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NOTE

Nitrogen self-doped porous carbon nanosheets derived from azo dye flocs for efficient supercapacitor electrodes

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Abstract
The present work introduces a new method for the recycling of waste flocculation sludge to prepare electrode materials for supercapacitor. Hazardous azo dye was removal from textile dying wastewater by a new chitosan-based flocculant, and the generated dye sludge flocs was used as a nitrogen-containing precursor for the fabrication of N-doped carbon materials. The influence of azo dye on specific surface areas, nitrogen content, pore evolution of the resulting products and their electrochemical performance were investigated in detail. The results demonstrated a dual role of azo dye worked as both a nitrogen resource and pore-forming agent. The resulting N-doped carbon nanosheets derived from azo dye flocs demonstrated high electrochemical capacitance and good stability for supercapacitor electrode, which is attributed to the unique nitrogen doping, higher specific surface area and efficient charge transfer ability.

Keywords Textile dying effluents · Flocs · N-doped carbon · Supercapacitors

1 Introduction

Nitrogen-doped carbon materials are one of the most widely studied electrodes to construct supercapacitors with the desired physical and chemical characterizations. In comparison to other heteroatoms, nitrogen-doped carbon materials show interesting properties such as high capacity, electric conductivity and wettability of materials, and excellent cycle ability [1]. N-doped carbon materials can be prepared by a one-step carbonization reaction employing N-containing precursors, such as melamine, polypyrrole, and polyaniline [2]. However, it often uses expensive nitrogen-enriched precursors, making the synthetic processes costly and difficult to scale-up. Thus, the generation of a low-cost and abundant N-containing resource as a precursor to produce high-performance electrode materials is highly desirable.

Sewage sludge, an important byproduct from coagulation/flocculation processes for the textile dying effluents, is considered hazardous waste, likely to cause health problems in humans and/or damage the environment [3]. As the costs to dispose of environmental wastes increases, more emphasis is placed on the recycling and conversion of flocculation sludge into high value-added products. The textile dye sludge, a by-product of wastewater treatment, mainly consists of polymeric flocculants and azo dyes molecules. Azo dye is an attractive source of nitrogen for the preparation of N-doped carbon materials by one-pot pyrolysis process. The use of flocculation sludge precursors to obtain advanced energy conversion and storage materials is an extremely attractive prospect to simultaneously resolve environmental problems and energy crises [4, 5].

In this work, chitosan-based flocculants (CBF) were synthesized by incorporation of 2,4-bis(dimethylamino)-6-chloro-[1,3,5]-triazine (BDAT) onto the chitosan. Azo dye in dying effluents can be removed efficiently by CBF. Then, sewage sludge was used as a nitrogen-contained precursor to produce nitrogen-doped carbon nanosheets by one-pot pyrolysis process. The roles of the dye on the pore evolution, nitrogen content, and species of the resulting products and their electrochemistry performance were measured in detail.

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2 Experimental

2.1 Materials

Chitosan was purchased from Sinopharm Chemical Reagent Co., Ltd. Cyanuric chloride was obtained from Tokyo Chemical Industry Co., Ltd. Reactive brilliant red K-2BP was obtained from Longsheng Dyestuff Co., Ltd.

2.2 Procedure for manufacturing the carbon nanosheets from azo dye flocs

Flocculant (CBF) was first prepared via an etherifying reaction between chitosan and 2,4-bis(dimethylamino)-6-chloro-[1,3,5]-triazine according to our previous research [6]. The Flocculation experiments for the K-2BP were employed by the jar tests to determine the optimum flocculation conditions according to the previous report [7]. CBF showed excellent flocculation performance for K-2BP, an extensively used commercial dyes, and dye flocs with saturated adsorption capacity of 2.0 g g^{-1} (color removal > 99%) can be obtained in the optimal flocculation conditions. Then, the dye flocs and pure flocculants were used as precursor source to prepare nitrogen self-doped porous carbon materials through direct carbonization at 800 °C in a N_2 atmosphere, which were defined as CBF-dye-N and CBF-N. Using flocculation sludge as precursors to prepare N-doped carbon materials as described in Scheme 1.

2.3 Characterization of materials

The detailed surface structures of the resulting annealed product were examined with scanning electron microscopy (SEM, Sigma 300, Carl Zeiss Jena) and transmission electron microscopy (TEM, JEM-2010, JEOL). X-ray photoelectron spectra (XPS) measurements were carried out using an ESCALAB 250Xi system (Thermo Scientific). The BET surface area and pore structures of CBF-N and CBF-dye-N were determined by measuring volumetric N_2 adsorption–desorption isotherms at 77 K in a Micromeritics ASAP 2020 HD88 instrument (Micromeritics, USA).

2.4 Electrochemical measurements

The electrochemical capacitors of the carbon-based electrodes were evaluated in a standard three-electrode setup in a 6 M KOH by a Chenhua CHI 760D model Electrochemical Workstation (Shanghai, China). A saturated Hg/Hg_2Cl_2 was used as reference electrodes, and platinum foil was used as counter electrode, respectively. The test electrode was prepared by dispersing certain amounts of the active material (80 wt%), carbon black (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in *N*-methyl-pyrrolidone (NMP) solvent. Then, the slurry was brush-coated onto a nickel foam with an active area of 1 cm^2 and dried at 100 °C for 3 h. The as-prepared samples were then evaluated with different mass loading from 3.5 to 4.1 mg. The calculation of specific capacitance (C_s) from GCD curves according to the following Eq. (1):

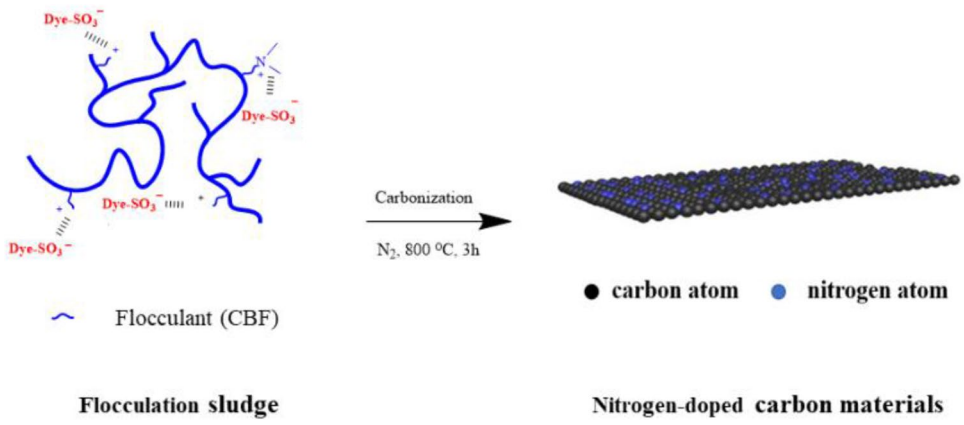
$$C_s = \frac{I\Delta t}{m\Delta V}, \tag{1}$$

where I represents the current (A), Δt denotes the discharge time (s), m is the mass of active material in each electrode (g), and ΔV refers to the potential change (V).

3 Results and discussion

3.1 Characterization of the resulting annealed product

The SEM images for CBF-dye-N and CBF-N are shown in Fig. 1a, b. It was clear that the whole surface of CBF-dye-N was comparatively rougher, with plenty of hierarchical pores



Scheme 1 Using flocculation sludge as precursors to prepare N-doped carbon materials

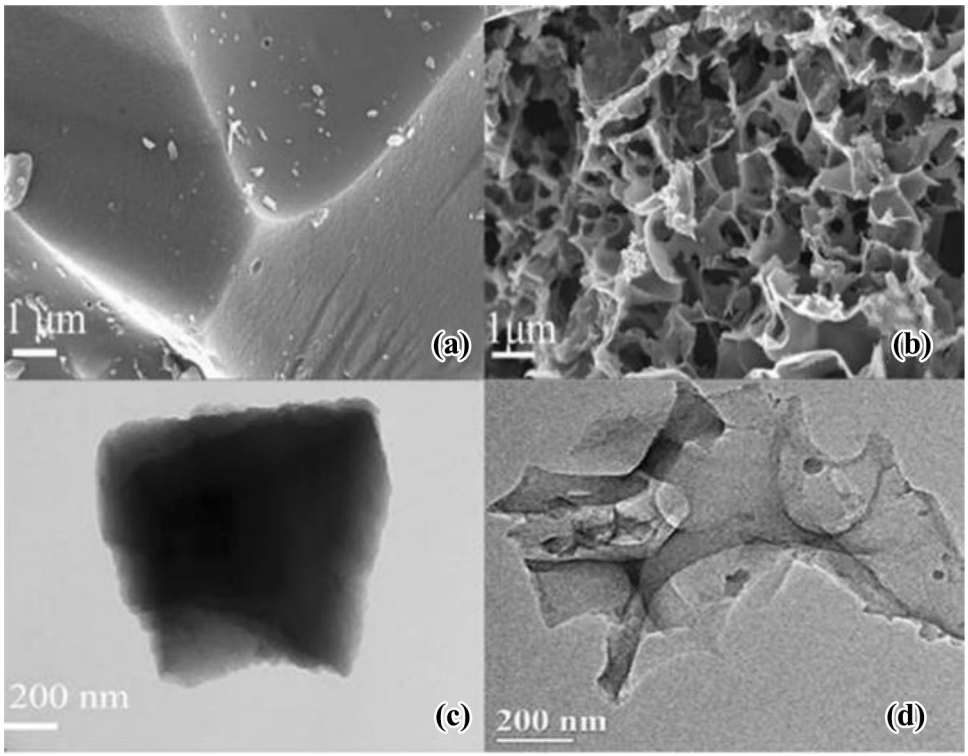


Fig. 1 SEM image of the CBF-N (**a**) and CBF-dye-N (**b**). TEM image of CBF-N (**c**) and CBF-dye-N (**d**)

and irregular cracks. This indicated that dye increased the porosity of the carbon materials. To further reveal its microstructures, a TEM image of CBF-N and CBF-dye-N are shown in Fig. 1c, d. Clearly, a two-dimensional nanosheet structure was still observed in CBF-dye-N. The nanosheet was about several hundred nanometers, with inter-crossed mesopores. The entire surface area of the nanosheet was highly accessible to electrolyte ions, which also enlarged the specific contact area of the electrodes/electrolyte, further enhancing the electrochemical performance [8, 9].

In Fig. 2a, there are three strong signals at ~ 286 eV, ~ 400 eV, and ~ 534 eV that correspond with the characteristic peaks from carbon, nitrogen and oxygen elements, respectively [10]. Compared with CBF-N (6.9 at%), which was prepared using the pure flocculant as precursor, CBF-dye-N showed much higher nitrogen doping (9 at%) by adding azo dye as the nitrogen source. The deconvolutions of N 1s revealed four different types of doped N at 398.6 (pyridinic nitrogen), 400.3 (pyrrolic nitrogen), 401.2 (graphitic nitrogen) and 403.7 (pyridine-N-oxide) (Fig. 2b) [11, 12]. The plentiful accessible nitrogen dopants in carbon materials, especially the charged pyridinic and pyrrolic can provide pseudocapacitance and enhance the capacity of supercapacitors [13].

N_2 adsorption–desorption isotherms of CBF-dye-N and CBF-N are demonstrated in Fig. 3. The pore structure parameters and specific surface area (S_{BET}) are listed in Table 1. The S_{BET} of the CBF-dye-N was measured to be 649.5 $m^2\ g^{-1}$, clearly much larger than that of pure flocculant (17.5 $m^2\ g^{-1}$). Furthermore, the resulting N-doped carbon materials derived from pure flocculant, exhibited a type between II and IV (in the IUPAC classification) [14]. As the CBF-dye-N, N_2 isotherms resembled type IV and displayed an H1-type hysteresis loop at high relative pressure ranges. Furthermore, N_2 adsorption was observed at low pressure with a steep uptake below 0.03 relative pressure. These results clearly indicated that pore size increased gradually and micro-, meso- and/or macro-pores coexisted in CBF-dye-N [11]. The dye likely acted as the pore-forming agent during the carbonization process, and the emission of many non-carbon or carbon elements resulted in the formation of many pores within the carbon matrix [15, 16]. CBF-dye-N had a higher specific surface area, which also greatly increased the contact area of electrodes within the electrolytes, further enhancing the electrochemical behaviors [17].

3.2 Electrochemical performance of the N-doped carbon nanosheets

The electrochemical properties of as-prepared N-doped materials were evaluated as supercapacitor electrode materials in a three-electrode cell. CV curve of CBF-dye-N shows a larger area, which means a higher specific capacitance compares to that of CBF-N electrode (Fig. 4a). The specific capacitance (C_s, F g^{-1}) of CBF-dye-N was calculated using galvanostatic charge/discharge curves (Fig. 4b). A high Cs of

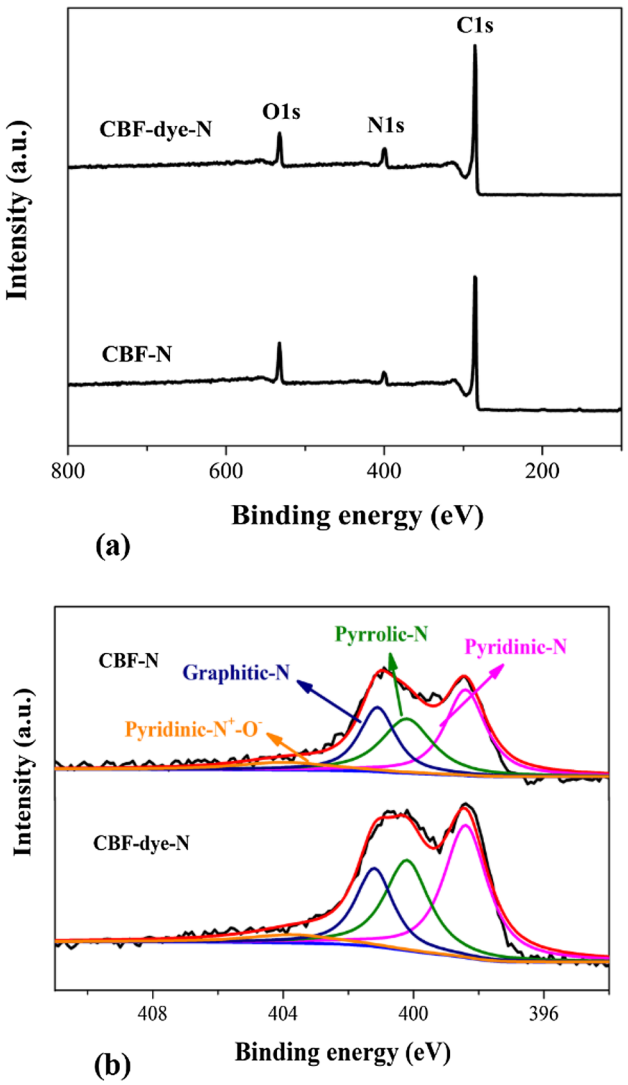


Fig. 2 XPS survey and high-resolution XPS spectra for CBF-N and CBF-dye-N

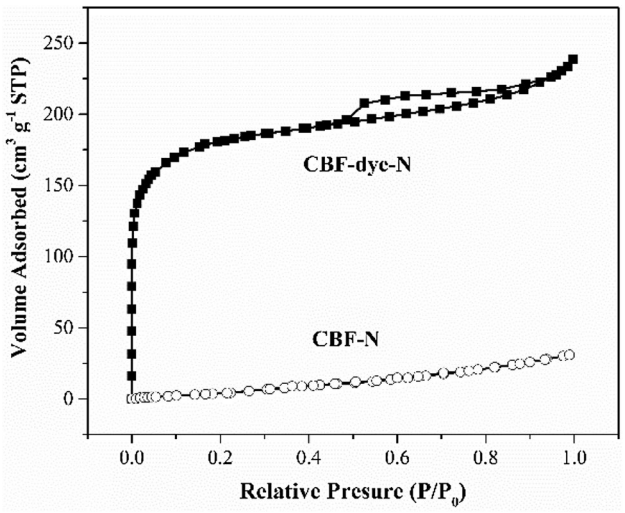


Fig. 3 N_2 adsorption–desorption isotherms of CBF-dye-N and CBF-N

Table 1 Porous property calculated from N_2 adsorption–desorption isotherms

Sample	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Meso-pore size (nm)	Micro-pore size (nm)
CBF-N	17.5	0.0649	10.93	1.09
CBF-dye-N	649.5	0.142	2.27	0.519

139 F g^{-1} can be reached at 0.5 A g^{-1}. Moreover, it is found that electrode CBF-dye-N shows better coulombic efficiency than CBF-dye (82.7% vs 72.7%). This can be interpreted that the surface area of CBF-dye-N is much larger than that of CBF-N, which could increase the contact area of electrodes within the electrolytes and improve the electrochemical behaviors. Furthermore, the content of pyridinic nitrogen increases significantly from ca. 38.2 at% for CBF-N to 48.2 at% for CBF-dye-N by the addition of dye to flocculant (Fig. 2). A previous study has reported pyridinic-N has a significant contribution in pseudocapacitance through the redox reactions. The results from electrochemistry performance of the electrodes are well consistent with the XPS data [18].

To assess the influence of dye on Warburg impedance of resulting N-doped materials, Nyquist plots were obtained under open circuit potential (Fig. 5a). It can be clearly seen that the CBF-dye-N had a nearly vertical line at low frequency region, indicating a very low internal resistance within the electrode. This phenomenon is mainly because a high surface area of CBF-dye-N, which providing smooth diffusion/transport for electrolyte ion through the electrode material [19].

Figure 5b demonstrates the specific capacitances and capacity retention of CBF-N and CBF-dye-N at different current densities. Clearly, the Cs of the samples decreased when increasing discharge current densities from 0 to 10 A g^{-1}. For CBF-dye-N, the specific capacitance reached 157 F g^{-1} at a discharge current of 0.2 A g^{-1}, which was maintained as high as 102 F g^{-1} under a higher discharge current density of 10 A g^{-1}. The excellent retention capability could be explained by the high surface area and appropriate pore size distribution of CBF-dye-N, which are good reservoirs and bring the easy migration of electrolyte ions even at a higher moving speed for electrolytes [20].

4 Conclusions

In summary, chitosan-based flocculant and dye flocs were used as nitrogen-rich precursors to manufacture nitrogen-doped carbon materials by a one-step carbonization reaction.

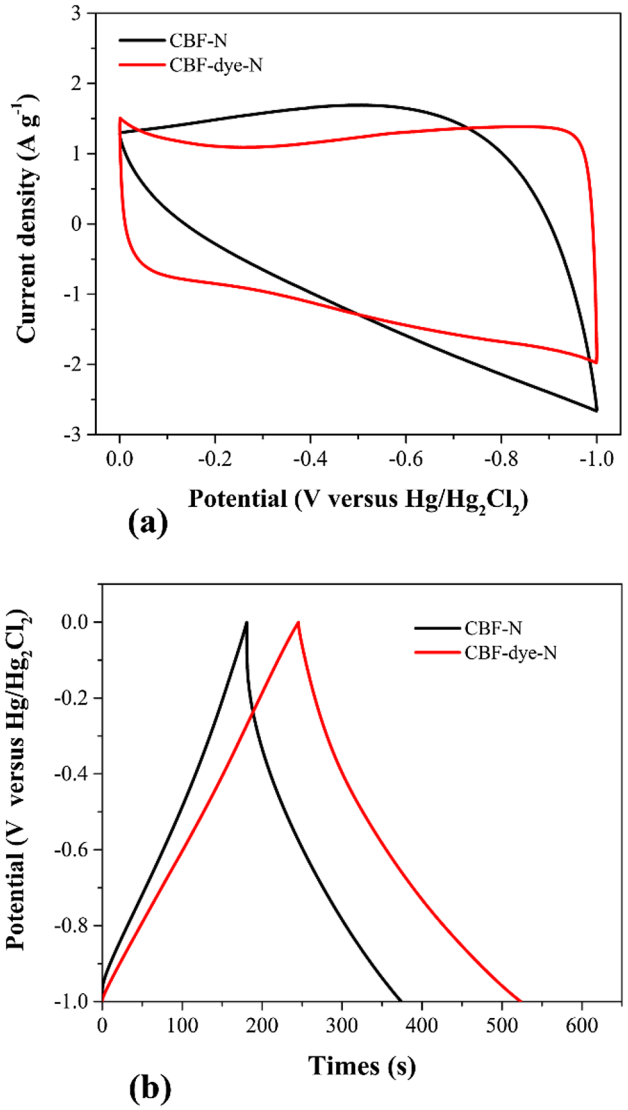


Fig. 4 **a** Cyclic voltammetry curves for CBF-dye-N and CBF-N at a scan rate of 20 mV s^{-1}. **b** Galvanostatic charge/discharge curves for CBF-dye-N and CBF-N at a current density of 0.5 A g^{-1}

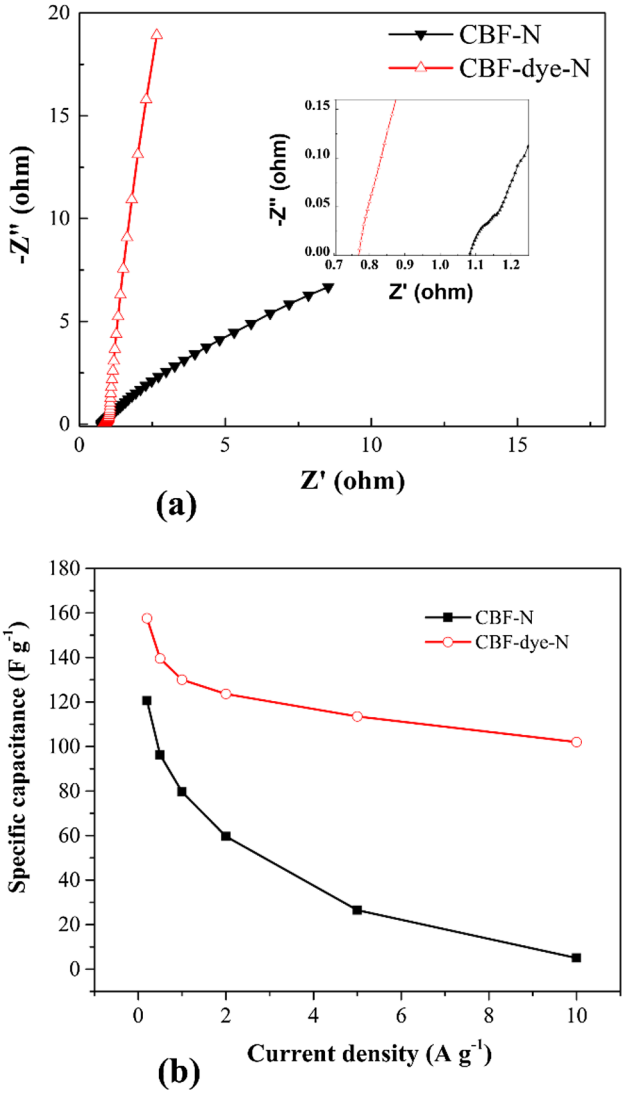


Fig. 5 Nyquist plots (**a**) and specific capacitance at various scan rates (**b**) of CBF-N and CBF-dye-N

Introduced azo dye played dual roles as a nitrogen resource and pore-forming agent. Using flocculation sludge as precursor source, the resulting annealed product exhibited a high specific capacity (157 F g^{-1} at 0.2 A g^{-1}) and good cycling stability as electrode material for supercapacitor. This work presents a new concept to recycle dye-contained sludge to produce advanced energy storage materials, which is highly promising for resolve environmental problems and energy crises simultaneously.

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Compliance with ethical standards

Conflict of interest There are no conflicts to declare.

References

1. 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 27:3541. https://doi.org/10.1002/adma.201500945
2. Qu K, Zheng Y, Dai S, Qiao SZ (2016) Graphene oxide-polydopamine derived N, S-codoped carbon nanosheets as superior bifunctional electrocatalysts for oxygen reduction and evolution. Nano Energy 19:373. https://doi.org/10.1016/j.nanoen.2015.11.027

3. Feng L, Luo J, Chen Y (2015) Dilemma of sewage sludge treatment and disposal in china. Environ Sci Technol 49:4781. https://doi.org/10.1021/acs.est.5b01455
4. Yuan SJ, Dai XH (2016) An efficient sewage sludge-derived bifunctional electrocatalyst for oxygen reduction and evolution reaction. Green Chem 18:4004. https://doi.org/10.1039/C5GC02729B
5. Lei Z, Feng W, Feng C, Zhou W, Wei C, Wang X (2017) Nitrified coke wastewater sludge flocs: an attractive precursor for N, S dual-doped graphene-like carbon with ultrahigh capacitance and oxygen reduction performance. J Mater Chem A 5:2012. https://doi.org/10.1039/C6TA09887H
6. Zhang K, Shi Y, Wu L, Chen L, Wei T, Jia X, Chen Z, Li M, Xu Y, Wang Y (2018) Thermo- and pH-responsive starch derivatives for smart window. Carbohydr Polym 196:209. https://doi.org/10.1016/j.carbpol.2018.05.039
7. Wang Y, Shi Y, Xu M, Wu L, Jia X, Wei T, Zhang S, Guo X (2016) Smart flocculant with temperature and pH response derived from starch. RSC Adv 6:44383. https://doi.org/10.1039/c6ra04060h
8. Yuan C, Yang L, Hou L, Shen L, Zhang X, Lou XW (2012) Growth of ultrathin mesoporous Co_3O_4 nanosheet arrays on Ni foam for high-performance electrochemical capacitors. Energy Environ Sci 5:7883. https://doi.org/10.1039/C2EE21745G
9. Yuan C, Li J, Hou L, Zhang X, Shen L, Lou XW (2012) Ultrathin mesoporous $NiCo_2O_4$ nanosheets supported on ni foam as advanced electrodes for supercapacitors. Adv Funct Mater 22:4592. https://doi.org/10.1002/adfm.201200994
10. Shi Y, Zhang LL, Schon TB, Li HH, Fan CY, Li XY, Wang HF, Wu XL, Xie H, Sun H (2017) Porous carbon with willow leaf shaped pores for high performance supercapacitors. ACS Appl Mater Inter 9:42699. https://doi.org/10.1021/acsami.7b12776
11. Chen LF, Zhang XD, Liang HW, Kong M, Guan QF, Chen P, Wu ZY, Yu SH (2012) Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors. ACS Nano 6:7092. https://doi.org/10.1021/nn302147s
12. Ruili L, Dongqing W, Xinliang F, Klaus M (2010) Nitrogen-Doped ordered mesoporous graphitic arrays with high electrocatalytic activity for oxygen reduction. Angew Chem Int Ed 122:2619. https://doi.org/10.1002/ange.200907289
13. Liu H, Song H, Chen X, Zhang S, Zhou J, Ma Z (2015) Effects of nitrogen- and oxygen-containing functional groups of activated carbon nanotubes on the electrochemical performance in supercapacitors. J Power Sources 285:303. https://doi.org/10.1016/j.jpowsour.2015.03.115
14. Kang S, Yu JS, Kruk M, Jaroniec M (2002) Synthesis of an ordered macroporous carbon with 62 nm spherical pores that exhibit unique gas adsorption properties. Chem Commun 16:1670. https://doi.org/10.1039/B204756J
15. Jing T, Jian L, Cuiling L, Yunqi L, Tade MO, Sheng D, Yusuke Y (2015) Synthesis of nitrogen-doped mesoporous carbon spheres with extra-large pores through assembly of diblock copolymer micelles. Angew Chem Int Ed 54:588. https://doi.org/10.1002/anie.201407629
16. Nie R, Yang H, Zhang H, Yu X, Lu X, Zhou D, Xia QH (2017) Mild-temperature hydrodeoxygenation of vanillin over porous nitrogen-doped carbon black supported nickel nanoparticles. Green Chem 19:3126. https://doi.org/10.1039/C7GC00531H
17. Nguyen VH, Shim J-J (2015) Three-dimensional nickel foam/graphene/$NiCo_2O_4$ as high-performance electrodes for supercapacitors. J Power Sources 273:110. https://doi.org/10.1016/j.jpowsour.2014.09.031
18. Lee YH, Chang KH, Hu CC (2013) Differentiate the pseudocapacitance and double-layer capacitance contributions for nitrogen-doped reduced graphene oxide in acidic and alkaline electrolytes. J Power Sources 227:300. https://doi.org/10.1016/j.jpowsour.2012.11.026
19. Tang J, Ge Y, Shen J, Ye M (2016) Facile synthesis of $CuCo_2S_4$ as a novel electrode material for ultrahigh supercapacitor performance. Chem Commun 52:1509. https://doi.org/10.1039/C5CC09402J
20. Chou T-C, Huang C-H, Doong R-A, Hu C-C (2013) Architectural design of hierarchically ordered porous carbons for high-rate electrochemical capacitors. J Mater Chem A 1:2886. https://doi.org/10.1039/C2TA01190E