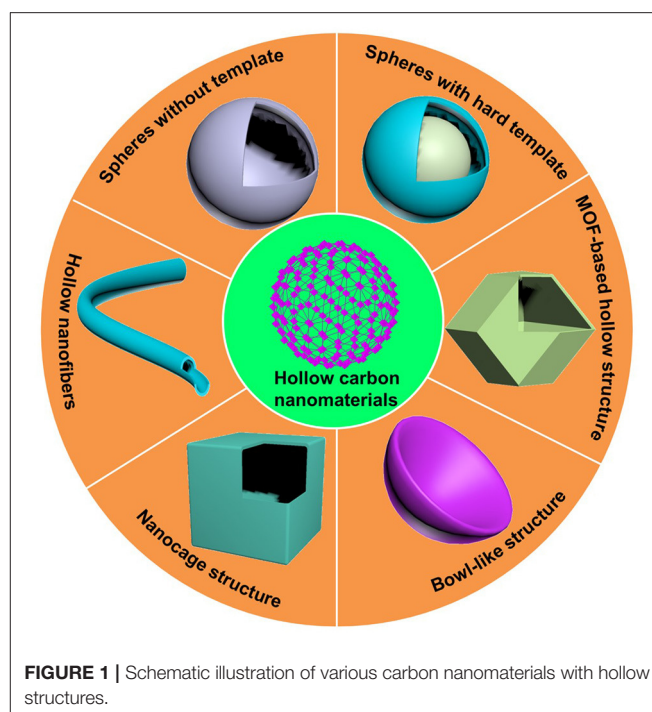


FIGURE 1 | Schematic illustration of various carbon nanomaterials with hollow structures.

800°C for 3 h, PAA vesicles transformed into hollow carbon spheres (Sun et al., 2016). Similarly, initiated by ammonium sulfate, 2, 6-Diaminopyridine polymerized and then heated at 950°C for 1 h, N, S co-doped hollow carbon spheres were prepared (Zhang X. et al., 2019).

HOLLOW CARBON WITH HARD-TEMPLATE METHOD

As an effective strategy, hard-template method, in which the materials with low price and easily controlled are used as templates, followed by being removed with physical or chemical procedure, is widely applied to synthesize HCNs. In general, hard-template method involves four steps. Firstly, a rigid solid template is prepared with specific morphology. Then, the surface of as-prepared template was modified or functionalized in order to increasing absorption ability. Furthermore, carbon precursor (i.e., dopamine, PAN, PAA, P123, P127) was coated on the surface of as-prepared template. Finally, as-prepared template was removed by solution etching or high temperature degradation.

Since hard-template method was discovered in 1999, numerous nanostructures have been prepared. Yoon and co-authors synthesized hollow core/mesoporous shell for the first time by using silica spheres as templates (Yoon et al., 2002). Subsequently Joo et al. developed a facile hydrothermal approach to prepare hollow carbon sphere by using silica as template and sucrose as carbon source. First, silica particles were prepared by a classical Stöber approach and impregnated with AlCl₃ aqueous solution. Next, sucrose was added as carbon precursor and treated by a benign hydrothermal process. After annealing

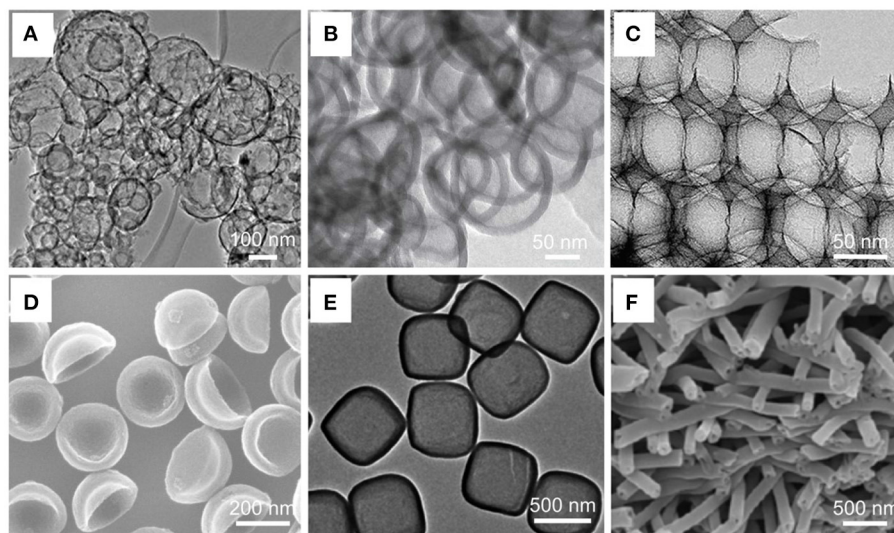


FIGURE 2 | (A) TEM image of template-free synthesized carbon hollow spheres (CHS). Natarajan et al. (2019) with permission from Royal Society of Chemistry. **(B)** TEM image of hollow carbon nanospheres with latex templates. Tang et al. (2012) with permission from Wiley-VCH. **(C)** TEM image of bicontinuous hierarchical porous carbon (BHPC-950) after hydrofluoric acid etching. Yang et al. (2017) with permission from Wiley-VCH. **(D)** SEM image of N-doped hollow porous carbon bowls (N-HPCB). Pei et al. (2016) with permission from Wiley-VCH. **(E)** TEM image of carbon nanoboxes. Yu et al. (2015) with permission from Wiley-VCH. **(F)** SEM image of N-doped hollow carbon nanofibers. Ramakrishnan et al. (2015) with permission from Royal Society of Chemistry.

(850°C) and etching (HF) treatment, the hollow carbon spheres were obtained (with specific surface of 788 cm²/g, pore volume of 1.15 cm³/g) (Joo et al., 2008). In addition, Tang and co-workers demonstrated that hollow carbon spheres can be prepared via a facile hydrothermal carbonization method. Polystyrene latexes and glucose were mixed and hydrothermally treated at 180°C for 20 h, and subsequently heated at 1000°C (**Figure 2B**) (Tang et al., 2012).

METAL ORGANIC FRAMEWORKS DERIVED HOLLOW CARBON NANOMATERIALS

Since the metal organic frameworks (MOFs) were synthesized in the 1990s, they have been widely used in adsorption, separation, catalysis, energy storage, pharmaceutical, and other fields due to their large specific surface area, porosity, convenient synthesis, good thermal stability, variable skeleton size, and chemical modification (Ren et al., 2018; Sun et al., 2020a,b). Selecting the precursors and calcination conditions of MOFs is an effective strategy to prepare new carbon nanomaterials with controllable size, shape, and composition. In 2008, Liu and co-authors reported that MOF was applied as template to synthesize porous carbon nanomaterials (Liu et al., 2008). MOF-5 and furfuryl alcohol were used as template and carbon source, respectively, followed by dynamic vacuum (200°C, 24 h) and carbonizing process (1000°C, 8 h, N₂), porous carbon with high specific surface area (2872 m²/g) was obtained. Since then, various HCNs have been prepared and applied in many fields. For instance, through a controlled etching approach, novel nanosize monocrystalline hollow MOF nanobubbles with

a uniform size of <100 nm and a thin shell of around 10 nm were prepared (Zhang et al., 2017). Moreover, Yang and co-workers reported a dual-template route to nitrogen-rich porous carbon. Typically, 3D ordered SiO₂ infiltrated into ZIF-8, then heated at 800–1000°C and etched by hydrofluoric acid, the obtained product exhibited ultralarge surface area of 2546 m²/g and ultrahigh total pore volume of 13.42 cm³/g (**Figure 2C**) (Yang et al., 2017).

On the other hand, combining MOFs with various functional materials is also an effective and feasible strategy. In 2012, Jahan and co-authors used reduced graphene oxide (rGO) sheets, which were functionalized with pyridine ligands on either side of the surface, acting as pillars connecting metalloporphyrin nodes to form a hybrid grapheme-MOF framework. Their excellent work demonstrated that the addition of functionalized rGO can influence the crystallization process of MOF and improve the electrocatalytic properties of the composites (Jahan et al., 2012). Additionally, hybridizing with carbon nanotubes is a widely adopted strategy in recent years. By dispersing and penetrating carbon nanotubes with MOF precursors, a large number of hybrid structures, such as multi-walled carbon nanotube/zeolitic ZIF-8 composite (MWNT@ZIF) (Yue et al., 2014), interpenetrated and self-standing conductive framework (ISCF) were successfully prepared (Liu Y. et al., 2017). In 2018, Zhang and co-authors reported a 3D porous MOF@CNT hybrid structure through a facile impregnation and solvothermal reaction approach. A carbon tube sponge which used as template was produced first, and then immersed into precursor solution. After solvothermal treatment, the ZIF-8 was *in situ* synthesized and MOF@CNT hybrid was obtained (Zhang H. et al., 2018).

HOLLOW BOWL-LIKE CARBON NANOMATERIALS

Hollow bowl-like carbon nanomaterials have attracted great interests due to their excellent properties, such as large surface area, tunable pore sizes, high pore volume, high packing density, high electrical conduction (Liang et al., 2020). Just as their hollow carbon spheres counterparts, hollow bowl-like carbon nanomaterials can be prepared via template-assisted method or template-free method as mentioned above.

In 2016, Pei used SiO₂ and polybenzoxazine as hard template and carbon precursor, respectively, and N-Doped hollow porous carbon bowls (N-HPCB) were synthesized with the treatments of carbonizing and etching (Figure 2D). The as-prepared N-HPCB exhibited a high specific surface area up to 2161 m²/g and pore volume of 1.5 m³/g (Pei et al., 2016). Without carbonization, Gao and co-authors developed a generalized strategy for the synthesis of “dual carbon”-protected bowl-like hollow particles. Similarly, SiO₂ and resorcinol formaldehyde (RF) were used as hard template and carbon source, respectively. A low-temperature refluxing procedure and a vapor-phase process were utilized during the preparation process (Gao et al., 2019). Interestingly, many facile strategies have been developed that hollow bowl-like carbon can be obtained just by tuning mass ratio of RF and tetraethyl orthosilicate (TEOS) (Fei et al., 2020; Yi et al., 2020).

As known, compared with its counterpart, template-free method requires fewer steps and cause less waste. Hence, scientists have focused their interests on synthesizing hollow bowl-like carbon materials with template-free method. With a facile sulfuric acid treatment and drying route, Liang and co-workers prepared hollow bowl-like carbon with specific surface area of 103.8 m²/g (Liang et al., 2014). In addition, Duan and co-authors prepared hollow bowl-like carbon supported AuPd with an average size of 175 nm by traditional hydrothermal carbonization (Duan et al., 2020).

CARBON NANOCAGES

Unlike sphere-shaped carbon nanomaterials, mass production of nanocages from carbon materials is still a great challenge. Template-assisted method is an effective strategy for the synthesis of carbon based nanocages. Xie et al. reported a facile route to prepare carbon nanocages by using MgO and benzene as template and carbon source, respectively (Xie et al., 2012). Typically, basic magnesium carbonate was heated in a tubular furnace, and then benzene was added into the tubular furnace, followed by treated with hydrochloric acid solution, the carbon nanocages with specific surface area up to 2053 m²/g were obtained. Similarly, Zang and co-workers prepared carbon nanocages by using SiO₂ and resorcinol formaldehyde resin as template and carbon source, respectively (Zang et al., 2020). In addition, Fe₃O₄, TiO₂, and CaO also were used as templates to prepare carbon nanocages (Wu Q. et al., 2020). Such as, novel N-doped carbon nanoboxes were synthesized with Fe₂O₃ nanocubes as the template, and a thin layer of polydopamine (PDA) were coated on their surface, followed by carbonization

process (500°C, 3 h) and being etched by hydrochloric acid, which resulted in the preparation of N-doped carbon nanoboxes (Figure 2E) (Yu et al., 2015).

More recently, pyrolysis has become a new strategy to prepare carbon nanocages. In 2019, Zhang and co-workers successfully synthesized carbon nanocages by the pyrolysis (600°C, 3 h) of PE and magnesium powder (Zhang Y. et al., 2019). Moreover, Wang and co-workers prepared N-doped carbon nanocages by a spay pyrolysis of pyridine (C₅H₅N) and pentacarbonyl [Fe(CO)₅] at 700 and 1000°C (Wang et al., 2014).

HOLLOW CARBON FIBERS

As early as 1997, by introducing alumina membrane as template, Hulteen and co-authors prepared hollow carbon fibers (Hulteen et al., 1997). Typically, porous alumina membrane was immersed in acrylonitrile solution, then the polymerization reaction was initiated by adding 1, 1'-azobis(cyclohexane carbonitrile), resulting in the formation of PAN/alumina composite. Similarly, in 2011, Zheng and co-workers reported a hollow carbon nanofiber-encapsulated sulfur electrode structure (Zheng et al., 2011). Anodic aluminum oxide (AAO) membrane and polystyrene (PS) were chosen as template and carbon source, respectively, through a carbonization process (750°C, 4 h), carbon coated AAO membranes were prepared, followed by removing the AAO templates, hollow carbon fibers of diameters range between 200 and 300 nm were obtained. Interestingly, biomass material, such as crab shell can also be used as template to prepare hollow carbon fibers (Liu et al., 2010).

On the other hand, electrospinning is also widely used for the synthesis of hollow carbon fibers. Larsen and co-workers reported a facile coaxial route for the fabrication of hollow nanofibers. TEOS and olive oil were used as outside and inner nanojet liquid, respectively. And they were injected into two coaxial capillaries with different diameters. After co-electrospinning process, hollow nanofibers were obtained (Loscertales et al., 2004). Similarly, Xia and Li fabricated hollow nanofibers by using Poly(vinyl pyrrolidone) (PVP) and Ti(OiPr)₄ as the core and shell materials, followed by co-electrospinning and carbonizing process (500°C, 1 h) (Li and Xia, 2004). Since then, various materials such as, polyacrylonitrile (PAN), poly(styrene-co-acrylonitrile) (SAN) (Le et al., 2016), poly (methyl methacrylate) (PMMA) have been used to synthesize hollow carbon fibers (Wang Y. et al., 2017). For instance, Ramakrishnan and co-workers reported a facile coaxial electrospinning approach to prepare hollow carbon fibers. PAN and PVP were used as carbon source and sacrificial material, respectively. After coaxial electrospinning and carbonization process (800°C, 1 h), the as-prepared hollow carbon fibers exhibited surface area of 557 m²/g and ultrahigh total pore volume of 0.5681 cm³/g (Figure 2F) (Ramakrishnan et al., 2015). In addition, with the development of nanotechnology, combing electrospinning with other technologies has become a new research hotspot in recent years. For example, by combing electrospinning with template-assisted method, Sun et al. prepared fantastic bamboo-like hollow carbon fibers

(Sun et al., 2015). Firstly, PAN and TEOS were used as precursors to prepare white nanofibers by electrospinning. Then bamboo-like hollow carbon fibers were obtained after carbonization treatment followed by removing SiO₂ template in hydrofluoric acid.

DISCUSSION

In summary, recent advances in synthesis of carbon nanomaterials with hollow structures are reviewed and discussed. The synthesis methods and applications of hollow carbon spheres, metal organic framework-derived carbon structures, bowl-like, cage-like, and carbon fibers hollow structures are presented. Although great progress has been made in this field, its synthesis, application and precise structural adjusting of HCNs are still facing great challenges. (1) Although template-free method is simple, the dynamics process of structure formation is not clarified. (2) Hard-template method is one of the most effective methods for synthesizing HCNs. However, sodium hydroxide or hydrofluoric acids are inevitably used in the process of template etching, especially for SiO₂ template, which not only pollutes the environment, but also increase the cost. Therefore, developing a novel template which could be removed under mild conditions is becoming to be the emphasis of research. (3) A large amount of metal organic frameworks have been reported over the years. Nonetheless, only few of them (i. e., MOF-5, ZIF-8, ZIF-67) could be derived to hollow carbon nanomaterials, due to their poor thermal structure stability. It is apparent that exploiting a series of ligands for high stability MOF or developing new carbonization approaches will broad their application on HCNs. (4) Compared with single layer hollow carbon nanomaterials (i.e., bow-like carbon nanomaterials, carbon nanocages, and hollow carbon

fiber), multilayer hollow structure, or hollow hierarchical structure, which could increase the specific surface area, modify properties of different layer, enhance the connection of each hollow structure, will be the key point in the development of hollow carbon nanomaterials.

Hollow carbon nanomaterials undoubtedly become a hot spot of novel materials research due to their unique structures with high specific area, rich exposed active sites, and mass loading vacancies. It is believed that with the combined efforts in traditional methods and in-depth kinetic analysis, more strategies will be realized in building unified size, stable, environmentally friendly, and low cost hollow carbon nanomaterials. These insightful ideas, raised during the exploration, will eventually benefit the understanding and development of conventional hollow structure, as well as other nanomaterials based on hollow structure.

AUTHOR CONTRIBUTIONS

FL and JT wrote the manuscript. FL and YC collected and read papers and contributed to the Discussion section. JL and SZ contributed to the paper design and refine. HC, HH, and CD contributed to the proofreading of the paper. ML and YY revised and approved the manuscript. All the authors collected and read papers and contributed to paper writing.

FUNDING

The authors are grateful for financial support from the National Natural Science Foundation of China (51908256), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (19KJA460004), the Priority Academic Program Development of Jiangsu Higher Education Institutions.

REFERENCES

- Chen, C., Huang, H., Yu, Y., Shi, J., He, C., Albilali, R., et al. (2018). Template-free Synthesis of hierarchical porous carbon with controlled morphology for CO₂ efficient capture. *Chem. Eng. J.* 353, 584–594. doi: 10.1016/j.cej.2018.07.161
- Chen, X., Gao, J., Liu, S., Yang, Z., Wang, S., Su, Z., et al. (2020). 1D bamboo-like N-doped carbon nanotubes with encapsulated iron-based nanoparticles as an advanced Zn-Air battery cathode electrocatalyst. *J. Alloy Compd.* 828:154435. doi: 10.1016/j.jallcom.2020.154435
- Duan, Y., Liu, Z., Zhao, B., and Liu, J. (2020). Bowl-like carbon supported and phosphotungstic acid composite for electrooxidation of ethylene glycol and glycerol. *Inorg. Chem. Commun.* 117:107976. doi: 10.1016/j.inoche.2020.107976
- Fei, R., Wang, H., Wang, Q., Qiu, R., Tang, S., Wang, R., et al. (2020). *In situ* hard-template synthesis of hollow bowl-like carbon: a potential versatile platform for sodium and zinc ion capacitors. *Adv. Energy Mater.* 10:2002741. doi: 10.1002/aenm.202002741
- Gao, J., Li, Y., Peng, B., Wang, G., and Zhang, G. (2019). The general construction of asymmetric bowl-like hollow nanostructures by grafting carbon-sheathed ultrasmall iron-based compounds onto carbon surfaces for use as superior anodes for sodium-ion hybrid capacitors. *J. Mater. Chem. A* 7, 24199–24204. doi: 10.1039/C9TA09181E
- Gao, J., Liu, S., Zhu, P., Zhao, X., and Wang, G. (2020). Fe–N₄ Engineering of S and N Co-doped hierarchical porous carbon-based electrocatalysts for enhanced oxygen reduction in Zn–air batteries. *Dalton Trans.* 49, 14847–14853. doi: 10.1039/D0DT02704A
- Guo, C., Wang, Q., He, J., Wu, C., Xie, K., Liu, Y., et al. (2020). Rational design of unique ZnO/ZnS@N-C heterostructures for high-performance lithium-ion batteries. *J. Phys. Chem. Lett.* 11, 905–912. doi: 10.1021/acs.jpclett.9b03677
- Guo, C., Zhang, W., Liu, Y., He, J., Yang, S., Liu, M., et al. (2019). Constructing CoO/Co₃S₄ heterostructures embedded in N-doped carbon frameworks for high-performance sodium-ion batteries. *Adv. Funct. Mater.* 29:1901925. doi: 10.1002/adfm.201901925
- Han, F.-D., Bai, Y.-J., Liu, R., Yao, B., Qi, Y.-X., Lun, N., et al. (2011). Template-free synthesis of interconnected hollow carbon nanospheres for high-performance anode material in lithium-ion batteries. *Adv. Energy Mater.* 1, 798–801. doi: 10.1002/aenm.201100340
- Hu, B., Wang, K., Wu, L., Yu, S.-H., Antonietti, M., and Titirici, M.-M. (2010). Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv. Mater.* 22, 813–828. doi: 10.1002/adma.200902812
- Hulteen, J. C., Chen, H. X., Chambliss, C. K., and Martin, C. R. (1997). Template synthesis of carbon nanotubule and nanofiber arrays. *Nanostruct. Mater.* 9, 133–136. doi: 10.1016/S0965-9773(97)00036-6
- Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature* 354, 56–58. doi: 10.1038/354056a0
- Jahan, M., Bao, Q., and Loh, K. P. (2012). Electrocatalytically active graphene-porphyrin MOF composite for oxygen reduction reaction. *J. Am. Chem. Soc.* 134, 6707–6713. doi: 10.1021/ja211433h

- Joo, J. B., Kim, P., Kim, W., Kim, J., Kim, N. D., and Yi, J. (2008). Simple preparation of hollow carbon sphere via templating method. *Curr. Appl. Phys.* 8, 814–817. doi: 10.1016/j.cap.2007.04.038
- Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., and Smalley, R. E. (1985). C₆₀: Buckminsterfullerene. *Nature* 318, 162–163. doi: 10.1038/318162a0
- Le, T. H., Yang, Y., Yu, L., Gao, T., Huang, Z., and Kang, F. (2016). Polyimide-based porous hollow carbon nanofibers for supercapacitor electrode. *J. Appl. Polym. Sci.* 133:43397. doi: 10.1002/app.43397
- Li, B. M., Yan, Y., Shen, C. T., Yu, Y., Wang, Q. H., and Liu, M. K. (2018). Extraordinary lithium ion storage capability achieved by SnO₂ nanocrystals with exposed {221} facets. *Nanoscale* 10, 16217–16230. doi: 10.1039/C8NR04513E
- Li, D., and Xia, Y. (2004). Direct fabrication of composite and ceramic hollow nanofibers by electrospinning. *Nano Lett.* 4, 933–938. doi: 10.1021/nl049590f
- Liang, J., Kou, H., and Ding, S. (2020). Complex hollow bowl-like nanostructures: synthesis, application, and perspective. *Adv. Funct. Mater.* 2020:2007801. doi: 10.1002/adfm.202007801
- Liang, J., Yu, X.-Y., Zhou, H., Wu, H. B., Ding, S., and Lou, X. W. (2014). Bowl-like SnO₂@Carbon hollow particles as an advanced anode material for lithium-ion batteries. *Angew. Chem. Int. Ed.* 53, 12803–12807. doi: 10.1002/anie.201407917
- Liang, J.-Y., Wang, C.-C., and Lu, S.-Y. (2015). Glucose-derived nitrogen-doped hierarchical hollow nest-like carbon nanostructures from a novel template-free method as an outstanding electrode material for supercapacitors. *J. Mater. Chem. A* 3, 24453–24462. doi: 10.1039/C5TA08007J
- Liu, B., Shioyama, H., Akita, T., and Xu, Q. (2008). Metal-organic framework as a template for porous carbon synthesis. *J. Am. Chem. Soc.* 130, 5390–5391. doi: 10.1021/ja7106146
- Liu, H.-J., Wang, X.-M., Cui, W.-J., Dou, Y.-Q., Zhao, D.-Y., and Xia, Y.-Y. (2010). Highly ordered mesoporous carbon nanofiber arrays from a crab shell biological template and its application in supercapacitors and fuel cells. *J. Mater. Chem.* 20, 4223–4230. doi: 10.1039/b925776d
- Liu, M., Zhang, P., Qu, Z., Yan, Y., Lai, C., Liu, T., et al. (2019). Conductive carbon nanofiber interpenetrated graphene architecture for ultra-stable sodium ion battery. *Nat. Commun.* 10:3917. doi: 10.1038/s41467-019-11925-z
- Liu, M. K., Li, B. M., Zhou, H., Chen, C., Liu, Y. Q., and Liu, T. X. (2017a). Extraordinary rate capability achieved by a 3D “skeleton/skin” carbon aerogel-polyaniline hybrid with vertically aligned pores. *Chem. Commun.* 53, 2810–2813. doi: 10.1039/C7CC00121E
- Liu, M. K., Liu, Y. Q., Yan, Y., Wang, F. S., Liu, J. H., and Liu, T. X. (2017b). A highly conductive carbon-sulfur film with interconnected mesopores as an advanced cathode for lithium-sulfur batteries. *Chem. Commun.* 53, 9097–9100. doi: 10.1039/C7CC04523A
- Liu, M. K., Meng, Q. H., Yang, Z., Zhao, X. S., and Liu, T. X. (2018). Ultra-long-term cycling stability of an integrated carbon-sulfur membrane with dual shuttle-inhibiting layers of graphene “Nets” and a porous carbon skin. *Chem. Commun.* 54, 5090–5093. doi: 10.1039/C8CC01889H
- Liu, Y., Li, G., Fu, J., Chen, Z., and Peng, X. (2017). Strings of porous carbon polyhedrons as self-standing cathode host for high-energy-density lithium-sulfur batteries. *Angew. Chem. Int. Ed.* 56, 6176–6180. doi: 10.1002/anie.201700686
- Liu, Y. Q., Yan, Y., Li, K., Yu, Y., Wang, Q. H., and Liu, M. K. (2019). A high-areal-capacity lithium-sulfur cathode achieved by a boron-doped carbon-sulfur aerogel with consecutive core-shell structures. *Chem. Commun.* 55, 1084–1087. doi: 10.1039/C8CC07594H
- Loscertales, I. G., Barrero, A., Márquez, M., Spretz, R., Velarde-Ortiz, R., and Larsen, G. (2004). Electrically forced coaxial nanojets for one-step hollow nanofiber design. *J. Am. Chem. Soc.* 126, 5376–5377. doi: 10.1021/ja049443j
- Natarajan, S., Bajaj, H. C., and Aravindan, V. (2019). Template-free synthesis of carbon hollow spheres and reduced graphene oxide from spent lithium-ion batteries towards efficient gas storage. *J. Mater. Chem. A* 7, 3244–3252. doi: 10.1039/C8TA11521D
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., et al. (2004). Electric field effect in atomically thin carbon films. *Science* 306:666. doi: 10.1126/science.1102896
- Pei, F., An, T., Zang, J., Zhao, X., Fang, X., Zheng, M., et al. (2016). From hollow carbon spheres to N-doped hollow porous carbon bowls: rational design of hollow carbon host for Li-S batteries. *Adv. Energy Mater.* 6:1502539. doi: 10.1002/aenm.201502539
- Ramakrishnan, P., Park, S.-G., and Shanmugam, S. (2015). Three-dimensional hierarchical nitrogen-doped arch and hollow nanocarbons: morphological influences on supercapacitor applications. *J. Mater. Chem. A* 3, 16242–16250. doi: 10.1039/C5TA03384E
- Ren, Q., Wang, H., Lu, X.-F., Tong, Y.-X., and Li, G.-R. (2018). Recent progress on MOF-derived heteroatom-doped carbon-based electrocatalysts for oxygen reduction reaction. *Adv. Sci.* 5:1700515. doi: 10.1002/advs.201700515
- Shen, Q., Sun, L., Zhuang, Y., Zhan, W., Wang, X., and Han, X. (2020). Hollow dodecahedral structure of In₂O₃-In₂S₃ heterojunction encapsulated by N-doped C as an excellent visible-light-active photocatalyst for organic transformation. *Inorg. Chem.* 59, 17650–17658. doi: 10.1021/acs.inorgchem.0c02892
- Sun, H., Zhu, Y., Yang, B., Wang, Y., Wu, Y., and Du, J. (2016). Template-free fabrication of nitrogen-doped hollow carbon spheres for high-performance supercapacitors based on a scalable homopolymer vesicle. *J. Mater. Chem. A* 4, 12088–12097. doi: 10.1039/C6TA04330E
- Sun, L., He, X., Yuan, Y., Chen, J., Zhan, W., Wang, X.-J., et al. (2020a). Tuning interfacial sequence between nitrogen-doped carbon layer and Au nanoparticles on metal-organic framework-derived TiO₂ to enhance photocatalytic hydrogen production. *Chem. Eng. J.* 397:125468. doi: 10.1016/j.cej.2020.125468
- Sun, L., Li, R., Zhan, W., Yuan, Y., Wang, X., Han, X., et al. (2019a). Double-shelled hollow rods assembled from nitrogen/sulfur-codoped carbon coated indium oxide nanoparticles as excellent photocatalysts. *Nat. Commun.* 10:2270. doi: 10.1038/s41467-019-10302-0
- Sun, L., Yuan, Y., Li, R., Zhan, W., Wang, X.-J., Zhao, Y., et al. (2019b). Significantly enhanced photocatalytic performance of In₂O₃ hollow spheres via the coating effect of an N,S-codoped carbon layer. *J. Mater. Chem. A* 7, 25423–25432. doi: 10.1039/C9TA07891F
- Sun, L., Yuan, Y., Wang, F., Zhao, Y., Zhan, W., and Han, X. (2020b). Selective wet-chemical Etching to create TiO₂@MOF frame heterostructure for efficient photocatalytic hydrogen evolution. *Nano Energy* 74:104909. doi: 10.1016/j.nanoen.2020.104909
- Sun, L., Zhuang, Y., Yuan, Y., Zhan, W., Wang, X.-J., Han, X., et al. (2019c). Nitrogen-doped carbon-coated CuO-In₂O₃ p-n heterojunction for remarkable photocatalytic hydrogen evolution. *Adv. Energy Mater.* 9:1902839. doi: 10.1002/aenm.201902839
- Sun, X., and Li, Y. (2004). Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angew. Chem. Int. Ed.* 43, 597–601. doi: 10.1002/anie.200352386
- Sun, Y., Sills, R. B., Hu, X., Seh, Z. W., Xiao, X., Xu, H., et al. (2015). A bamboo-inspired nanostructure design for flexible, foldable, and twistable energy storage devices. *Nano Lett.* 15, 3899–3906. doi: 10.1021/acs.nanolett.5b00738
- Tang, K., Fu, L., White, R. J., Yu, L., Titirici, M.-M., Antonietti, M., et al. (2012). Hollow carbon nanospheres with superior rate capability for sodium-based batteries. *Adv. Energy Mater.* 2, 873–877. doi: 10.1002/aenm.201100691
- Wang, Q., Li, H., Chen, L., and Huang, X. (2001). Monodispersed hard carbon spherules with uniform nanopores. *Carbon* 39, 2211–2214. doi: 10.1016/S0008-6223(01)00040-9
- Wang, Q., Zhang, W., Guo, C., Liu, Y., Wang, C., and Guo, Z. (2017). In situ construction of 3D interconnected FeS@Fe₃C@Graphitic carbon networks for high-performance sodium-ion batteries. *Adv. Funct. Mater.* 27:1703390. doi: 10.1002/adfm.201703390
- Wang, S., Sun, W., Yang, D.-S., and Yang, F. (2019). Conversion of soybean waste to sub-icron porous-hollow carbon spheres for supercapacitor via a reagent and template-free route. *Mater. Today Energy* 13, 50–55. doi: 10.1016/j.mtener.2019.04.015
- Wang, T., Yang, C., Liu, Y., Yang, M., Li, X., He, Y., et al. (2020). Dual-shelled multidoped hollow carbon nanocages with hierarchical porosity for high-performance oxygen reduction reaction in both alkaline and acidic media. *Nano Lett.* 20, 5639–5645. doi: 10.1021/acs.nanolett.0c00081
- Wang, X. X., Tan, Z. H., Zeng, M., and Wang, J. N. (2014). Carbon nanocages: a new support material for Pt catalyst with remarkably high durability. *Sci. Rep.* 4:4437. doi: 10.1038/srep04437
- Wang, Y., Li, G., Jin, J., and Yang, S. (2017). Hollow porous carbon nanofibers as novel support for platinum-based oxygen reduction reaction electrocatalysts. *Int. J. Hydrog. Energy* 42, 5938–5947. doi: 10.1016/j.ijhydene.2017.02.012

- Wen, Z., Wang, Q., Zhang, Q., and Li, J. (2007). Hollow carbon spheres with wide size distribution as anode catalyst support for direct methanol fuel cells. *Electrochem. Commun.* 9, 1867–1872. doi: 10.1016/j.elecom.2007.04.016
- Wu, C., Xie, K., Ren, K., Yang, S., and Wang, Q. (2020). Dendrite-free Zn anodes enabled by functional nitrogen-doped carbon protective layers for aqueous zinc-ion batteries. *Dalton Trans.* 49, 17629–17634. doi: 10.1039/D0DT03459B
- Wu, Q., Yang, L., Wang, X., and Hu, Z. (2020). Carbon-based nanocages: a new platform for advanced energy storage and conversion. *Adv. Mater.* 32:1904177. doi: 10.1002/adma.201904177
- Xie, K., Qin, X., Wang, X., Wang, Y., Tao, H., Wu, Q., et al. (2012). Carbon nanocages as supercapacitor electrode materials. *Adv. Mater.* 24, 347–352. doi: 10.1002/adma.201103872
- Yan, Y., Zhang, P., Qu, Z., Tong, M., Zhao, S., Li, Z., et al. (2020). Carbon/sulfur aerogel with adequate mesoporous channels as robust polysulfide confinement matrix for highly stable lithium–sulfur battery. *Nano Lett.* 20, 7662–7669. doi: 10.1021/acs.nanolett.0c03203
- Yang, M., Hu, X., Fang, Z., Sun, L., Yuan, Z., Wang, S., et al. (2017). Bifunctional MOF-derived carbon photonic crystal architectures for advanced Zn–air and Li–S batteries: highly exposed graphitic nitrogen matters. *Adv. Funct. Mater.* 27:1701971. doi: 10.1002/adfm.201701971
- Yang, Z., Gao, J., Liu, S., Zhu, P., Huang, S., Zeng, D., et al. (2020). Exploiting S,N co-doped 3D hierarchical porous carbon with Fe_{II}-N₄ moiety as an efficient cathode electrocatalyst for advanced Zn–air battery. *Electrochim. Acta* 364:137301. doi: 10.1016/j.electacta.2020.137301
- Yang, Z. Y., Zhang, P., Wang, J., Yan, Y., Yu, Y., Wang, Q. H., et al. (2018). Hierarchical Carbon@SnS₂ aerogel with “Skeleton/Skin” architectures as a high-capacity, high-rate capability and long cycle life anode for sodium ion storage. *ACS Appl. Mater. Interfaces* 10, 37434–37444. doi: 10.1021/acsami.8b14861
- Yi, W., Chen, X., Zhu, Y., Chen, H., and Liu, J. (2020). Self-organized bowl-like hollow carbon submicrospheres with hierarchical mesopore-rich structure as superior electrode materials for supercapacitors. *Appl. Surf. Sci.* 509:144841. doi: 10.1016/j.apsusc.2019.144841
- Yoon, S. B., Sohn, K., Kim, J. Y., Shin, C. H., Yu, J. S., and Hyeon, T. (2002). Fabrication of carbon capsules with hollow macroporous core/mesoporous shell structures. *Adv. Mater.* 14, 19–21. doi: 10.1002/1521-4095(20020104)14:1<19::AID-ADMA19>3.0.CO;2-X
- Yu, X.-Y., Hu, H., Wang, Y., Chen, H., and Lou, X. W. (2015). Ultrathin MoS₂ nanosheets supported on n-doped carbon nanoboxes with enhanced lithium storage and electrocatalytic properties. *Angew. Chem. Int. Ed.* 54, 7395–7398. doi: 10.1002/anie.201502117
- Yuan, Y., Sheng, K., Zeng, S., Han, X., Sun, L., Lončarić, I., et al. (2020a). Engineering Cu/TiO₂@N-doped C interfaces derived from an atom-precise heterometallic CuII4TiIV5 cluster for efficient photocatalytic hydrogen evolution. *Inorg. Chem.* 59, 5456–5462. doi: 10.1021/acs.inorgchem.0c00084
- Yuan, Y., Sun, L., Li, Y., Zhan, W., Wang, X., and Han, X. (2020b). Synergistic modulation of active sites and charge transport: N/S Co-doped C encapsulated NiCo₂O₄/NiO hollow microrods for boosting oxygen evolution catalysis. *Inorg. Chem.* 59, 4080–4089. doi: 10.1021/acs.inorgchem.0c00089
- Yuan, Y., Sun, L., Wu, G., Yuan, Y., Zhan, W., Wang, X., et al. (2020c). Engineering nickel/palladium heterojunctions for dehydrogenation of ammonia borane: improving the catalytic performance with 3d mesoporous structures and external nitrogen-doped carbon layers. *Inorg. Chem.* 59, 2104–2110. doi: 10.1021/acs.inorgchem.9b03607
- Yuan, Y., Sun, L., Zeng, S., Zhan, W., Wang, X., and Han, X. (2020d). Modulating the charge-transfer step of a p–n heterojunction with nitrogen-doped carbon: a promising strategy to improve photocatalytic performance. *Chem. Eur. J.* 26, 921–926. doi: 10.1002/chem.201904467
- Yue, Y., Guo, B., Qiao, Z.-A., Fulvio, P. F., Chen, J., Binder, A. J., et al. (2014). Multi-wall carbon nanotube@Zeolite imidazolate framework composite from a nanoscale zinc oxide precursor. *Microporous Mesoporous Mater.* 198, 139–143. doi: 10.1016/j.micromeso.2014.07.026
- Zang, X., Xue, Y., Ni, W., Li, C., Hu, L., Zhang, A., et al. (2020). Enhanced electrosorption ability of carbon nanocages as an advanced electrode material for capacitive deionization. *ACS Appl. Mater. Interfaces* 12, 2180–2190. doi: 10.1021/acsami.9b12744
- Zhan, W., Yuan, Y., Sun, L., Yuan, Y., Han, X., and Zhao, Y. (2019). Hierarchical NiO@N-doped carbon microspheres with ultrathin nanosheet subunits as excellent photocatalysts for hydrogen evolution. *Small* 15:1901024. doi: 10.1002/smll.201901024
- Zhang, H., Zhao, W., Zou, M., Wang, Y., Chen, Y., Xu, L., et al. (2018). 3D, mutually embedded MOF@carbon nanotube hybrid networks for high-performance lithium-sulfur batteries. *Adv. Energy Mater.* 8:1800013. doi: 10.1002/aenm.201800013
- Zhang, P., Liu, Y. Q., Yan, Y., Yu, Y., Wang, Q. H., and Liu, M. K. (2018). High areal capacitance for lithium ion storage achieved by a hierarchical carbon/MoS₂ aerogel with vertically aligned pores. *ACS Appl. Energy Mater.* 1, 4814–4823. doi: 10.1021/acsami.8b00897
- Zhang, P., and Lou, X. W. (2019). Design of heterostructured hollow photocatalysts for solar-to-Chemical Energy Conversion. *Adv. Mater.* 31:1900281. doi: 10.1002/adma.201900281
- Zhang, W., Jiang, X., Zhao, Y., Carné-Sánchez, A., Malgras, V., Kim, J., et al. (2017). Hollow carbon nanobubbles: monocrystalline MOF nanobubbles and their pyrolysis. *Chem. Sci.* 8, 3538–3546. doi: 10.1039/C6SC04903F
- Zhang, X., Wang, Y., Du, Y., Qing, M., Yu, F., Tian, Z. Q., et al. (2019). Highly Active N,S Co-doped hierarchical porous carbon nanospheres from green and template-free method for super capacitors and oxygen reduction reaction. *Electrochim. Acta* 318, 272–280. doi: 10.1016/j.electacta.2019.06.081
- Zhang, Y., Yu, Y., Liang, K., Liu, L., Shen, Z., and Chen, A. (2019). Hollow mesoporous carbon cages by pyrolysis of waste polyethylene for supercapacitors. *N. J. Chem.* 43, 10899–10905. doi: 10.1039/C9NJ01534E
- Zheng, G., Yang, Y., Cha, J. J., Hong, S. S., and Cui, Y. (2011). Hollow carbon nanofiber-encapsulated sulfur cathodes for high specific capacity rechargeable lithium batteries. *Nano Lett.* 11, 4462–4467. doi: 10.1021/nl2027684

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2021 Liu, Cheng, Tan, Li, Cheng, Hu, Du, Zhao, Yan and Liu. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.