Liquid–liquid micromixing strategy enables low KOH-amount synthesis of ultrahighly porous carbon for zinc-ion storage

Peifeng Yu^{1,2} · Yuan Zeng^{1,2} · Qiaoying Cao^{1,2} · Xiaoyan Chen^{1,2} · Mingtao Zheng^{1,2} · Hang Hu^{1,2} · Yong Xiao^{1,2} · Yingliang Liu^{1,2} · Yeru Liang^{1,2}

Received: 27 February 2020 / Accepted: 31 March 2020 / Published online: 6 April 2020
© Springer Nature Switzerland AG 2020

Abstract

Ultrahigh specific surface area and low KOH amount are normally mutually exclusive and hard to attain simultaneously when using the traditional KOH activation. In this work, we report a facile approach to synthesize a series of porous carbons with ultrahigh specific surface area about $3000 \text{ m}^2 \text{ g}^{-1}$ by using a very low mass ratio of KOH to carbon precursor, *e.g.*, 0.42. The key to this preparation strategy is development of a liquid–liquid micromixing strategy for mixing KOH with biomass-based carbon precursors that can be well dispersed in KOH aqueous solution. Compared with solid–solid mixing strategy normally used in traditional KOH activation methods, the liquid–liquid micromixing strategy enables to form a homogeneous solution with highly mixing between macromolecular-scale carbon precursor and ion-scale KOH at the microscopic level, which significantly increases the activation reaction efficiency. The typical porous carbon obtained based on the liquid–liquid micromixing strategy exhibits a specific surface area as high as $3009 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that of porous carbon prepared through a solid–solid mixing strategy, *i.e.*, $2228 \text{ m}^2 \text{ g}^{-1}$. Benefiting from the ultrahigh specific surface area, the resultant carbon materials show very attractive electrochemical performances when used as the cathode material in zinc-ion hybrid supercapacitor, such as an intriguing average specific capacity of 344 mAh g^{-1} and a remarkable cycling stability of 98.5% capacity retention after 10,000 cycles.

Keywords Liquid–liquid micromixing strategy · Low KOH-amount · Ultrahigh specific surface area · Porous carbon · Zinc-ion storage

1 Introduction

Porous carbons have attracted great attention over the past decades due to their unique characteristics such as high specific surface area, superior conductivity, adjustable pore structure and excellent chemical stability [1–5]. These features are of great interests in versatile applications for energy storage, catalysis, adsorption, separation,

and many other areas [6–12]. In general, porosity is considered as the most vital role in determining porous carbon's performance in applications, especially in those fields where abundant active sites are needed [13]. Thus, exploring highly porous structure has always been a long-term goal for the development of advanced porous carbons, which can provide a chance to boost their performance to a new stage [14–16].

Peifeng Yu and Yuan Zeng authors have contributed equally to this work.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-2666-7>) contains supplementary material, which is available to authorized users.

✉ Yeru Liang, liangyr@scau.edu.cn | ¹College of Materials and Energy, South China Agricultural University, Guangzhou 510642, People's Republic of China. ²Guangdong Laboratory of Lingnan Modern Agriculture, Guangzhou 510642, People's Republic of China.

SN Applied Sciences (2020) 2:829 | <https://doi.org/10.1007/s42452-020-2666-7>

Porous carbons are usually prepared through template, activation and direct carbonization methods [17–21]. To date, activation is still the most frequently used method to prepare porous carbons, *e.g.*, commercial activated carbons. Among various activation techniques, KOH activation, which involves semi-carbonization, mixing with KOH, activation and purification, has been demonstrated as the most efficient one [22]. Nevertheless, in order to obtain very large specific surface areas (*e.g.*, above $2000 \text{ m}^2 \text{ g}^{-1}$), KOH activation always requires usage of high-amount KOH (*i.e.*, the mass ratio of KOH to carbon precursor is normally 4 or higher values) [23–25]. It will not only induces the corrosion of production equipment but also outputs extensive environmental unfriendly wastewater, which is inconsistent with the urgent need of energy conservation and environmental protection. While decreasing the KOH amount, the resultant porous carbon possesses a typically specific surface area below $2000 \text{ m}^2 \text{ g}^{-1}$ [26–29]. Ultrahigh specific surface area and low KOH amount are normally mutually exclusive and hard to attain simultaneously. Additionally, various porous carbons with high specific surface area are prepared from unsustainable chemical petroleum-based chemical products, which yield a negative effect on the fossil-fuel and environmental crisis [30]. As ubiquitous, nontoxic, and low-cost natural renewable resources, biomass has been demonstrated as a promising and green raw material for porous carbons [31–33]. Nevertheless, with the aforementioned issue, the employment of high-amount KOH still remain formidable restriction on their large-scale applications. Therefore, exploring an efficient and sustainable strategy to prepare high-surface-area carbon materials is still a remaining challenge.

Herein, we report a facile strategy to synthesize porous carbons with ultrahigh specific surface area about $3000 \text{ m}^2 \text{ g}^{-1}$ by using a very low mass ratio of KOH to carbon precursor (K/CP), *e.g.*, 0.42. Such a K/CP value is much lower than those obtained in a conventional chemical activation way to porous carbons with similar specific surface area (Table S1, in Supporting Information). The key to this preparation strategy is development of a liquid–liquid micromixing strategy for mixing KOH with biomass-based carbon precursors that can be well dispersed in KOH aqueous solution. Compared with solid–solid mixing strategy normally used in traditional KOH activation methods, the liquid–liquid micromixing strategy enables to form a homogeneous solution with highly mixing between macromolecular-scale carbon precursor and ion-scale KOH at the microscopic level. This favours KOH to better contact with the carbon precursor and thus significantly increases the activation reaction efficiency. The typical porous carbon obtained based on the liquid–liquid micromixing strategy exhibits a specific surface area as high as $3009 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that of porous

carbon prepared through a solid–solid mixing strategy, *i.e.*, $2228 \text{ m}^2 \text{ g}^{-1}$. Benefiting from the ultrahigh specific surface area, the resultant carbon materials show very attractive electrochemical performances when used as the cathode material in zinc-ion hybrid supercapacitor. For example, the typical porous carbon cathode shows remarkable cycling stability of 98.5% capacity retention over 10,000 cycles and an intriguing average specific capacity of 344 mAh g^{-1} , which are superior to those of most of previously reported electrodes. Furthermore, considering that the carbon precursors are renewable biomass with abundant yield, the preparation of ultrahighly porous carbon through the liquid–liquid micromixing strategy could be scalable and sustainable, opening up remarkable avenues to high-value materials from natural biomass.

2 Experimental

2.1 Preparation of porous carbons based on liquid–liquid micromixing strategy

Typically, 0.84 g KOH was dissolved in 50 mL deionized water to form KOH solution. Then 2 g of silkworm cocoon was mixed with the KOH solution to form a homogeneous solution. After being freeze-dried, the obtained solid product was heated to 800°C with a heating rate of 5°C min^{-1} under N_2 atmosphere and then held for 2 h. The resulting product was treated with 2 mol L^{-1} HCl and rinsed with deionized water several times, leading to formation of porous carbon derived from silkworm cocoon based on liquid–liquid micromixing strategy (PC-SC-LLMM). The synthetic procedures of other porous carbon materials with high specific surface area are similar to that of PC-SC-LLMM except for using different carbon precursors that can be well dispersed in the low concentration of KOH aqueous solution.

2.2 Preparation of porous carbons based on solid–solid micromixing strategy

For comparison, 2.0 g of raw silkworm cocoon was heated to 500°C with a heating rate of 5°C min^{-1} under N_2 atmosphere and then held for 1 h. After that, 0.84 g of KOH was mixed with the semi-carbonized silkworm cocoon in an agate mortar by grinding. The resultant mixture was heated to 800°C with a heating rate of 5°C min^{-1} under N_2 atmosphere and held for 2 h. The resulting product was treated with 2 mol L^{-1} HCl and rinsed with deionized water several times, leading to formation of porous carbon derived from silkworm cocoon based on solid–solid mixing strategy (PC-SC-SSM). The synthetic procedures of

other porous carbon materials are similar to that of PC-SC-SSM except for using different carbon precursors.

2.3 Structure characterization

The microstructures of the samples were characterized by high-resolution transmission electron microscopy (TECANI10). The morphology characterization was obtained by the field emission electron microscope (FE-SEM, HITACHI SU8220). The pore structure was gained from N_2 adsorption–desorption isotherms in 77 K by using Micromeritics ASAP 3flex analyzer. Before analysing, all samples were outgassed at 350 °C for 8 h. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) theory. Micropore specific surface area (S_{mic}) was determined by t-plot method, and then external specific surface area (S_{ext}) was obtained by subtracting S_{mic} from BET specific surface area (S_{BET}). The total pore volume (V_t) was calculated according to the nitrogen absorption at a saturation relative pressure of *ca.* 0.99. The micropore volume was calculated by t-plot analysis. Moreover, the pore size distribution was analyzed by the nonlocal density functional theory.

2.4 Electrochemical characterization

The cathodes were prepared by mixing the carbon samples, super-P and polyvinylidene fluoride with the mass rate of 8:1:1 in N-methyl pyrrolidone solvent and then coating the mixture onto carbon cloth. The total mass loading onto each electrode was about 1.6 mg cm^{−1}. The thickness of Zn metal foil was 60 μm, which was used as the anode after polishing. The zinc-ion hybrid supercapacitors were assembled with two layers of non-woven fabric separator, electrolyte of 2 mol L^{−1} ZnSO₄ aqueous solution with 1 mol L^{−1} Na₂SO₄ as an additive in deionized water, and CR2025 coin battery shell. Cyclic voltammetry (CV) tests were carried out on Chenhua electrochemical workstation (CHI760E, Shanghai, China) with a voltage range of 0.01–1.8 V. Galvanostatic charge–discharge (GCD) measurements were performed on Neware battery (CT-4008, Shenzhen, China) tester.

3 Results and discussion

In general, traditional KOH activation involves semi-carbonization, mixing with KOH, activation and purification. During this process, KOH is mixed with semi-carbonized carbon precursor through a grinding-assisted solid–solid mixing technique (Fig. 1). As a model study, silkworm cocoon is selected as raw materials of porous carbons. The semi-carbonized silkworm cocoon is mixed with KOH

Fig. 1 Schematic diagram of synthesis of porous carbon based on liquid–liquid micromixing and solid–solid mixing strategies

powder by grinding based on the solid–solid mixing strategy (Fig. 2a). However, the resulting mixture looks inhomogeneous through the scanning electron microscopy observation, which is unfavorable for high-efficiency activation (Fig. S1, in Supporting Information). In a significant deviation from the above conventional solid–solid mixing technique, silkworm cocoon is directly well dispersed in a low concentration of KOH aqueous solution by using ultrasound dispersion, leading to formation of a homogeneous solution with a very low K/CP of 0.42 (Fig. S2, in Supporting Information). After freeze-drying, a homogeneous pale yellow powder is obtained, implying that ion-scale KOH is uniformly mixed with macromolecular-scale silkworm cocoon at the microscopic level (Fig. 2b).

The mixture is subsequently heated at high temperature in N_2 flow. After washing and drying, the targeted porous carbons are obtained. N_2 adsorption–desorption measurements are performed to evaluate the porosity of the as-prepared samples. As shown in N_2 adsorption–desorption isotherms of Fig. 2c, the resulting PC-SC-LLMM exhibits a type I isotherm. The nitrogen adsorption amount increases sharply at low relative pressure (P/P_0), which indicates the presence of plenty of micropores [34]. The high-resolution transmission electron microscopy (TEM) image confirms that numerous small-sized nanopores are observed in the framework of the PC-SC-LLMM (Fig. 2d). According to the density functional theory (DFT) pore size distribution curves (Fig. S3, in Supporting Information), the size of these micropores is mainly centered at around 1.2 and 1.7 nm.

In comparison, the as-prepared PC-SC-SSM obviously shows lower nitrogen adsorption amount, implying a poorer porosity in PC-SC-SSM [35]. The calculated BET specific surface area of PC-SC-LLMM is as high as 3009 m² g^{−1}, which is almost 1.4 times larger than 2228 m² g^{−1} of PC-SC-SSM (Fig. 2e). Besides the specific surface area, the PC-SC-LLMM also possesses a higher pore volume of 1.35 cm³ g^{−1} when compared with PC-SC-SSM

Fig. 2 **a** Digital photograph of semi-carbonized silkworm cocoon mixed with KOH by grinding based on solid–solid mixing strategy. **b** Digital photograph of after freeze drying of homogeneous solution containing silkworm cocoon and KOH based on liquid–liquid micromixing strategy. **c** N_2 adsorption–desorption isotherms of

PC-SC-LLMM and PC-SC-SSM. **d** High-resolution TEM image of PC-SC-LLMM. **e** BET specific surface area and micropore specific surface area of PC-SC-LLMM and PC-SC-SSM. **f** Total pore volume and micropore volume of PC-SC-LLMM and PC-SC-SSM

(i.e., $1.06 \text{ cm}^3 \text{ g}^{-1}$, Fig. 2f). Such a difference is mainly derived from the different micropore structure. The micropore surface area and micropore volume of PC-SC-LLMM reaches $2591 \text{ m}^2 \text{ g}^{-1}$ and $1.04 \text{ cm}^3 \text{ g}^{-1}$, respectively, which is larger than those of PC-SC-SSM (i.e., $1929 \text{ m}^2 \text{ g}^{-1}$ and $0.77 \text{ cm}^3 \text{ g}^{-1}$, Fig. 2e, f). Considering the fact that KOH activation mainly generates micropores, the higher porosity in micropore structure of PC-SC-LLMM demonstrates the fabrication of PC-SC-LLMM possesses a higher activation efficiency when compared with that of PC-SC-SSM [36]. As illustrated in the Raman spectra (Fig. S4, in Supporting Information), two characteristic peaks at about 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band) can be observed, which are related to disordered carbon structure and graphitic structure in carbon materials, respectively. In generally, I_D/I_G ratio is usually used to evaluate the defect degree of the carbon materials. The I_D/I_G of PC-SC-LLMM is calculated to be 1.26, which is higher than that of PC-SC-SSM (i.e., 1.01), further illustrating the higher activation efficiency in liquid–liquid micromixing strategy when compared with traditional activation approach. It should be noted that high K/CP value (e.g., 4–10) is general even essential for preparing porous carbons with BET specific surface area about $3000 \text{ m}^2 \text{ g}^{-1}$ (Table S1, in Supporting Information). In comparison, our liquid–liquid micromixing strategy only needs a very low K/CP value (i.e., 0.42), providing

an efficient and new way to the fabrication of ultrahigh-surface-area porous carbons.

This facile strategy can be well extended to other carbon precursors such as mushroom stalk (MS) that can be well dispersed in low concentration of KOH aqueous solution (Fig. S5, in Supporting Information). Similarly, the porous carbon obtained from MS based on the liquid–liquid micromixing strategy (PC-MS-LLMM) possesses a higher nitrogen adsorption amount when compared with the porous carbon obtained from MS based on the solid–solid mixing strategy (PC-MS-SSM), especially at low P/P_0 (Fig. 3a). The specific surface area is further calculated by using the BET method, which is shown in Fig. 3b. Obviously, the specific surface area of sample PC-MS-LLMM follows the same trend as PC-SC-LLMM, rising from $2231 \text{ m}^2 \text{ g}^{-1}$ for sample PC-MS-SSM to $2903 \text{ m}^2 \text{ g}^{-1}$ for PC-MS-LLMM. All the above results illustrate that liquid–liquid micromixing strategy is an effective way for improving the KOH activation efficiency.

Benefiting from the well-developed porous structure, the as-prepared PC-SC-LLMM holds promise for many applications. As a demonstration, the PC-SC-LLMM is applied as the cathode for zinc-ion hybrid supercapacitors. As shown in Fig. 4a and Fig. S6 in Supporting Information, the CV curves of PC-SC-LLMM show regular shapes, which indicates that PC-SC-LLMM-based zinc-ion hybrid supercapacitor is rechargeable and has a stable work voltage

Fig. 3 **a** N_2 adsorption–desorption isotherms of PC-MS-LLMM and PC-MS-SSM. **b** Total pore volume and micropore volume of PC-MS-LLMM and PC-MS-SSM

range of 0.01 ~ 1.8 V. It should note that the measured CV plots hold similar shapes even the sweep rates increases to 500 mV s^{-1} , which implies the rapid kinetics and effectively storing zinc ion of PC-SC-LLMM cathode during the fast electrochemical reaction process.[37, 38]

To evaluate the preeminence of the PC-SC-LLMM cathode during charge–discharge process, the control samples PC-SC-SSM and a commercial activated carbon (AC) are investigated under the same experimental conditions (Table S2 and Figs. S7 and S8, in Supporting Information). As shown in galvanostatic charge–discharge curves tested at various current densities from 0.1 to 5 A g^{-1} , the PC-SC-LLMM cathode obviously possesses longer charge or discharge times, indicating larger zinc-ion storage capacities in the PC-SC-LLMM cathode (Fig. 4b). The superior electrochemical performance of PC-SC-LLMM can be a further calculation based on the discharge curves, which illustrates that the specific capacities of the PC-SC-LLMM cathode are significantly larger than those of PC-SC-SSM and AC under different current densities (Fig. 4c and Fig. S9 in Supporting Information). For instance, when the current density is 0.1 A g^{-1} , an appealing average specific capacity value of 5 cycles is as high as 344 mAh g^{-1} for the PC-SC-LLMM cathode, which is higher than that of PC-SC-SSM cathode (*i.e.*, 211 mAh g^{-1}) and that of the AC cathode (*i.e.*, 186 mAh g^{-1}). Furthermore, the difference in specific capacity becomes more obvious at higher current densities. When the current density increases 50 times (*i.e.*, 5 A g^{-1}), a high average specific capacity of 152 mAh g^{-1} for the PC-SC-LLMM cathode still can be achieved, which is much larger than 74 mAh g^{-1} of PC-SC-SSM and 50 mAh g^{-1} of AC. Moreover, the PC-SC-LLMM cathode still exhibits a high specific capacity of 282 mAh g^{-1} when the charge/discharge density is recovered to 0.1 A g^{-1} , indicating its good rate and stable cycling stability. These

values also make the PC-SC-LLMM cathode outperform the majority of the reported carbonaceous cathodes (Table S3, in Supporting Information).

The long-term cycle life is further demonstrated by cycling stability measurement (Fig. 4d). After 10,000 charge–discharge cycles at a high current density of 3 A g^{-1} , the discharge capacity of the PC-SC-LLMM cathode still maintains 98.5% of the initial capacity, while the coulombic efficiency retains almost 100% during all cycles. It demonstrates its preminent cycling stability.

4 Conclusion

In summary, a very low mass ratio of KOH to carbon precursor, *i.e.*, 0.42, for synthesizing porous carbon materials with ultrahigh specific surface area about $3000 \text{ m}^2 \text{g}^{-1}$ is achieved by development of a liquid–liquid micromixing strategy. It is shown that the liquid–liquid micromixing strategy significantly increases the activation efficiency comparing with the traditional solid–solid mixing strategy, mainly due to the highly homogeneous mixing between macromolecular-scale carbon precursor and ion-scale KOH at the microscopic level. The as-prepared PC-SC-LLMM electrode shows excellent zinc-ion storage performance with excellent reversible capacities, high rate performance and attractive long-term cycle stability, demonstrating a great potential for practical applications. These findings provide a facile and effective strategy for potentially large-scale production of porous carbon with high specific surface area by using a low mass ratio of KOH to carbon precursor that can be well dispersed in KOH aqueous solution. In addition, this type of highly porous carbon could trigger significant potential in plenty of applications including adsorption, catalysis, and other energy storage devices.

Fig. 4 **a** CV curves and **b** GCD curves of PC-SC-LLMM-based zinc-ion hybrid supercapacitor. **c** Specific capacities of PC-SC-LLMM and AC obtained at various current densities from 0.1 to 5 A g^{-1} .

d Long-term cycling stability at a current density of 3 A g^{-1} over 10,000 cycles of PC-SC-LLMM-based zinc-ion hybrid supercapacitor

Acknowledgements This study was funded by the National Natural Science Foundation of China (Grant Nos. 51972121, 21671069), Top-Notch Scientific and Technical Innovative Youth Talents of Guangdong Special Support Program (Grant No. 2017TQ04C419), Guangdong Province Universities and Colleges Pearl River Scholar Funded Scheme (Grant No. 2017), Guangdong Basic and Applied Basic Research Foundation (Grant No. 2019A1515011502) and Program for Pearl River New Star of Science and Technology in Guangzhou (Grant No. 201710010104).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Wang J, Nie P, Ding B, Dong SY, Hao XD, Dou H, Zhang XG (2017) Biomass derived carbon for energy storage devices. *J Mater Chem A* 5(6):2411–2428
- Liu Y, Xiao Z, Liu Y, Fan L-Z (2018) Biowaste Derived 3D honeycomb-like porous carbon with binary-heteroatom doping for high performance flexible solid-state supercapacitors. *J Mater Chem A* 6:160–166
- Sevilla M, Mokaya R (2014) Energy storage applications of activated carbons: supercapacitors and hydrogen storage. *Energy Environ Sci* 7(4):1250–1280
- Liang YR, Liang FX, Li ZH, Wu DC, Yan FY, Li SY, Fu RW (2010) The role of mass transport pathway in wormholelike mesoporous carbon for supercapacitors. *Phys Chem Chem Phys* 12(36):10842–10845
- Xu F, Qiu Y, Jiang G, Ding B, Li J, Liu Q, Wu J, Xu X, Wang H, Liang Y (2019) Unraveling the correlation between structures of carbon nanospheres derived from polymeric spheres and their electrochemical performance to achieve high-rate supercapacitors. *Macromol Rapid Commun* 40(17):1800770
- Liang YR, Zhang WC, Wu DC, Ni QQ, Zhang MQ (2018) Interface engineering of carbon-based nanocomposites for advanced electrochemical Energy Storage. *Adv Mater Interfaces* 5(14):1800430
- Blankenship TS, Mokaya R (2017) Cigarette butt-derived carbons have ultra-high surface area and unprecedented hydrogen storage capacity. *Energy Environ Sci* 10(12):2552–2562
- Zhang YM, Li BY, Williams K, Gao WY, Ma SQ (2013) A new microporous carbon material synthesized via thermolysis of a porous aromatic framework embedded with an extra carbon source for low-pressure CO₂ uptake. *Chem Commun* 49(87):10269–10271
- Pei YR, Choi G, Asahina S, Yang JH, Vinu A, Choy JH (2019) A novel geopolymer route to porous carbon: high CO₂ adsorption capacity. *Chem Commun* 55(22):3266–3269
- Liang Y, Chen L, Zhuang D, Liu H, Fu R, Zhang M, Wu D, Matyjaszewski K (2018) Fabrication and nanostructure control of super-hierarchical carbon materials from heterogeneous bottlebrushes. *Chemical Science* 8:2101
- Deng J, Xiong TY, Xu F, Li MM, Han CL, Gong YT, Wang HY, Wang Y (2015) Inspired by bread leavening: one-pot synthesis of hierarchically porous carbon for supercapacitors. *Green Chem* 17(7):4053–4060
- Wu MJ, Qiao JL, Li KX, Zhou XJ, Liu YY, Zhang JJ (2016) A large-scale synthesis of heteroatom (N and S) co-doped hierarchically porous carbon (HPC) derived from polyquaternium for superior oxygen reduction reactivity. *Green Chem* 18(9):2699–2709
- Lin TQ, Chen IW, Liu FX, Yang CY, Bi H, Xu FF, Huang FQ (2015) Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage. *Science* 350(6267):1508–1513
- Yu PF, Liang YR, Dong HW, Hu H, Liu SM, Peng L, Zheng MT, Xiao Y, Liu YL (2018) Rational synthesis of highly porous carbon from waste bagasse for advanced supercapacitor application. *ACS Sustain Chem Eng* 6(11):5325–5332
- He JJ, To JWF, Psarras PC, Yan HP, Atkinson T, Holmes RT, Nordlund D, Bao ZN, Wilcox J (2016) Tunable polyaniline-based porous carbon with ultrahigh surface area for CO₂ capture at elevated pressure. *Adv Energy Mater* 6(14):1502491
- Adeniran B, Mokaya R (2015) Low temperature synthesized carbon nanotube superstructures with superior CO₂ and hydrogen storage capacity. *J Mater Chem A* 3(9):5148–5161
- Gonzalez-Garcia P (2018) Activated carbon from lignocellulosics precursors: a review of the synthesis methods, characterization techniques and applications. *Renew Sustain Energy Rev* 82:1393–1414
- Xia YD, Yang ZX, Mokaya R (2010) Templated nanoscale porous carbons. *Nanoscale* 2(5):639–659
- Chen XY, Chen C, Zhang ZJ, Xie DH (2013) High performance porous carbon through hard–soft dual templates for supercapacitor electrodes. *J Mater Chem A* 1(25):7379–7383
- Yang XY, Chen LH, Li Y, Rooke JC, Sanchez C, Su BL (2017) Hierarchically porous materials: synthesis strategies and structure design. *Chem Soc Rev* 46(2):481–558
- Benzigar MR, Talapaneni SN, Joseph S, Ramadass K, Singh G, Scaranto J, Ravon U, Al-Bahily K, Vinu A (2018) Recent advances in functionalized micro and mesoporous carbon materials: synthesis and applications. *Chem Soc Rev* 47(8):2680–2721
- Wang JC, Kaskel S (2012) KOH activation of carbon-based materials for energy storage. *J Mater Chem* 22(45):23710–23725
- Blankenship TS, Blankenship TS, Balahmar N, Mokaya R (2017) Oxygen-rich microporous carbons with exceptional hydrogen storage capacity. *Nat Commun* 8:1545
- Zhu G, Ma L, Lv H, Hu Y, Chen T, Chen R, Liang J, Wang X, Wang Y, Yan C (2017) Pine needle-derived microporous nitrogen-doped carbon frameworks exhibit high performances in electrocatalytic hydrogen evolution reaction and supercapacitors. *Nanoscale* 9(3):1237
- Sevilla M, Ferrero GA, Fuertes AB (2017) Beyond KOH activation for the synthesis of superactivated carbons from hydrochar. *Carbon* 114:50–58
- Ncibi MC, Ranguin R, Pintor MJ, Jeanne-Rose V, Sillanpää M, Gaspard S (2014) Preparation and characterization of chemically activated carbons derived from Mediterranean *Posidonia oceanica* (L.) fibres. *J Anal Appl Pyroly* 109:205–214
- Jibril B, Houache O, Al-Maamari R, Al-Rashidi B (2008) Effects of H₃PO₄ and KOH in carbonization of lignocellulosic material. *J Anal Appl Pyroly* 83(2):151–156
- Hesas RH, Arami-Niya A, Daud WMAW, Sahu JN (2015) Microwave-assisted production of activated carbons from oil palm shell in the presence of CO₂ or N₂ for CO₂ adsorption. *J Ind Eng Chem* 24:196–205
- Ruiz B, Ruisanchez E, Gil RR, Ferrera-Lorenzo N, Lozano MS, Fuente E (2015) Sustainable porous carbons from lignocellulosic wastes obtained from the extraction of tannins. *Micropor Mesopor Mat* 209:23–29
- Liu DC, Zhang WL, Lin HB, Li Y, Lu HY, Wang Y (2016) A green technology for the preparation of high capacitance rice husk-based activated carbon. *J Clean Prod* 112:1190–1198
- Deng J, Li MM, Wang Y (2016) Biomass-derived carbon: synthesis and applications in energy storage and conversion. *Green Chem* 18(18):4824–4854
- Zhu B, Liu B, Qu C, Zhang H, Guo W, Liang Z, Chen F, Zou R (2018) Tailoring biomass-derived carbon for high-performance supercapacitor from controllably cultivated algae microspheres. *J Mater Chem A* 6:1523–1530
- Long WY, Fang BZ, Ignaszak A, Wu ZZ, Wang YJ, Wilkinson D (2017) Biomass-derived nanostructured carbons and their composites as anode materials for lithium ion batteries. *Chem Soc Rev* 46(23):7176–7190
- Wang HL, Gao QM, Hu J, Chen Z (2009) High performance of nanoporous carbon in cryogenic hydrogen storage and electrochemical capacitance. *Carbon* 47(9):2259–2268
- Balahmar N, Mitchell AC, Mokaya R (2015) Generalized mechanochemical synthesis of biomass-derived sustainable carbons for high performance CO₂ storage. *Adv Energy Mater* 5(22):1500867
- Balahmar N, Al-Jumaily AS, Mokaya R (2017) Biomass to porous carbon in one step: directly activated biomass for high performance CO₂ storage. *J Mater Chem A* 5(24):12330–12339

37. Dong L, Ma X, Yang L, Ling Z, Liu W, Cheng J, Xu C, Li B, Yang QH, Kang F (2018) Extremely safe, high-rate and ultralong-life zinc-ion hybrid supercapacitors. *Energy Storage Mater* 13:96–102
38. Wang H, Wang M, Tang Y (2018) A novel zinc-ion hybrid supercapacitor for long-life and low-cost energy storage applications. *Energy Storage Mater* 13:1–7

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.