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Jia-Nan Zhang *Editor*

Carbon-Based Nanomaterials for Energy Conversion and Storage

Applications in Electrochemical Catalysis

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Jia-Nan Zhang
Editor

Carbon-Based Nanomaterials for Energy Conversion and Storage

Applications in Electrochemical Catalysis

Springer

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Preface

The increasing demand of energy and scarcity of fossil fuel are major concerns today and have attracted much attention on utilizing renewable energy sources for better storage and conversion of energy. To meet the increasing demand of energy, most researches have focused on developing high-performance energy conversion and storage. The extensive studies have been carried out on catalysts used in different types of electrochemical reaction. The optimal design of catalysts is considered as one of the main routes to achieve high performance of the electrochemical energy conversion and storage. In this regard, carbon-based nanomaterials have been drawn considerable attention due to their special properties of high surface areas which providing large number of active sites for electrochemical reaction and ion/electron diffusion. Among various materials, carbon-based materials can be used as effective catalytic materials for different electrochemical reactions, from metal-free carbon-based nanomaterials to metal-heteroatom-carbon-based nanomaterials, as well as metal nanoparticles supported or encapsulated to carbon-based materials with their unique properties, tailored sizes and morphologies and. With the flourishing development of diverse carbon-based nanomaterials, further insights into the design and mechanisms of ideal electrocatalysts have been gained.

This book aims to cover all these aspects and discuss recent achievements and various electrochemical reactions processes including energy conversion and storage, as well as the corresponding advanced electrocatalysts mechanism understanding. The book comprises four sections. The first section discusses the fundamental synthesis, characterization techniques, and catalytic effects related to the energy conversion and storage mechanism from different types of electrochemical reactions. The next section elaborately reviews different types of electrocatalytic reactions based on different carbon-based materials and their performance reported till date. The third section is focused on batteries based on different carbon-based materials with different storage mechanism and their performances as reported. Finally, the enlightenment in terms of theoretical development and experimental research will be provided to the general reader.

It is anticipated that the content will further supply unambiguous understanding for all these components and the importance of the field and discuss current trends of different carbon-based materials for current ongoing works.

Zhengzhou, China Prof. Jia-Nan Zhang

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Chapter 1
Introduction

Siran Xu, Yajin Wang, Dongping Xue, Huicong Xia, and Jia-Nan Zhang

Nanotechnology refers to the study of the properties and interactions of substances (including the manipulation of atoms and molecules) on the nanometer scale (between 1 and 100 nm), as well as the multidisciplinary science and technology that utilizes these properties, covering multiple fields such as physics, chemistry, materials, science, engineering, biology and medicine [1]. Its ultimate goal is to directly synthesis products with specific functions based on the novel physical, chemical, and biological properties of atoms, molecules, and nanoscale substances. Nanotechnology is another major technology that profoundly affects social development after information technology and biotechnology [2].

Nanomaterials are the core component of nanotechnology. When the substance reaches nanometer scale (about 1–100 nm), quantum effect, locality of substance, huge surface, and interface effects make many properties of the substance qualitatively change, showing lots of differences from macroscopic objects and the strange phenomenon of single atoms [2, 3]. However, if only the scale reaches nanometers without special properties, it cannot be called nanomaterials. After 1990, nanomaterials have developed rapidly. The most worth mentioning before this is the discovery of carbon nano-atom cluster—buckminsterfullerene (C_{60}) in 1985 [3]. The successful

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development of this material has made people see that it has special properties that ordinary carbon material does not have. Pure C_{60} solid is an insulator, but it becomes a material with good conductivity after being doped with alkali metals, which can be compared with metals and even become superconductors [4]. With the development of nanotechnology, the classification of nanomaterials has become more detailed, including nano-particles, nano-blocks, nano-films, and nano-assembly systems [5]. At the beginning of the twenty-first century, people are more and more interested in the emerging fields of modern nanotechnology. With the help of various special properties of nanomaterials, which have a wide range of applications in the fields of catalytic, environmental protection, construction materials, [6] biomedical materials, [7] electromagnetic materials, [8] optical materials, [9] degradable materials [10] and so on. After decades of research and exploration on nanotechnology, it has been developed by leaps and bounds, and now scientists have been able to manipulate individual atoms in the laboratory, making nanomaterials the basis for preparing various required functional devices.

Some people say that electricity has brought about human civilization; others say that it is a human civilization that has created electricity. Regardless of the judgment, we can be sure that the emergence of electricity has changed the history of mankind, and the energy that brings electricity is an important driving force for the progress of mankind, society, and civilization. Because of this, our huge social system still relies on fossil energy which has naturally penetrated all aspects of our lives until now. 85% of the energy used by human beings is fossil energy sources, such as coal, oil, and natural gas, and overuse of these fossil energy sources has caused them to be in a crisis of energy exhaustion [11]. Moreover, the excessive use of traditional fossil energy has brought about global warming, ecological system destruction, endangerment of rare species, frequent extreme weather events, sea-level rise crisis, air pollution, and other problems, which seriously threaten survival and development of human society. If there is clean, safe, efficient, inexhaustible energy for our use, the "energy crisis" will cease to exist. Therefore, it is urgent to find clean energy, get rid of fossil energy dependence, promote economic growth, eliminate energy inequality and poverty, and protect the environment, to realize the sustainable development of all mankind [12]. Electrochemical energy storage and conversion systems, such as fuel cells, [13] metal-air batteries, [14] electrolytic water devices, [15] and carbon dioxide reduction technology [16] have become important means to deal with environmental and energy crises. In energy conversion equipment, catalyst design is an important link. Traditional electrocatalysts and energy storage materials still face technical problems such as complex preparation processes, low porosity, poor catalytic activity and stability, which severely restrict their commercial applications. Therefore, there is an urgent need to develop catalytic materials with high conversion efficiency and excellent stability. In recent years, researchers have focused their attention on nanocatalysts. Because of their unique crystal structure and surface characteristics, they have the advantages of large specific surface area, excellent stability, and high surface activity. Moreover, the bonding and electronic state on the surface of the nanocatalysts are different from the inside of the particle, and the incomplete coordination of surface atoms will also lead to an increase in surface active sites,

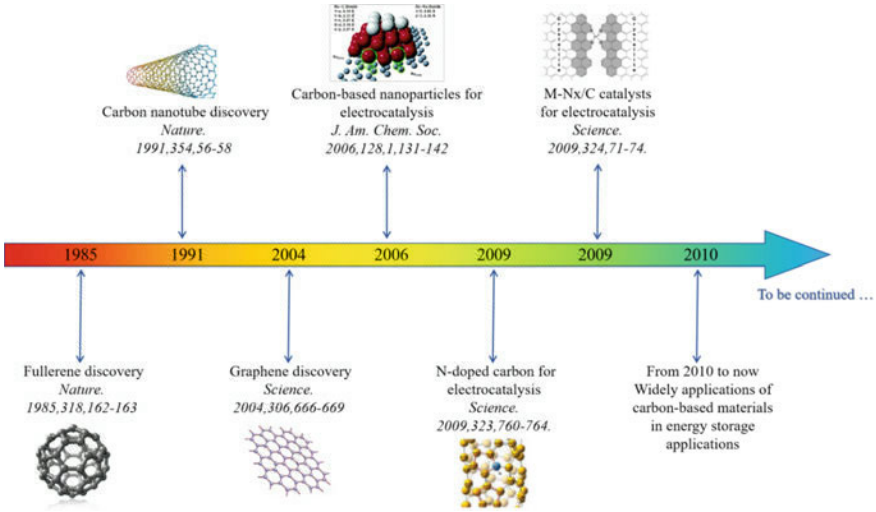

Fig. 1.1 Timeline of the important breakthrough of the development of carbon nanomaterials

and improve the catalytic performance [17]. Therefore, nanocatalysts show great application prospects in energy conversion and storage [18].

Carbon nanomaterials (CNMs) stand out to be one of the highly efficient nanomaterials due to it is vast availability and lower cost compared to other nanomaterials [19, 20]. The development history of carbon-based nanomaterials is shown in Fig. 1.1. Meanwhile, CNMs, benefiting from their unique properties in exceptional electrical, thermal, chemical, and mechanical fields, have occupied a unique position in nanoscience [20–22]. Indeed, CNMs, thanks to the various allotropes (graphite, diamond, fullerenes), as well as the abundant dimensions from zero-dimensional (0D) to three-dimensional (3D) and variable forms of existence (powders, fibers, films, foams, fabrics, and hybrids) have captured immense attention as attractive materials with great potential and promising applications in massive fields [23]. In recent years, fullerenes, expanded graphite (EG), carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, reduced graphene oxide (rGO), and other CNMs have been extensively applied in energy storage, electronics, catalysis, biomaterials, and medical fields [24–26]. CNMs are widely popular because of their low cost, abundant resources, various morphologies, excellent electrical and thermal conductivity, large surface areas, highly tunable electronic structures, and mechanical/chemical strength [24, 27]. These properties are all advantageous for advanced development in catalysis. The diversification of carbon nanostructures also provides more possibilities and directions for further exploration of electrochemical properties, mainly involving 0D fullerenes, carbon dots, one-dimensional (1D) CNTs, nanofibres, two-dimensional (2D) graphene, and 3D nanocrystal or self-assembled carbon [28]. Fullerenes, as typical 0D CNMs, usually exhibit hollow spheres or ellipsoidal shapes [29]. Among them, C_{60} as an allotrope of carbon with an ideal spherical structure has been considered as the most representative 0D carbon material [30]. Subsequently, fullerenes have been studied extensively since 1990, when Kratschmer et al. [4] successfully achieved scalable production of C_{60} by evaporating graphite electrodes in a helium atmosphere. Numerous studies have reported that fullerene C_{60}, with its precise structure and abundant unsaturated bonds, can be easily functionalized to produce various derivatives, which can effectively reduce the structural/combinatorial heterogeneity problems that plague many CNMs [29, 31, 32]. Fullerenes also exhibit excellent redox properties, endowing them unique research properties in batteries and catalysis [31, 33]. 1D CNMs have shown extensive potential for energy conversion and storage as well as for commercial industrial production due to their low-cost, large specific surface areas, and controlled synthesis [23, 25, 34]. CNTs, as the most studied 1D carbon material, exhibit a tubular structure rolled by graphene sheets with a high length-to-diameter ratio [35, 36]. CNTs are usually divided into single-walled carbon nanotube (SWCNTs) and multi-walled carbon nanotube (MWCNTs) [21]. SWCNTs consists of a single layer graphene sheet, while MWCNTs are composed of multiple layers of graphene nanosheet, both of which have hollow lamellar structure, ultra-high electrical conductivity, significant charge transport mobility, good thermal stability, and large specific surface areas [37, 38]. Since the discovery of 2D graphene as a new member of the carbon family by Novoselov et al. in 2004, a new chapter in the development of graphene in materials science has been opened [39]. 2D graphene, a single layer of carbon atoms with a hexagonal lattice, consists of sp^2 carbon atoms bonded to adjacent carbon atoms in 3σ bonds [8, 40, 41]. The unique structural advantages of graphene endow the large theoretical specific surface areas with numerous mass transfer channels to fast deliver electrolyte to the active centers, high electrical conductivity to fast catalytic reaction kinetics, and strong corrosion resistance and chemical stability [40, 42, 43]. In addition, 2D graphene is an ideal carrier for dispersed active materials; graphene can not only modulate the morphology and microstructure of active materials and expose more electrochemical active sites, but also induce strong synergistic coupling effects [44, 45]. 3D nanocarbon material represents the growth in all dimensions, unlike 1D and 2D CNMs that expand only along one and two directions [25, 41]. Apart from the traditional activated carbon, mesoporous carbon and nanocrystals, more reports have focused on the self-assembly of low-dimensional CNMs, and flexible and highly selective assembly materials make it possible to design 3D CNMs in a controlled manner [25]. Thus, they not only inherit the characteristics of individual components, but also obtain some new features endowed by the assembly of all the components.

In 2009, Dai and his colleagues successfully fabricated nitrogen (N)-doped vertically aligned carbon nanotubes as metal-free catalysts to replace Pt for oxygen reduction reaction (ORR) in alkaline fuel cells, which exhibit extremely high catalytic activity, ultra-high long-term stability [46]. Since then, metal-free carbon-based materials have been widely explored as a new class of potential catalysts and have shown excellent catalytic performance in energy conversion and storage, green catalysis, and industrial production [47]. Various CNMs, including heteroatom doping (B, O, P, S, N, F), edge doping, defect doping, and charge transfer doping, have attracted immense attention as high-efficient metal-free catalysts for various key reactions in energy conversion and storage processes [16, 48, 49]. Although metal-based materials often suffer from some shortcomings, such as high cost, low utilization, easy deactivation, and poor stability, the outstanding electrochemical activity decided that metal-based materials occupy the dominant status during nanomaterials [47, 50]. Therefore, the use of CNMs as a carrier to support or encapsulate metal-based carbon catalysts can effectively solve the above challenges. In addition, there are multiple advantages for diverse CNMs as a carrier to construct carbon-based materials: (1) Numerous researches imply that loading the active phases into the carbon skeleton not only improves the overall electrical conductivity and accelerates the electron transfer rate, but also modulates the electronic density of states of carbon and generates new active sites [51]. (2) The introduction of defects or heteroatoms can cause a positive impact on the charge state of the carbon skeleton, resulting in an increase in the variety and density of potential active sites [48, 52, 53]. (3) Metal-support interaction, confinement effect, and other catalytic effects can induce rapid charge transfer between metal site and carbon matrix, modulate the electronic structure of the loaded metal, and thus significantly enhance the electrochemical performance of carbon-based electrocatalysts [54, 55]. It is worth mentioning that the highly agglomerative nature of metal nanoparticles greatly limits the atomic utilization of metal sites and reduces the number of accessible active sites. In 2011, Zhang et al. [56] reported the preparation and performance of single-atom catalysts consisting of isolated single Pt atoms supported on the surface of iron oxide (Pt_1/FeO_x) for the first time, which exhibited outstanding activity and strong stability for CO oxidation and proposed the concept of "single-atom catalysis" on this basis. It is not difficult to speculate that the uniform dispersion of single metal atoms on CNMs can maximize the utilization of metal atoms and expose a large number of active sites [57, 58]. Single-atom catalysis is now a foreword and a hot object in the field of nanomaterials.

Previously, 0D metal nanoparticles have been the focus of materials research due to their high surface-to-volume ratio, better exposure of metal sites compared with their bulk counterparts, and their excellent electrical, magnetic, optical, and catalytic properties [59, 60]. However, due to the high surface energy of metal nanoparticles, migration and agglomeration of nanoparticles are very likely to occur during the catalytic process, and these structural and morphological changes often have a great negative impact on catalytic activity, selectivity, and stability, resulting in a dramatic decrease in catalytic performance, which greatly limits the further exploration of metal nanoparticles in energy conversion and storage [61–63]. Since 1994, when Planeix et al. [64] first reported the synthesis and application of nanohybrids consisting of Ru nanoparticles supported on carbon nanotube, the development of carbon-based nanomaterials has entered a new phase, with the exponential growth of a large amount of literature about metal nanoparticles supported on CNMs. Although the stability of conventional carbon-based supported metal nanoparticles can be improved by strong metal-support interactions, they may still undergo migration and agglomeration under harsh conditions. Fortunately, with the continuous innovation and development of carbon-based nanomaterials, a class of encapsulated metal nanoparticles has emerged. Since CNMs are ideal carriers for metal nanoparticles due to their large surface areas, good thermal stability, tunable electronic structure, rich structural variety, good electrical conductivity, and acid and base resistance, encapsulating metal nanoparticles into CNMs have become a mainstream trend [65]. Numerous researches imply that encapsulated metal nanoparticles into CNMs can endow dramatically enhanced stability (due to the combination of spatial constraints and metal-support interactions) and recyclability, improved catalytic selectivity, strong electronic transfer, and interfacial catalysis between metal nanoparticles and carbon matrix [61, 66, 67]. In recent years, a great deal of research has focused on the development of low-cost, high-abundance, highly active and stable nanomaterials for energy conversion and storage applications. The emergence of carbon-based nanomaterials has brought a new light to the advanced development in this field.

To address the global energy crisis and the growing environmental pollution problem, various advanced electrochemical energy conversion devices (e.g., fuel cells, metal-air batteries, electrochemical water splitting, etc.) has been intensively studied to develop a green, economical, sustainable, and reliable alternative to traditional fossil fuel [68, 69]. However, their in-depth development is limited by the lack of ideal electrocatalysts to drive key electrode reactions, such as the cathode ORR reaction in proton exchange membrane fuel cells (PMFC), the oxygen evolution reaction (OER) and ORR processes in rechargeable Zn-air batteries, and the two half-reactions of hydrogen evolution reaction (HER) and OER in water splitting [15, 70, 71]. In addition, converting the greenhouse gas CO_2 into valuable chemical fuels using renewable electricity (CO_2 reduction reaction (CO_2RR)) offers new opportunities to reduce resource extraction and achieve a carbon–neutral [16, 19]. In addition, the conversion of airborne N_2 to NH_3 by electrochemical reduction (Nitrogen reduction reaction (NRR)) is considered to be a sustainable alternative process [72]. Although the specific mechanisms involved in each of the catalytic reactions mentioned above are different, they all undergo sluggish electron transfer kinetics and all require low-cost, highly active, and strong stable electrochemical catalysts to speed up the reaction process. Currently, carbon-based nanomaterials have emerged as the most promising candidates to replace precious metal catalysts due to the complex catalytic effects between active phase and carbon matrix, and CNMs' unique properties: (1) Natural reserves are abundant and cost-effective; (2) Excellent acid and alkali resistance and chemical stability; (3) High theoretical specific surface area; (4) Strong electric conductivity; (5) Various structures available. Meanwhile, with the advanced development of carbon-based nanomaterials, numerous studies were reported about various key reactions of energy conversion, such as ORR, HER, OER, CO_2RR, and NRR, as shown in Fig. 1.2 [19, 26, 71, 73–76].

Electrochemical energy storage (EES) devices, especially lithium-ion batteries (LIBs), have become the most commonly used power source due to their high energy density, safety, long cycle life, and environmental friendliness, as well as being the most widely used rechargeable battery today [77, 78]. In addition to these, the other electrochemical energy storage devices such as metal-sulfur (selenium) batteries (especially Li–S(Se) batteries) and metal-air batteries are also receiving

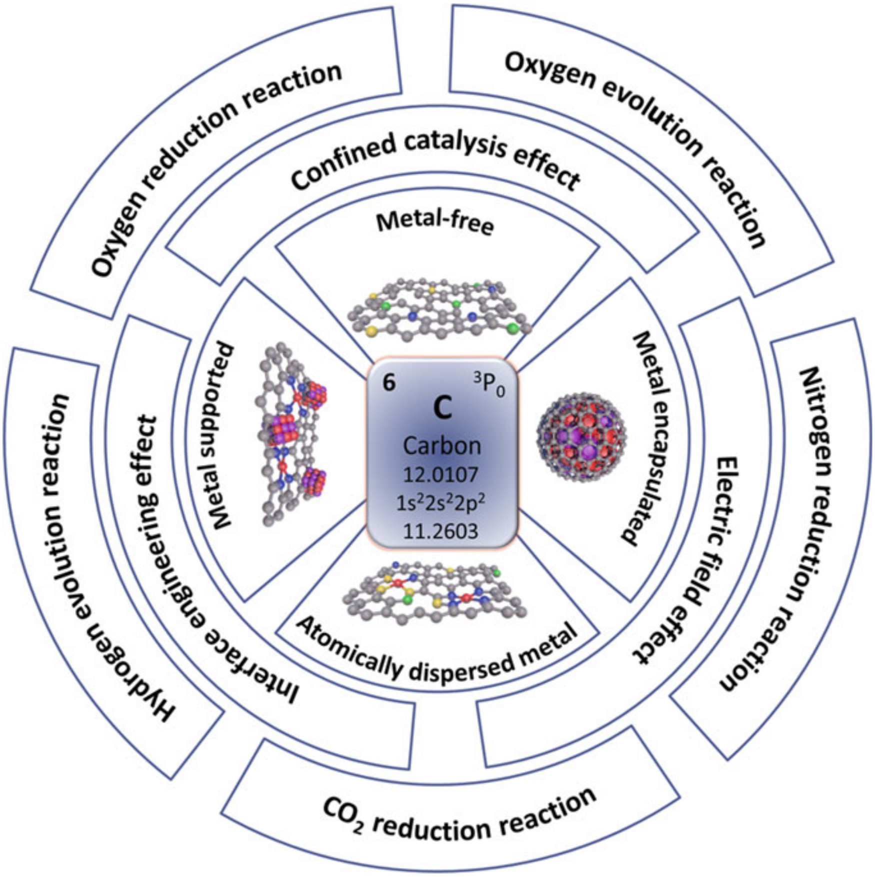

Fig. 1.2 Illustration of carbon-based nanomaterials for electrochemical catalysis

increasing attention due to their unique characteristics [77, 79, 80]. However, all these EES devices are facing the defects of low energy density and need to be recharged frequently, so it is crucial to develop a lightweight, large volume EES device that can be recharged quickly and has a long life, which has become an inevitable trend for future development [77]. Therefore, the development of suitable battery electrode materials to limit their energy density and specific density is essential for the development of EES devices. CNMs exhibit high electrical conductivity, high specific surface area, and good stability with low volume expansion during charging and discharging. The high conductivity facilitates charge transfer, and the high specific surface area provides a channel for the diffusion of electrolytes and oxygen. The adjustable pore structure with a high specific surface area enables rapid diffusion and charge transfer of electrolyte, which is conducive to rapid charging and discharging (Fig. 1.3) [81, 82]. These properties of carbon materials make them show great potential in the EES field.

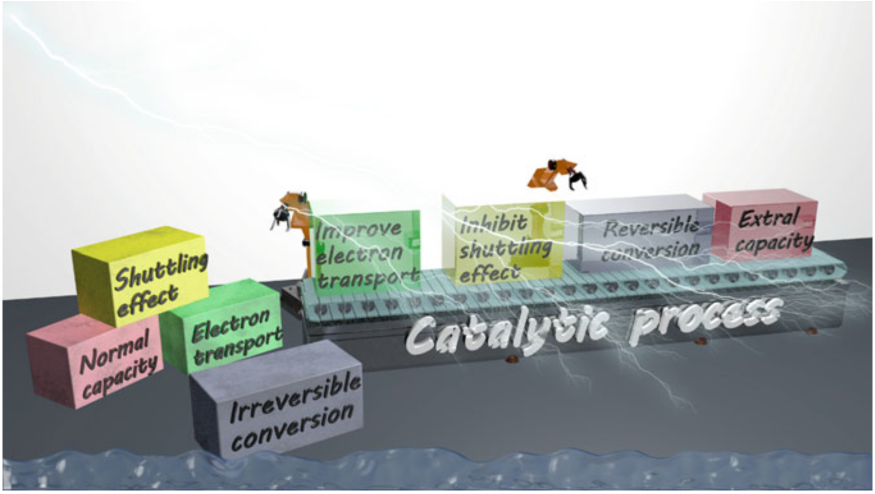

Fig. 1.3 Challenges and perspectives of catalytic processes for energy storage devices

In this chapter, first of all, according to the current environment and energy development status, we propose that an electrochemical-based energy conversion and storage system is one of the cleanest and renewable ways to alleviate energy and environmental problems. Secondly, based on the application of electrochemical energy conversion and storage, we propose that the key to these applications is the catalyst and electrode materials. Among the catalytic materials, carbon-based nanomaterials have been widely studied in energy conversion and storage applications due to their rich sources, low price, large specific surface area, adjustable morphology, and electronic structure. Finally, we propose that this book will comprehensively and deeply reveal the regulation rules and catalytic mechanism of carbon-based catalyst surface and interface defect structures by combining the current synthesis design principles of carbon-based nanomaterials and advanced characterization techniques, hoping to help scientific researchers, especially new researchers, quickly get in touch with cutting-edge science.

This book aims to systematically summarize the advanced development of carbon-based nanomaterials for electrochemical catalysis. It is our sincere hope that this book will provide researchers with further knowledge about carbon-based nanomaterials and that researchers interested in carbon-based nanomaterials will explore new ideas or answers in this book, which is the real meaning of this book. We also hope that new researchers will develop a stronger scientific interest through the interpretation of this book. We apologize to the authors of many outstanding research papers that we have missed due to the large amount of literature produced in this field over time.

References

1. R.P. Andres, R.S. Averback, W.L. Brown, L.E. Brus, W.A. Goddard, A. Kaldor, S.G. Louie, M. Moscovits, P.S. Peercy, S.J. Riley, R.W. Siegel, F. Spaepen, Y. Wang, Research opportunities on clusters and cluster-assembled materials—A department of energy, council on materials science panel report. J. Mater. Res. **4**, 704–736 (2011). https://doi.org/10.1557/jmr.1989.0704
2. P. Moriarty, Nanostructured materials. Rep. Prog. Phys. **64**, 297–381 (2001). https://doi.org/10.1088/0034-4885/64/3/201
3. R.F. Curl, R.E. Smalley, Probing C_{60}. Science **242**, 1017–1022 (1988). https://doi.org/10.1126/science.242.4881.1017
4. W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, Solid C_{60}: A new form of carbon. Nature **347**, 354–358 (1990). https://doi.org/10.1038/347354a0
5. H. Gleiter, Nanostructured materials: Basic concepts and microstructure. Acta Mater. **48**, 1–29 (2000). https://doi.org/10.1016/s1359-6454(99)00285-2
6. A.S. Dahlan, Smart and functional materials based nanomaterials in construction styles in nano-architecture. SILICON **11**, 1949–1953 (2019). https://doi.org/10.1007/s12633-018-0015-x
7. Gkika DA, Vordos N, Nolan JW, Mitropoulos AC, Vansant EF, Cool P, Braet J (2017) Price tag in nanomaterials?. J. Nanopart. Res. 19. https://doi.org/10.1007/s11051-017-3875-x
8. P. Kumar, Ultrathin 2D nanomaterials for electromagnetic interference shielding. Adv. Mater. Interfaces **6**, 1901454 (2019). https://doi.org/10.1002/admi.201901454
9. S. Muhammad, M. Nakano, A.G. Al-Sehemi, Y. Kitagawa, A. Irfan, A.R. Chaudhry, R. Kishi, S. Ito, K. Yoneda, K. Fukuda, Role of a singlet diradical character in carbon nanomaterials: A novel hot spot for efficient nonlinear optical materials. Nanoscale **8**, 17998–18020 (2016). https://doi.org/10.1039/c6nr06097h
10. P. Qu, M. Zhang, K. Fan, Z. Guo, Microporous modified atmosphere packaging to extend shelf life of fresh foods: A review. Crit. Rev. Food Sci. Nutr. **62**, 51–65 (2022). https://doi.org/10.1080/10408398.2020.1811635
11. S. Erker, R. Stangl, G. Stoeglehner, Resilience in the light of energy crises—Part I: A framework to conceptualise regional energy resilience. J. Clean. Prod. **164**, 420–433 (2017). https://doi.org/10.1016/j.jclepro.2017.06.163
12. H.J. Smith, The PACE of clean energy development. Science **355**, 921–922 (2017). https://doi.org/10.1126/science.355.6328.921-c
13. A. Bailey, L. Andrews, A. Khot, L. Rubin, J. Young, T.D. Allston, G.A. Takacs, Hydrogen storage experiments for an undergraduate laboratory course—clean energy: Hydrogen/fuel cells. J. Chem. Educ. **92**, 688–692 (2014). https://doi.org/10.1021/ed5006294
14. H.-F. Wang, Q. Xu, Materials design for rechargeable metal-air batteries. Matter **1**, 565–595 (2019). https://doi.org/10.1016/j.matt.2019.05.008
15. J. Zhang, Q. Zhang, X. Feng, Support and interface effects in water-splitting electrocatalysts. Adv. Mater. **31**, 1808167 (2019). https://doi.org/10.1002/adma.201808167
16. M. de Jesus Gálvez-Vázquez, P. Moreno-García, H. Xu, Y. Hou, H. Hu, I.Z. Montiel, A.V. Rudnev, S. Alinejad, V. Grozovski, B.J. Wiley, M. Arenz, P. Broekmann, Environment matters: CO_2RR electrocatalyst performance testing in a gas-fed zero-gap electrolyzer. ACS Catal. **10**, 13096–13108 (2020). https://doi.org/10.1021/acscatal.0c03609
17. H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, Nano-photocatalytic materials: Possibilities and challenges. Adv. Mater. **24**, 229–251 (2012). https://doi.org/10.1002/adma.201102752
18. Q. Zhang, E. Uchaker, S.L. Candelaria, G. Cao, Nanomaterials for energy conversion and storage. Chem. Soc. Rev. **42**, 3127–3171 (2013). https://doi.org/10.1039/c3cs00009e
19. D. Xue, H. Xia, W. Yan, J. Zhang, S. Mu, Defect engineering on carbon-based catalysts for electrocatalytic CO_2 reduction. Nano-Micro Lett. **13**, 5 (2020). https://doi.org/10.1007/s40820-020-00538-7
20. N. Choudhary, S. Hwang, W. Choi, Carbon nanomaterials: A review, in *Handbook of nanomaterials properties*. ed. by B. Bhushan, D. Luo, S.R. Schricker, W. Sigmund, S. Zauscher (Springer, Berlin Heidelberg, Berlin, 2014), pp. 709–769

21. F. Ghaemi, M. Ali, R. Yunus, R.N. Othman, Synthesis of carbon nanomaterials using catalytic chemical vapor deposition technique, in *Synthesis, technology and applications of carbon nanomaterials*, eds. by S.A. Rashid, R.N.I. Raja Othman, M.Z. Hussein (Elsevier, 2019), pp. 1–27
22. A.D. Goswami, D.H. Trivedi, N.L. Jadhav, D.V. Pinjari, Sustainable and green synthesis of carbon nanomaterials: A review. J. Environ. Chem. Eng. **9**, 106118 (2021). https://doi.org/10.1016/j.jece.2021.106118
23. S. Kumar, G. Saeed, L. Zhu, K.N. Hui, N.H. Kim, J.H. Lee, 0D to 3D carbon-based networks combined with pseudocapacitive electrode material for high energy density supercapacitor: A review. Chem. Eng. J. **403**, 126352 (2021). https://doi.org/10.1016/j.cej.2020.126352
24. K.P. Gopinath, D.-V.N. Vo, D. Gnana Prakash, A. Adithya Joseph, S. Viswanathan, J. Arun, Environmental applications of carbon-based materials: A review. Environ. Chem. Lett. **19**, 557–582 (2020). https://doi.org/10.1007/s10311-020-01084-9
25. J. Ni, Y. Li, Carbon nanomaterials in different dimensions for electrochemical energy storage. Adv. Energy Mater. **6**, 1600278 (2016). https://doi.org/10.1002/aenm.201600278
26. S. Peng, L. Li, J. Kong Yoong Lee, L. Tian, M. Srinivasan, S. Adams, S. Ramakrishna, Electrospun carbon nanofibers and their hybrid composites as advanced materials for energy conversion and storage. Nano Energy 22, 361–395 (2016). https://doi.org/10.1016/j.nanoen.2016.02.001
27. D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Carbon nanomaterials for electronics, optoelectronics, photovoltaics, and sensing. Chem. Soc. Rev. **42**, 2824–2860 (2013). https://doi.org/10.1039/c2cs35335k
28. H. Yi, D. Huang, L. Qin, G. Zeng, C. Lai, M. Cheng, S. Ye, B. Song, X. Ren, X. Guo, Selective prepared carbon nanomaterials for advanced photocatalytic application in environmental pollutant treatment and hydrogen production. Appl. Catal. B **239**, 408–424 (2018). https://doi.org/10.1016/j.apcatb.2018.07.068
29. T. Xu, W. Shen, W. Huang, X. Lu, Fullerene micro/nanostructures: Controlled synthesis and energy applications. Mat. Today Nano **11**, 100081 (2020). https://doi.org/10.1016/j.mtnano.2020.100081
30. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C_{60}: Buckminsterfullerene. Nature **318**, 162–163 (1985). https://doi.org/10.1038/318162a0
31. Z. Jiang, Y. Zhao, X. Lu, J. Xie, Fullerenes for rechargeable battery applications: Recent developments and future perspectives. J. Energy Chem. **55**, 70–79 (2021). https://doi.org/10.1016/j.jechem.2020.06.065
32. M. Chen, R. Guan, S. Yang, Hybrids of fullerenes and 2D nanomaterials. Adv. Sci. **6**, 1800941 (2019). https://doi.org/10.1002/advs.201800941
33. C. Shan, H.-J. Yen, K. Wu, Q. Lin, M. Zhou, X. Guo, D. Wu, H. Zhang, G. Wu, H.-L. Wang, Functionalized fullerenes for highly efficient lithium ion storage: Structure-property-performance correlation with energy implications. Nano Energy **40**, 327–335 (2017). https://doi.org/10.1016/j.nanoen.2017.08.033
34. J. Restivo, O.S. Gonçalves Pinto Soares, M.F. Ribeiro Pereira, Processing methods used in the fabrication of macrostructures containing 1D carbon nanomaterials for catalysis. Processes **8**, (2020). https://doi.org/10.3390/pr8111329
35. S.S. Mahmood, A.J. Atiya, F.H. Abdulrazzak, A.F. Alkaim, F.H. Hussein, A review on applications of carbon nanotubes (CNTs) in solar cells. J. Med. Chem. Sci. **4**, 225–229 (2021). https://doi.org/10.26655/jmchemsci.2021.3.2
36. S. Iijima, Helical microtubules of graphitic carbon. Nature **354**, 56–58 (1991). https://doi.org/10.1038/354056a0
37. R.K. Thines, N.M. Mubarak, S. Nizamuddin, J.N. Sahu, E.C. Abdullah, P. Ganesan, Application potential of carbon nanomaterials in water and wastewater treatment: A review. J. Taiwan Inst. Chem. Eng. **72**, 116–133 (2017). https://doi.org/10.1016/j.jtice.2017.01.018
38. Q. Wu, L. Yang, X. Wang, Z. Hu, From carbon-based nanotubes to nanocages for advanced energy conversion and storage. Acc. Chem. Res. **50**, 435–444 (2017). https://doi.org/10.1021/acs.accounts.6b00541

39. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films. Science **306**, 666–669 (2004). https://doi.org/10.1126/science.1102896
40. N.G. Sahoo, Y. Pan, L. Li, S.H. Chan, Graphene-based materials for energy conversion. Adv. Mater. **24**, 4203–4210 (2012). https://doi.org/10.1002/adma.201104971
41. Y. Wang, P. Yang, L. Zheng, X. Shi, H. Zheng, Carbon nanomaterials with sp^2 or/and sp hybridization in energy conversion and storage applications: A review. Energy Storage Mater. **26**, 349–370 (2020). https://doi.org/10.1016/j.ensm.2019.11.006
42. S. Stankovich, D.A. Dikin, G.H. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials. Nature **442**, 282–286 (2006). https://doi.org/10.1038/nature04969
43. F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov, Detection of individual gas molecules adsorbed on graphene. Nat. Mater. **6**, 652–655 (2007). https://doi.org/10.1038/nmat1967
44. A. Ali, P.K. Shen, Nonprecious metal's graphene-supported electrocatalysts for hydrogen evolution reaction: Fundamentals to applications. Carbon Energy **2**, 99–121 (2019). https://doi.org/10.1002/cey2.26
45. X. Li, X. Yang, J. Zhang, Y. Huang, B. Liu, In situ/operando techniques for characterization of single-atom catalysts. ACS Catal. **9**, 2521–2531 (2019). https://doi.org/10.1021/acscatal.8b04937
46. K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. Science **323**, 760–764 (2009). https://doi.org/10.1126/science.1168049
47. S. Zhao, D.W. Wang, R. Amal, L. Dai, Carbon-based metal-free catalysts for key reactions involved in energy conversion and storage. Adv. Mater. **31**, 1801526 (2019). https://doi.org/10.1002/adma.201801526
48. W. Chen, M. Wan, Q. Liu, X. Xiong, F. Yu, Y. Huang, Heteroatom-doped carbon materials: Synthesis, mechanism, and application for sodium-ion batteries. Small Methods **3**, 1800323 (2018). https://doi.org/10.1002/smtd.201800323
49. T. Asefa, X. Huang, Heteroatom-doped carbon materials for electrocatalysis. Chemistry **23**, 10703–10713 (2017). https://doi.org/10.1002/chem.201700439
50. X. Wang, A. Vasileff, Y. Jiao, Y. Zheng, S.Z. Qiao, Electronic and structural engineering of carbon-based metal-free electrocatalysts for water splitting. Adv. Mater. **31**, 1803625 (2019). https://doi.org/10.1002/adma.201803625
51. W. Zhou, J. Jia, J. Lu, L. Yang, D. Hou, G. Li, S. Chen, Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction. Nano Energy **28**, 29–43 (2016). https://doi.org/10.1016/j.nanoen.2016.08.027
52. L. Tao, Y. Wang, Y. Zou, N. Zhang, Y. Zhang, Y. Wu, Y. Wang, R. Chen, S. Wang, Charge transfer modulated activity of carbon-based electrocatalysts. Adv. Energy Mater. **10**, 1901227 (2019). https://doi.org/10.1002/aenm.201901227
53. A. Ferre-Vilaplana, E. Herrero, Charge transfer, bonding conditioning and solvation effect in the activation of the oxygen reduction reaction on unclustered graphitic-nitrogen-doped graphene. Phys. Chem. Chem. Phys. **17**, 16238–16242 (2015). https://doi.org/10.1039/c5cp00918a
54. J. Yang, W. Li, D. Wang, Y. Li, Electronic metal-support interaction of single-atom catalysts and applications in electrocatalysis. Adv. Mater. **32**, 2003300 (2020). https://doi.org/10.1002/adma.202003300
55. A. Beck, X. Huang, L. Artiglia, M. Zabilskiy, X. Wang, P. Rzepka, D. Palagin, M.G. Willinger, J.A. van Bokhoven, The dynamics of overlayer formation on catalyst nanoparticles and strong metal-support interaction. Nat. Commun. **11**, 3220 (2020). https://doi.org/10.1038/s41467-020-17070-2
56. B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, Single-atom catalysis of CO oxidation using Pt_1/FeO_x. Nat. Chem. **3**, 634–641 (2011). https://doi.org/10.1038/nchem.1095

57. M.B. Gawande, P. Fornasiero, R. Zbořil, Carbon-based single-atom catalysts for advanced applications. ACS Catal. **10**, 2231–2259 (2020). https://doi.org/10.1021/acscatal.9b04217
58. Y. Peng, B. Lu, S. Chen, Carbon-supported single atom catalysts for electrochemical energy conversion and storage. Adv. Mater. **30**, e1801995 (2018). https://doi.org/10.1002/adma.201801995
59. B. Wu, Y. Kuang, X. Zhang, J. Chen, Noble metal nanoparticles/carbon nanotubes nanohybrids: Synthesis and applications. Nano Today **6**, 75–90 (2011). https://doi.org/10.1016/j.nantod.2010.12.008
60. R. Narayanan, M.A. El-Sayed, Catalysis with transition metal nanoparticles in colloidal solution: Nanoparticle shape dependence and stability. J. Phys. Chem. B **109**, 12663–12676 (2005). https://doi.org/10.1021/jp051066p
61. C. Gao, F. Lyu, Y. Yin, Encapsulated metal nanoparticles for catalysis. Chem. Rev. **121**, 834–881 (2021). https://doi.org/10.1021/acs.chemrev.0c00237
62. N. Wang, Q. Sun, J. Yu, Ultrasmall metal nanoparticles confined within crystalline nanoporous materials: A fascinating class of nanocatalysts. Adv. Mater. **31**, 1803966 (2019). https://doi.org/10.1002/adma.201803966
63. Q.-L. Zhu, Q. Xu, Immobilization of ultrafine metal nanoparticles to high-surface-area materials and their catalytic applications. Chem **1**, 220–245 (2016). https://doi.org/10.1016/j.chempr.2016.07.005
64. J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier, P.M. Ajayan, Application of carbon nanotubes as supports in heterogeneous catalysis. J. Am. Chem. Soc. **116**, 7935–7936 (2002). https://doi.org/10.1021/ja00096a076
65. X. Yan, Y. Jia, X. Yao, Defects on carbons for electrocatalytic oxygen reduction. Chem. Soc. Rev. **47**, 7628–7658 (2018). https://doi.org/10.1039/c7cs00690j
66. J. Lu, S. Yin, P.K. Shen, Carbon-encapsulated electrocatalysts for the hydrogen evolution reaction. Electrochem Energy Rev **2**, 105–127 (2018). https://doi.org/10.1007/s41918-018-0025-9
67. N. Rao, R. Singh, L. Bashambu, Carbon-based nanomaterials: Synthesis and prospective applications. Mater. Today Proc. **44**, 608–614 (2021). https://doi.org/10.1016/j.matpr.2020.10.593
68. Y. Zhang, M. Luo, Y. Yang, Y. Li, S. Guo, Advanced multifunctional electrocatalysts for energy conversion. ACS Energy Lett. **4**, 1672–1680 (2019). https://doi.org/10.1021/acsenergylett.9b01045
69. Z.P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler, Z. Chen, Batteries and fuel cells for emerging electric vehicle markets. Nat. Energy **3**, 279–289 (2018). https://doi.org/10.1038/s41560-018-0108-1
70. H. Yin, H. Xia, S. Zhao, K. Li, J. Zhang, S. Mu, Atomic level dispersed metal–nitrogen–carbon catalyst toward oxygen reduction reaction: Synthesis strategies and chemical environmental regulation. Energy Environ. Mater. **4**, 5–18 (2020). https://doi.org/10.1002/eem2.12085
71. Y. Qiao, P. Yuan, Y. Hu, J. Zhang, S. Mu, J. Zhou, H. Li, H. Xia, J. He, Q. Xu, Sulfuration of an Fe-N-C catalyst containing Fe_xC/Fe species to enhance the catalysis of oxygen reduction in acidic media and for use in flexible Zn-air batteries. Adv. Mater. **30**, 1804504 (2018). https://doi.org/10.1002/adma.201804504
72. W. Tong, B. Huang, P. Wang, L. Li, Q. Shao, X. Huang, Crystal-phase-engineered PdCu electrocatalyst for enhanced ammonia synthesis. Angew. Chem. Int. Ed. **59**, 2649–2653 (2020). https://doi.org/10.1002/anie.201913122
73. Y. Guo, P. Yuan, J. Zhang, H. Xia, F. Cheng, M. Zhou, J. Li, Y. Qiao, S. Mu, Q. Xu, Co_2P-CoN double active centers confined in N-doped carbon nanotube: Heterostructural engineering for trifunctional catalysis toward HER, ORR, OER, and Zn-air batteries driven water splitting. Adv. Func. Mater. **28**, 1805641 (2018). https://doi.org/10.1002/adfm.201805641
74. Y. Guo, P. Yuan, J. Zhang, Y. Hu, I.S. Amiinu, X. Wang, J. Zhou, H. Xia, Z. Song, Q. Xu, S. Mu, Carbon nanosheets containing discrete Co-N_x-B_y-C active sites for efficient oxygen electrocatalysis and rechargeable Zn-air batteries. ACS Nano **12**, 1894–1901 (2018). https://doi.org/10.1021/acsnano.7b08721

75. X. Xue, J. Zhang, I.A. Saana, J. Sun, Q. Xu, S. Mu, Rational inert-basal-plane activating design of ultrathin 1T' phase MoS_2 with a MoO_3 heterostructure for enhancing hydrogen evolution performances. Nanoscale **10**, 16531–16538 (2018). https://doi.org/10.1039/c8nr05270k
76. K. Shen, X. Chen, J. Chen, Y. Li, Development of MOF-derived carbon-based nanomaterials for efficient catalysis. ACS Catal. **6**, 5887–5903 (2016). https://doi.org/10.1021/acscatal.6b01222
77. C. Zhang, W. Lv, Y. Tao, Q.-H. Yang, Towards superior volumetric performance: Design and preparation of novel carbon materials for energy storage. Energy Environ. Sci. **8**, 1390–1403 (2015). https://doi.org/10.1039/c5ee00389j
78. M.S. Dresselhaus, I.L. Thomas, Alternative energy technologies. Nature **414**, 332–337 (2001). https://doi.org/10.1038/35104599
79. H. Xia, G. Qu, H. Yin, J. Zhang, Atomically dispersed metal active centers as a chemically tunable platform for energy storage devices. J. Mater. Chem. A **8**, 15358–15372 (2020). https://doi.org/10.1039/d0ta04019c
80. K. Guo, G. Qu, J. Li, H. Xia, W. Yan, J. Fu, P. Yuan, J. Zhang, Polysulfides shuttling remedies by interface-catalytic effect of Mn_3O_4-MnP_x heterostructure. Energy Storage Mater. **36**, 496–503 (2021). https://doi.org/10.1016/j.ensm.2021.01.021
81. Y. Pan, K. Xu, C. Wu, Recent progress in supercapacitors based on the advanced carbon electrodes. Nanotechnol. Rev. **8**, 299–314 (2019). https://doi.org/10.1515/ntrev-2019-0029
82. X. Wang, L. Liu, Z. Niu, Carbon-based materials for lithium-ion capacitors. Mater. Chem. Frontiers **3**, 1265–1279 (2019). https://doi.org/10.1039/c9qm00062c