Large scale synthesis of nitrogen-doped nanoporous carbon spheres based on miniemulsion polymerization for efficient dye removal

Jing Zhao^{1,3} · Jianan Zhang^{1,2} · Mingyuan Wu¹ · Qingyun Wu¹ · Jianjun Yang¹

© Springer Nature Switzerland AG 2019

Abstract

Functional nanoporous carbon spheres (NPCS) are important for applications ranging from adsorption, catalysis, separation to energy storage and biomedicine. We demonstrated a facile method to synthesize uniform NPCS, involving the formation of polyacrylonitrile@poly (γ -methacryloxypropyl trimethoxysilane) (PAN@PMPS) composite particles via seeded miniemulsion polymerization of PAN nanoparticles (NPs), carbonization, and subsequent removal of the outer PMPS shell. The influences of the addition of water phase inhibitor sodium nitrite and crosslinking agent divinylbenzene on the morphologies of PAN@PMPS composite particles were investigated. The adsorption performance of NPCS towards methylene blue (MB) was investigated. The results showed that uniform PAN@PMPS composite particles were obtained with average diameters of ~ 149 nm when using NaNO_2 as water phase inhibitor. PMPS layer prevented PAN core aggregation/fusion during the carbonization process, resulting in the formation of individual NPCS. Uniform NPCS exhibiting diameters of ~ 122 nm, with the accessible surface area (~ 202 m²/g), and high nitrogen content (13.75 wt%) was obtained. NPCS exhibited excellent adsorption capacity towards MB with the maximum value of 117.89 mg/g at 298 K from aqueous solution. This miniemulsion polymerization-based strategy provides a new, facile approach to prepare high-performance porous carbon spheres in industrialization promise.

✉ Jianan Zhang, jianan@ahu.edu.cn | ¹School of Chemistry and Chemical Engineering and Institute of Physical Science and Information Technology, Anhui University, Hefei 230601, China. ²Anhui Province Key Laboratory of Environment-friendly Polymer Materials, Hefei 230601, China. ³Chaohu University, Chaohu 238000, China.

Graphical abstract

Keywords Nanoporous carbon spheres · Polyacrylonitrile · Miniemulsion polymerization · Composite particles · Adsorption

1 Introduction

Nanoporous carbon spheres (NPCS) integrate the advantages of porous carbon materials with spherical morphology, which have been examined in catalysis, adsorption applications, water and air purification, biomedicine, and energy storage and conversion applications [1–6]. Over the past decade, there has been explosive growth in the synthesis, characterization and application of NPCS [7–9]. Various synthetic strategies have been developed to prepare NPCS, including templating [10–13], emulsion polymerization [14], self-assembly [15], hydro-thermal carbonization (HTC) [16, 17], and the Stöber methods [18].

Among these methods, templating method is the most straight forth way by using pre-prepared particles as the precursor of carbon spheres. Because of chain cross-linking and fusion between neighboring nanoparticles during high-temperature carbonization, NPCS materials often agglomerate [4], diminishing their performance. Thus, the synthesis of uniform “individual” NPCS presented a major challenge of significant technological relevance [19]. Furthermore, such highly hydrophobic carbons have a limited number of active sites which could impede their practical applications [20]. NPCS doped with heteroatoms such as nitrogen, sulfur, and boron resulted in significantly enhanced surface polarity, wettability, and electron-donor

tendency of carbon matrix [21–25]. The functional group of heteroatom doped NPCS bearing a lone pair of electrons could improve the sorption of cationic dyes such as methylene blue (MB) [26].

Recently, we prepared porous carbon with high surface areas templated from commercial silica/cellulose nanocrystals showing excellent ORR properties [13], nanoporous carbon templated from organosilica nanoparticles of 5 nm [27], and porous carbon spheres templated from core/shell structured composite microspheres [19], which are all based on ATRP process. Compared with our recently published work, we intend to prepare the precursor particles of porous carbon spheres by miniemulsion polymerization method, which, as we know, is easier to be industrialized. Herein, we demonstrate a novel core/shell strategy to prepare uniform NPCS with high nitrogen content. Core-shell structured polyacrylonitrile@poly(3-methacryloxypropyl trimethoxysilane) (PAN@PMPS) composite particles were obtained via one-pot seeded miniemulsion polymerization. The PMPS shells acting as sacrificial protective layers were introduced to prevent PAN core aggregation/fusion during the carbonization process, resulting in well-dispersed NPCS after etching of the protective shell with NaOH solution. This miniemulsion polymerization-based strategy provided a facile and scalable approach to prepare high-performance NPCS with potential numerous applications.

2 Experimental section

2.1 Chemicals

Acrylonitrile (AN) and divinylbenzene (DVB) were purified by passing through a short basic Al_2O_3 column before use. 3-Methacryloxypropyltrimethoxysilane (MPS, Aldrich) was used without purification. Hexadecane (HD, Fluka), sodium dodecyl sulfate (SDS), and sodium nitrite (NaNO_2) were used as received. 2, 2'-Azobis (2-methypropionitrile) (AIBN) was purified by recrystallization in ethanol before use. Methylene blue trihydrate (MB) was used without further purification. Unless otherwise noted, all chemicals were purchased from Shanghai Chemical Reagent Co. Deionized water was used for all purposes.

2.2 Preparation of PAN@PMPS composite particles

PAN@PMPS composite particles were synthesized by seeded miniemulsion copolymerization based on our previous work [28, 29]. In a typical synthesis, HD (0.80 g), DVB (0.15 g), and AIBN (0.30 g) were first added to the monomer of AN (15.00 g) to form an oil phase. A portion of 80.00 g of SDS (0.20 g) and NaNO_2 (0.05 g) aqueous solution was employed as a water phase. The pre-emulsion was obtained by the mixing of the oil phase and the water phase under mechanical stirring for 30 min. Then the miniemulsion was prepared under high speed shearing using a Fluko[®] FM200 homogenizer at 16,000 rpm for 5 min in an ice bath and then degassed by bubbling with nitrogen for 30 min. The polymerization took place at 65 °C in a 250 mL three-necked round flask equipped with an agitator and a reflux condenser. MPS monomer (6.00 g) was then added dropwise over 30 min after 1.0 h of polymerization. PAN@PMPS composite particles were obtained after polymerization at 65 °C for 8 h. Table 1 showed the polymerization conditions in the synthesis of PAN@PMPS composite particles.

2.3 Preparation of NPCS

A certain amount of PAN@PMPS composite particles were dried to obtain solid PAN@silica composites. The thermal stabilization of the PAN cores was achieved by heating the PAN@silica composites at 280 °C for 2 h under air, resulting in partial cross-linking and cyclization of PAN side chains. Carbon@silica composites were obtained after carbonization at 700 °C for 0.5 h under a nitrogen atmosphere [17]. Individual NPCSs were generated after etching of the protective silica shell by stirring in 1 M NaOH solution (an EtOH-H₂O mixture) for 24 h [30].

2.4 Characterization

Scanning electron microscopy (SEM) was carried out with a field emission scanning electron microanalyzer (S-4800, Japan) operating at 30 kV. Samples of transmission electron microscopy (TEM) were prepared by drying a drop of dilute nanocomposite dispersion onto a carbon-coated copper grid. The analysis was conducted by using a JEM-2100 (JEOL, Japan) electron microscope operating at 200 kV. The PAN NPs and PAN@PMPS composite particles were characterized by a Vertex 80v & Hyperion 2000, operating at a resolution of 4 cm⁻¹ and a wavenumber range of 4000–400 cm⁻¹, based on the KBr method. The hydrodynamic diameters and size distributions of PAN NPs, PAN@PMPS composite particles and NPCS were measured by DLS measurement using a Zetasizer Nano ZS90 (Malvern Instruments, MA). The powder X-ray diffraction patterns (XRD) were performed on an XD-3 X-ray diffractometer with CuK α radiation, $\lambda = 0.15418$ nm, and the 2θ angle varied from 10° to 90° at a scanning rate of 4° min⁻¹. Surface area and pore size distribution were taken with N₂ adsorption, following the Barrett–Joyner–Halenda algorithm and the calibration method. Raman spectra were collected on inVia-Reflex spectrometer (United Kingdom) with a 532 nm laser excitation. X-ray photoelectron spectrometer (XPS) studies were conducted to weight the chemical state of NPCS products by ESCALAB 250Xi, United States. The concentration of MB was measured by UV–vis spectrometer (UV756/756CRT) at room temperature.

Table 1 Synthetic conditions of PAN@PMPS composite particles

Samples	Oil phase				Water phase			Dropwise addition of monomer MPS (g)
	AN (g)	HD (g)	DVB (g)	AIBN (g)	H ₂ O (g)	SDS (g)	NaNO ₂ (g)	
1	15.00	0.80	1.80	0.30	80.00	0.20	0	6.00
2	15.00	0.80	1.80	0.30	80.00	0.20	0.05	6.00
3	15.00	0.80	0.75	0.30	80.00	0.20	0.05	6.00
4	15.00	0.80	0.15	0.30	80.00	0.20	0.05	6.00

2.5 Adsorption properties of MB

The solutions of MB (300 mg/L) were prepared by dissolving methylene blue trihydrate in 250 mL of distilled water. The suspension solution of MB and NPCS were put into the conical flask and then agitated in oscillation at 150 rpm for a certain period of time at room temperature. The samples were filtered for the measurements of residual MB concentration. The concentration was determined using a UV–vis spectrometer (UV756/756CRT) at a maximum adsorption of 665 nm wavelength [31]. The adsorption capacity of MB was calculated by the following equation [32]:

$$q_t = (C_0 - C_t)V/m \quad (1)$$

where q_t (mg/g) was adsorption amount of MB at time of t , C_0 (mg/L) and C_t (mg/L) were the concentration of MB solution at the initial and time of t , V (L) was the solution volume, and m (g) was the mass of NPCS.

3 Results and discussion

3.1 Formation of NPCS templated from PAN@PMPS composite particles

Scheme 1 illustrates the procedure for preparation of NPCS templated from PAN@PMPS composite particles. PAN NPs were prepared by miniemulsion polymerization

Scheme 1 Schematic illustration of the process to synthesize the individual NPCS. **a** Preparation of PAN NPs by miniemulsion polymerization, **b** preparation of PAN@PMPS composite particles by seeded miniemulsion polymerization, **c** thermal stabilization and carbonization of PAN@PMPS composite particles, and **d** etching of protective shell to generate individual NPCS

(Scheme 1a). Then PAN@PMPS core/shell composite particles were obtained after grafting of PMPS by seeded miniemulsion polymerization (Scheme 1b). The thermal stabilization process of PAN@PMPS core/shell composite particles was performed under air atmosphere, and carbonization of stabilized PAN nanodomains was carried out under a nitrogen atmosphere to obtain porous carbon/silica hybrids (Scheme 1c) [33]. The cross-linked PMPS layer acted as a protective shell avoiding thermofusion of neighboring PAN cores during the carbonization process, resulting in individual NPCS after removal of the outer shell (Scheme 1d) [19, 34].

3.2 Characterization of PAN NPs and PAN@PMPS composite particles

To confirm the successful copolymerization of AN with MPS, the obtained composite particles were characterized by FT-IR. The FT-IR spectra of PAN NPs and PAN@PMPS composite particles were presented in Fig. 1. The double peak bands at 2927 cm^{-1} and 2853 cm^{-1} were attributed to a C–H stretching vibration. The double peak bands at 1460 cm^{-1} and 1364 cm^{-1} were attributed to a C–H bending vibration. The existence of characteristic $\text{C}\equiv\text{N}$ peaks at 2247 cm^{-1} in both PAN NPs and the obtained composite particles indicated PAN NPs and PAN@PMPS were successfully synthesized (Fig. 1a, b). Furthermore, the typical peak at 1716 cm^{-1} attributed to $\text{C}=\text{O}$ stretch of MPS proved the formation of PAN@PMPS composite particles (Fig. 1b).

In order to confirm the successful formation of PAN@PMPS composite particles, the hydrodynamic diameters of PAN NPs and PAN@PMPS composite particles were characterized by DLS, which were shown in Fig. 2. PAN NPs of about 116 nm possessing a narrow particle size distribution demonstrated that monomer droplet nucleation

Fig. 1 FT-IR spectra of **a** PAN NPs and **b** PAN@PMPS composite particles

Fig. 2 Size distributions of PAN NPs and PAN@PMPS composite particles characterized by DLS at 298 K

predominated during the miniemulsion polymerization. As expected the size of PAN@PMPS composite particles would increase after continued growth of PMPS onto PAN seeds. When compared with the corresponding PAN NPs, the hydrodynamic diameters of PAN@PMPS composite particles increased obviously from about 116–149 nm confirming the successful growth of PMPS onto PAN seeded NPs.

Obviously, the fabrication of uniform precursor particles of PAN@PMPS was the prerequisite to obtain porous spheres after carbonization. Due to the insolubility of PAN in its monomer, PAN NPs were not accessible by classical emulsion polymerization. In our miniemulsion system, due to the high solubility of acrylonitrile in water (7.35 wt%), NaNO_2 was added to avoid/inhibit the water phase nucleation of PAN. As could be seen in Fig. 3a, without

the addition of NaNO_2 in the water phase, the agglomerations of PAN@PMPS-D12N (DVB:12 wt%, without NaNO_2) were observed. The addition of NaNO_2 enhances droplet nucleation in acrylonitrile miniemulsion polymerization by reducing water phase nucleation in the maximum extent [35, 36]. Figure 3b showed that PAN@PMPS composite particles had regular spherical morphologies with good dispersity. In order to obtain PAN@PMPS composite particles of uniform size, the effects of crosslinker contents on the final morphologies of PAN@PMPS composite particles were investigated by using 12 wt% of DVB, 5 wt% of DVB, and 1 wt% of DVB, which were donated as PAN@PMPS-D12, PAN@PMPS-D5, and PAN@PMPS-D1, respectively. As can be seen from Fig. 3b–d, PAN@PMPS-D1 exhibited uniform morphology with diameters of ~ 130 nm, which acted as the best candidate for the preparation of NPCS. The partially enlarged TEM image (inset in Fig. 3d) showed a crumpled appearance of PAN@PMPS particles. The precipitation of the formed PAN within the monomer droplets led to the formation of roughened surfaces during the crystallization processes [36].

3.3 Morphology and chemical identity of NPCS

As demonstrated in our previous work, without the protective PMPS shell, bare PAN NPs were aggregated and fused to form monolith carbons during the carbonization process [19]. In order to testify the protective effects of the outer PMPS shell, PAN@PMPS composite particles were carbonized to form carbon@silica hybrids and individual porous carbon spheres were released after treatment by NaOH solution. As shown in Fig. 4b, the as-prepared NPCS

Fig. 3 TEM images of **a** PAN@PMPS-D12N (DVB:12 wt%, without NaNO_2), **b** PAN@PMPS-D12 (DVB:12 wt%), **c** PAN@PMPS-D5 (DVB:5 wt%), and **d** PAN@PMPS-D1 (DVB:1 wt%)

Fig. 4 **a** SEM image of NPCS, **b** TEM image of NPCS, **c** enlarged TEM image of individual NPCS, and **d** size distribution of NPCS at 298 K by DLS

demonstrated spherical morphology with quite a uniform size of ~ 120 nm, which was in accordance with the SEM result. The successful preparation of individual porous carbon spheres also confirmed the formation of PAN@PMPS composite particles with PMPS shell acting as a protective layer. The porous structure of individual NPCS was demonstrated in enlarged TEM image (Fig. 4c). The uniformity of the as-prepared NPCS was further confirmed by DLS results with the average hydrodynamic diameter of about 122 nm (Fig. 4d), which is in accordance with that from TEM result.

XRD and Raman spectroscopy were used to study the chemical composition of NPCS. The observed broad diffraction peaks at 2θ of 24° and 44° could be identified as the (002) and (101) reflections of a partially graphitic structure shown in Fig. 5a, which indicated that the material contained graphite carbon [37]. Raman spectroscopy provided further information on the surface and topology of NPCS. As shown in Fig. 5b, the typical Raman spectrum of NPCS exhibited D bands at about 1341 cm^{-1} was assigned to disorder originating from sp^3 carbons and disordered structures and G bands located at 1587 cm^{-1} was associated with a hexagonal carbon structure [38]. It has been demonstrated that the integral intensity ratio I_D/I_G correlated strongly with the microstructure of solid carbons, and larger I_D/I_G value corresponded to a lower graphitic structural order [39, 40]. The I_D/I_G value of NPCS was estimated to be 1.57, indicating the defects and disorders of carbon spheres.

The type of nitrogen species and the surface elemental composition of NPCS were evaluated by XPS analysis. The C1s and N1s high resolution spectra of NPCS were

Fig. 5 **a** XRD profiles and **b** Raman scattering spectrum of NPCS

shown in Fig. 6c, d, respectively. The peaks of C–OH, C–C, C=C, and C=O configurations were observed at 285.6 eV, 284.8 eV, 284.2 eV, and 288.2 eV after C1s peak treatment, respectively [41]. The peak at 397.5 eV could be ascribed to pyridine N species, the peak at 400.2 eV corresponded to pyrrolic structure, and the peak at 401.2 eV belonged to graphite N species. The peak at 398.5 eV could be described to other nitrogen species [42–44]. The different nitrogen content diagrams of the NPCS was shown in Fig. 6b. According to the XPS data, the contents of carbon (C), nitrogen (N), and oxygen (O) were 76.15 wt%, 13.75 wt%, and 10.10 wt%, respectively, indicating that PAN precursor yielded NPCS with high nitrogen content under the selected pyrolysis conditions.

The N₂ sorption isotherm measurements at 77 K were carried out to examine the porosity of the as-prepared NPCS. Figure 7a, b show the N₂ adsorption and desorption isotherms and pore size distribution of NPCS. The BET surface area of NPCS was calculated to be 202 cm²/g with the pore volume of 0.35 cm³/g and the average pore size of 4.0 nm when calculated by the BJH method. NPCS revealed a typical IV pattern confirming mesoporous evidence. The hysteresis loop by the capillary condensation of N₂ inside the pores was typically caused by the existence of mesoporous structure [45]. Therefore, the prepared porous carbon spheres contained rich

mesoporosity with high specific surface area and large pore volume.

3.4 Adsorption capacity of MB

Increasing in adsorption capacity with increasing contact time, as shown in Fig. 8, was attributed to more time became available for MB to interaction with adsorption sites on the surface of the NPCS. The experiments were carried out at an initial dye concentration of 300 mg/L with 0.5 g/L absorbent mass at room temperature. The adsorption rate of MB was rapid within the first 2 h, then increased slowly, and the adsorption equilibrium was obtained within 24 h. This was attributed to a large number of vacant surface adsorption sites were available for adsorption during the initial stage. With the lapse of time, the remaining vacant surface adsorption sites of NPCS became difficult to be occupied due to repulsive forces between adsorbed MB on the adsorbent and bulk phases [46–48]. The adsorption capacity of MC onto NPCS was 117.89 mg/g at 298 K. Table 2 shows a comparative study of MB adsorption by different adsorbents and our synthesized NPCS. It is to be noted that NPCS shows the maximum adsorption capacities (q_m) of 117.89 mg/g for MB, which is higher than the previously reported data on carbon and carbon-based materials [49–54].

Fig. 6 **a** XPS survey of the NPCS, **b** the content of different types of nitrogen in NPCS, **c** high-resolution C1s XPS spectra, and **d** high-resolution N1s XPS spectra

Fig. 7 **a** Nitrogen adsorption and desorption isotherms and **b** the pore size distribution of NPCS

Fig. 8 Adsorption capacities for MB onto NPCS as a function of the contact time (adsorbent dose 0.5 g/L, initial MB concentration 300 mg/L, 298 K)

4 Conclusion

Uniform nitrogen-doped NPCSs were prepared using core/shell-structured PAN@PMPs composite particles as

Table 2 Comparison of the adsorption capacity (q_m) of NPCS with other different adsorbents for MB adsorption

Samples	Q_m (mg/g)	Ref. no.
Cellulose-based wastes	20.8	[49]
Acid activated carbon	60.61	[50]
Porous carbon nanospheres	68.49	[51]
Graphene/magnetite composite	43.82	[52]
Rattle-type magnetic carbon nanospheres	45.15	[53]
Carbon nanotubes	64.7	[54]
Porous carbon nanospheres	117.89	This work

the precursors via miniemulsion polymerization method. The introduction of PMS layer prevented PAN core aggregation/fusion during the pyrolytic process, resulting in individual NPCS exhibiting diameters of ~ 122 nm, with a relatively high surface area (~ 202 m²/g), and high nitrogen content (13.75 wt%). This miniemulsion polymerization-based strategy provided a simple, scalable approach to prepare high performance NPCS, which exhibited good adsorption capacity towards MB with the maximum value of 117.89 mg/g at 298 K from aqueous solution.

Acknowledgements This work was supported by the Open fund for Discipline Construction, Institute of Physical Science and Information Technology, Anhui University and University Natural Science Research Project of Anhui Province (KJ2018A0036).

Author contributions The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Liu D, Peng X, Wu B, Zheng X, Chuong TT, Li J, Sun S, Stucky GD (2015) Uniform concave polystyrene-carbon core-shell nanospheres by a swelling induced buckling process. *J Am Chem Soc* 137(31):9772–9775
- Dai L, Xue Y, Qu L, Choi H-J, Baek J-B (2015) Metal-free catalysts for oxygen reduction reaction. *Chem Rev* 115(11):4823–4892
- Fang Y, Lv Y, Gong F, Wu Z, Li X, Zhu H, Zhou L, Yao C, Zhang F, Zheng G (2015) Interface tension-induced synthesis of mono-dispersed mesoporous carbon hemispheres. *J Am Chem Soc* 137(8):2808–2811
- Liu J, Wickramaratne NP, Qiao SZ, Jaroniec M (2015) Molecular-based design and emerging applications of nanoporous carbon spheres. *Nat Mater* 14(8):763–774
- Ahmad A, Mohd-Setapar SH, Chuong CS, Khatoon A, Wani WA, Kumar R, Rafatullah M (2015) Recent advances in new generation

- dye removal technologies: novel search for approaches to reprocess wastewater. *RSC Adv* 5(39):30801–30818
6. Vakili M, Rafatullah M, Salamatinia B, Abdullah AZ, Ibrahim MH, Tan KB, Gholami Z, Amouzgar P (2014) Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: a review. *Carbohydr Polym* 113:115–130
 7. Deshmukh AA, Mhlanga SD, Coville NJ (2010) Carbon spheres. *Mater Sci Eng R Rep* 70(1):1–28
 8. Nieto-Márquez A, Romero R, Romero A, Valverde JL (2011) Carbon nanospheres: synthesis, physicochemical properties and applications. *J Mater Chem* 21(6):1664–1672
 9. Lu AH, Hao GP, Sun Q, Zhang XQ, Li WC (2012) Chemical synthesis of carbon materials with intriguing nanostructure and morphology. *Macromol Chem Phys* 213(10–11):1107–1131
 10. Ding L, Olesik SV (2004) Synthesis of polymer nanospheres and carbon nanospheres using the monomer 1, 8-dihydroxymethyl-1, 3, 5, 7-octatetrayne. *Nano Lett* 4(11):2271–2276
 11. Liu J, Yang T, Wang D-W, Lu GQM, Zhao D, Qiao SZ (2013) A facile soft-template synthesis of mesoporous polymeric and carbonaceous nanospheres. *Nat Commun* 4:2798
 12. Kim T-W, Chung P-W, Slowing II, Tsunoda M, Yeung ES, Lin VS-Y (2008) Structurally ordered mesoporous carbon nanoparticles as transmembrane delivery vehicle in human cancer cells. *Nano Lett* 8(11):3724–3727
 13. Zhang J, Song Y, Kopeć M, Lee J, Wang Z, Liu S, Yan J, Yuan R, Kowalewski T, Bockstaller MR (2017) Facile aqueous route to nitrogen-doped mesoporous carbons. *J Am Chem Soc* 139(37):12931–12934
 14. Ouyang Y, Shi H, Fu R, Wu D (2013) Highly monodisperse microporous polymeric and carbonaceous nanospheres with multifunctional properties. *Sci Rep* 3:1430
 15. Wang S, Li W-C, Hao G-P, Hao Y, Sun Q, Zhang X-Q, Lu A-H (2011) Temperature-programmed precise control over the sizes of carbon nanospheres based on benzoxazine chemistry. *J Am Chem Soc* 133(39):15304–15307
 16. Sun X, Li Y (2004) Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angew Chem Int Ed* 43(5):597–601
 17. Xu S, Liu C, Ye F, Guo Y, Wiezorek J (2017) Alkali-assisted hydrothermal route to control submicron-sized nanoporous carbon spheres with uniform distribution. *Colloids Surf A Physicochem Eng Asp* 515:1–11
 18. Liu J, Qiao SZ, Liu H, Chen J, Orpe A, Zhao D, Lu GQM (2011) Extension of the Stöber method to the preparation of monodisperse resorcinol-formaldehyde resin polymer and carbon spheres. *Angew Chem Int Ed* 50(26):5947–5951
 19. Zhang J, Yuan R, Natesakhawat S, Wang Z, Zhao Y, Yan J, Liu S, Lee J, Luo D, Gottlieb E, Kowalewski T, Bockstaller MR, Matyjaszewski K (2017) Individual nanoporous carbon spheres with high nitrogen content from polyacrylonitrile nanoparticles with sacrificial protective layers. *ACS Appl Mater Interfaces* 9(43):37804–37812
 20. Wei J, Zhou D, Sun Z, Deng Y, Xia Y, Zhao D (2013) A controllable synthesis of rich nitrogen-doped ordered mesoporous carbon for CO₂ capture and supercapacitors. *Adv Funct Mater* 23(18):2322–2328
 21. Gong K, Du F, Xia Z, Durstock M, Dai L (2009) Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. *Science* 323(5915):760–764
 22. Zhao J, Lai H, Lyu Z, Jiang Y, Xie K, Wang X, Wu Q, Yang L, Jin Z, Ma Y (2015) Hydrophilic hierarchical nitrogen-doped carbon nanocages for ultrahigh supercapacitive performance. *Adv Mater* 27(23):3541–3545
 23. Liu S, Cai Y, Zhao X, Liang Y, Zheng M, Hu H, Dong H, Jiang S, Liu Y, Xiao Y (2017) Sulfur-doped nanoporous carbon spheres with ultrahigh specific surface area and high electrochemical activity for supercapacitor. *J Power Sources* 360:373–382
 24. Feng S, Li W, Shi Q, Li Y, Chen J, Ling Y, Asiri AM, Zhao D (2014) Synthesis of nitrogen-doped hollow carbon nanospheres for CO₂ capture. *Chem Commun* 50(3):329–331
 25. Sun Y, Wu J, Tian J, Jin C, Yang R (2015) Sulfur-doped carbon spheres as efficient metal-free electrocatalysts for oxygen reduction reaction. *Electrochim Acta* 178:806–812
 26. Haque E, Lo V, Minett AI, Harris AT, Church TL (2014) Dichotomous adsorption behaviour of dyes on an amino-functionalised metal-organic framework, amino-MIL-101 (Al). *J Mater Chem A* 2(1):193–203
 27. Zhang J, Song Y, Zhao Y, Zhao S, Yan J, Lee J, Wang Z, Liu S, Yuan R, Luo D (2018) Organosilica with grafted polyacrylonitrile brushes for high surface area nitrogen-enriched nanoporous carbons. *Chem Mater* 30(7):2208–2212
 28. Zhang J, Ge X, Wang M, Wu M, Yang J, Wu Q (2012) Facile fabrication of flower-like nanocomposite microparticles via seeded miniemulsion polymerization. *Polym Chem* 3(8):2011–2017
 29. Zhang J, Yang J, Wu Q, Wu M, Liu N, Jin Z, Wang Y (2010) SiO₂/polymer hybrid hollow microspheres via double in situ miniemulsion polymerization. *Macromolecules* 43(3):1188–1190
 30. Lee J-S, Joo SH, Ryoo R (2002) Synthesis of mesoporous silicas of controlled pore wall thickness and their replication to ordered nanoporous carbons with various pore diameters. *J Am Chem Soc* 124(7):1156–1157
 31. Olgun A, Atar N (2009) Equilibrium and kinetic adsorption study of basic yellow 28 and basic red 46 by a boron industry waste. *J Hazard Mater* 161(1):148–156
 32. Wang X, Chen C, Hu W, Ding A, Xu D, Zhou X (2005) Sorption of 243Am (III) to multiwall carbon nanotubes. *Environ Sci Technol* 39(8):2856–2860
 33. Fitzer E (1989) Pan-based carbon fibers—present state and trend of the technology from the viewpoint of possibilities and limits to influence and to control the fiber properties by the process parameters. *Carbon* 27(5):621–645
 34. Liu W, Chen J, Yang T, Chou K-C, Hou X (2016) Enhancing photoluminescence properties of SiC/SiO₂ coaxial nanocables by making oxygen vacancies. *Dalton Trans* 45(34):13503–13508
 35. Zhou SX, Weng ZX, Huang ZM, Pan ZR (2001) Effects of water solubility of acrylonitrile on vinylidene chloride/acrylonitrile/styrene suspension polymerization. *J Appl Polym Sci* 79(8):1431–1438
 36. Landfester K, Antonietti M (2000) The polymerization of acrylonitrile in miniemulsions: “crumpled latex particles” or polymer nanocrystals. *Macromol Rapid Commun* 21(12):820–824
 37. Pol VG, Shrestha LK, Ariga K (2014) Tunable, functional carbon spheres derived from rapid synthesis of resorcinol-formaldehyde resins. *ACS Appl Mater Interfaces* 6(13):10649–10655
 38. Yun YS, Park MH, Hong SJ, Lee ME, Park YW, Jin H-J (2015) Hierarchically porous carbon nanosheets from waste coffee grounds for supercapacitors. *ACS Appl Mater Interfaces* 7(6):3684–3690
 39. Jawhari T, Roid A, Casado J (1995) Raman spectroscopic characterization of some commercially available carbon black materials. *Carbon* 33(11):1561–1565
 40. Hibino T, Kobayashi K, Heo P (2013) Oxygen reduction reaction over nitrogen-doped graphene oxide cathodes in acid and alkaline fuel cells at intermediate temperatures. *Electrochim Acta* 112:82–89
 41. Jia L, Wang H, Dhawale D, Anand C, Wahab MA, Ji Q, Ariga K, Vinu A (2014) Highly ordered macro-mesoporous carbon nitride film for selective detection of acidic/basic molecules. *Chem Commun* 50(45):5976–5979
 42. Chen P, Yang J-J, Li S-S, Wang Z, Xiao T-Y, Qian Y-H, Yu S-H (2013) Hydrothermal synthesis of macroscopic nitrogen-doped

- graphene hydrogels for ultrafast supercapacitor. *Nano Energy* 2(2):249–256
43. Arrigo R, Hävecker M, Wrabetz S, Blume R, Lerch M, McGregor J, Parrott EP, Zeitler JA, Gladden LF, Knop-Gericke A (2010) Tuning the acid/base properties of nanocarbons by functionalization via amination. *J Am Chem Soc* 132(28):9616–9630
 44. Chen P, Wang L-K, Wang G, Gao M-R, Ge J, Yuan W-J, Shen Y-H, Xie A-J, Yu S-H (2014) Nitrogen-doped nanoporous carbon nanosheets derived from plant biomass: an efficient catalyst for oxygen reduction reaction. *Energy Environ Sci* 7(12):4095–4103. <https://doi.org/10.1039/c4ee02531h>
 45. Park S-H, Jung H-R, Lee W-J (2013) Hollow activated carbon nanofibers prepared by electrospinning as counter electrodes for dye-sensitized solar cells. *Electrochim Acta* 102:423–428
 46. Zhang H, Li X, He G, Zhan J, Liu D (2013) Preparation of magnetic composite hollow microsphere and its adsorption capacity for basic dyes. *Ind Eng Chem Res* 52(47):16902–16910
 47. Zolfaghari G, Esmaili-Sari A, Anbia M, Younesi H, Amirmahmoodi S, Ghafari-Nazari A (2011) Taguchi optimization approach for Pb (II) and Hg (II) removal from aqueous solutions using modified mesoporous carbon. *J Hazard Mater* 192(3):1046–1055
 48. Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010) Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater* 177(1–3):70–80
 49. Annadurai G, Juang R-S, Lee D-J (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J Hazard Mater* 92(3):263–274
 50. Arivoli S, Hema M, Parthasarathy S, Manju N (2010) Adsorption dynamics of methylene blue by acid activated carbon. *J Chem Pharm Res* 2(5):626–641
 51. Kundu S, Chowdhury IH, Naskar MK (2018) Hierarchical porous carbon nanospheres for efficient removal of toxic organic water contaminants of phenol and methylene blue. *J Chem Eng Data* 63(3):559–573
 52. Ai L, Zhang C, Chen Z (2011) Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite. *J Hazard Mater* 192(3):1515–1524
 53. Shao Y, Zhou L, Bao C, Ma J (2015) A facile approach to the fabrication of rattle-type magnetic carbon nanospheres for removal of methylene blue in water. *Carbon* 89:378–391
 54. Yao Y, Xu F, Chen M, Xu Z, Zhu Z (2010) Adsorption behavior of methylene blue on carbon nanotubes. *Bioresour Technol* 101(9):3040–3046

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