Synergistic approach of high-performance N-NiCo/PC environment benign electrode material for energy storage device

Muhammad Irfan¹, Xianhua Liu¹*, Suraya Mushtaq¹, Jonnathan Cabrera¹ and Pingping Zhang¹

¹School of Environmental Science and Engineering, Tianjin University, Tianjin, 300354, PR China.
²College of Food Science and Engineering, Tianjin Agricultural University, Tianjin, 300384, PR China.

*Corresponding author. Tel.: +86-22-85356239; E-mail: lxh@tju.edu.cn
Synergistic approach of high-performance N-NiCo/PC environment benign electrode material for energy storage device

Muhammad Irfan¹, Xianhua Liu¹*, Suraya Mushtaq¹, Jonathan Cabrera¹ and Pingping Zhang²

Abstract
Development of sustainable electrochemical energy storage devices faces great challenge in exploring highly efficient and low cost electrode materials. Biomass waste derived carbonaceous materials can be used as an alternative to expensive metals in supercapacitor. However, their application limited by low performance. In this study, the combination use of persimmon waste derived carbon and transition metal nitride demonstrated strong potential for supercapacitor application. Persimmon based carbonaceous gel decorated with bimetallic-nitride (N-NiCo/PC) was firstly synthesized through a green hydrothermal method. Electrochemical properties of N-NiCo/PC as electrode in 6 M KOH electrolyte solution were evaluated by using cyclic voltammetry (CV) and charge-discharge measurements. The N-NiCo/PC exhibited 895.5 F/g specific capacitance at 1 A/g current density and maintained 91.5% capacitance retention after 900 cycles. Hence, the bimetallic nitride-based-composite catalyst is a potentially suitable material for high-performance energy storage devices. In addition, this work demonstrated a promising pathway for transforming environmental waste into sustainable energy conversion materials.

Keywords: Persimmon waste; aerogel; N-NiCo/PC electrode; supercapacitor
1. Introduction

Lately, there is a need to protect natural resources and control energy consumption because of global warming. With rapid population growth, the energy demand can be attained in the direction of unconventional sustainable and renewable energy devices[1], like fuel cells [2-5], batteries[6], and supercapacitors[7] that convert chemically stored energy into electrical energy through electrochemical reactions. Among these different technologies, the supercapacitor has received great attention because of its high-power density, good cycle stability, fast storage capacity, and excellent operational safety[8]. According to its energy-storage mechanism, a supercapacitor can be divided into a pseudo capacitor and an electric double-layer capacitor. The capacitance of the pseudo capacitor comes from the reversible faraday redox reaction of electroactive material at the electrode interface and electrolyte. The capacitance of electric double layer capacitor is caused by the accumulation of pure electrostatic charge at the electrode/electrolyte interface and it has more stable reversible electrochemical performance and longer cycle life than pseudo-capacitors because of these properties it grabbed researcher’s intention in last few decades[9]. However, supercapacitor performance based on the electrode material selection, the material having large specific surface area and good electrical conductivity is considered suitable for high-performance supercapacitor [10,11]. In various energy devices, carbon is the mainstream active component owing to its low cost, good conductivity, magnificent stability, and simple fabrication design. So far, porous carbon materials such as activated carbon (AC) [12], graphene [13], carbon nanotubes (CNT) [14], biomass-derived carbon hydro-aerogel [15-17], etc., have provoked wide-range utilization in energy storage systems. Commercially fabrication of energy storage devices largely depends on abundant electrode material resources, economical, eco-friendly, and sustainable manufacturing. These well-designed carbons are usually complex to synthesize, costly, and agglomeration are obstacles in their applied application. With rapid economic development, we still face many challenges. It has become a key issue to explore economical and effective electrode materials with excellent electrochemical performance. In this regard, biomass-based hydro-aerogels are a good candidate in energy storing systems.

The efficiency-stability of the hydro-aerogel-based electrode can be enhanced with the addition of metals and their oxides. The cost-effective transition metals (TM) or metal oxides having comparable specific
energies among noble metals or metalloids and attaining great importance recently. In supercapacitor application the transition metals, nickel (Ni) [18], cobalt (Co) [19], ruthenium (Ru) [20], vanadium (V) [21], manganese (Mn) [22], etc. are widely used because of their high faradic charge transference process[23]. To improve metals conductance and sustainability, the combination of transitional metals and nitrides are widely applied in supercapacitors [24]. Conductive TM provides a combination of electronic conductance, valance state diversity, and sustainability like unique properties and is potential candidates for energy storage systems in comparison with equivalent metals or metallic oxides [25-27]. Additionally, the presence of nitrogen strongly affects the electronic properties of the metal by increasing the electron density on the metal surface [2].

In the work presented here, we synthesized a biomass-derived (persimmon-waste) N-NiCo/PC decorated carbonaceous gel through a simple glass route method. The as-prepared composite material N-NiCo/PC was applied in the supercapacitor. The use of bimetallic transition metals along with nitride providing a renewable green synthetic route for catalytic carbon material for the electrode. The use of bimetallic PG along with nitride providing a renewable green-synthetic method for high-performance supercapacitor.

2. Experiment section

2.1. Preparation of persimmon fruit waste aerogel and N-NiCo/PC

The scheme 1 represents synthesis’s procedure of the N-NiCo/PC composite material. Briefly, the persimmon fruit waste was collected and washed with distilled water. The fruit was shacked and autoclaved at 150 °C by using 100 mL Teflon vessels for 10 hours. After naturally cooled the block of hydrogel was removed from the vessels and kept in ethanol solution for 3 days to get rid of impurities. The hydrogel block was cut into 1 cm² piece and dried through vacuum freeze-drying. An aerogel brown in color obtained after completely dried the annealed at 350 °C in tube furnace for 4 hours. The persimmon based carbonaceous gel was soaked in an ethanol solution containing nickel nitride Ni (NO₃)₂·6H₂O, cobalt nitride Co (NO₃)₂·6H₂O (molar ratio 1:1), urea (H₂NCONH₂) and stirred the solution by nitrogen supply for 8 hours. The soaking process continued for 8 hours and after that the material dried at 70 °C in a vacuum oven overnight. The dried composite material was then carbonized through a tube furnace at 350 °C for 5 hours under a nitrogen environment. The tube furnace naturally cooled down and the obtained persimmon based carbonaceous gel decorated with bimetallic-nitride (N-
NiCo/PC) composite and that was used for electrode preparation. N-Ni/PC and N-Co/PC were also prepared for comparison by following the same procedure.

**Scheme 1:** The schematic diagram for the preparation the N-NiCo/PC composite sample

### 2.2. Physical and electrochemical characterization

The EDS spectra was used for elemental analysis of the bimetallic nitride composite material. The electrochemical characterization was achieved by using CHI 660E electrochemical workstation (CH Instruments, Inc. Shanghai). An electrode was fabricated by loading N-NiCo/PC, carbon black, and PTFE (80:1:1) on HCL cleaned nickel foam. The fabricated electrode was dried over-night and pressed. 6 M KOH solution was used for three-electrode systems: 1) N-NiCo/PC working electrode; 2) Pt counter electrode; Hg/HgO reference electrode respectively. The other electrodes, N-Ni/PC, and N-Co/PC were synthesized followed the same methodology. For specific capacitance estimation of synthesized electrodes were obtained through cyclic voltammetry (CV) and charge-discharge measurements by using the following equations:

\[
C_{sp} = \frac{\int i dV}{S. \Delta V. m} \quad (1)
\]

\[
C_{sp} = \frac{I \Delta t}{m \Delta V} \quad (2)
\]

Where \(\int i dV\) represent the area under the CV curve, \(\Delta V\) represent the potential window, \(m\) indicates the loading material (mg), \(S\) indicates the scan rate (mV/s), \(I\) indicates the discharge current density (A), and \(\Delta t\) represent the discharge time (s), respectively.
3. Results and Discussion

The EDS spectra (Figure 1) represent contributing elements in the N-NiCo/PC material. The spectra showed the presence of Carbon (C), nitride, nickel, and cobalt. The strong peak of the carbon revealed that the major portion in composite comes from the persimmon fruit carbonaceous gel. The particle agglomeration can be seen from the figure 1. The composite material N-NiCo/PC showed interconnect channels between nickel and cobalt catalysts on the carbonaceous gel surface. These channels contribute to ions’ movement and transportation from the bulk solution-to-inner surface of the composite. The agglomerated particles contain small dots that can represent the nitride contribution in the synthesized composite material and these dots impart to enhance the composite surface area which leads to improving supercapacitor performance that justify the EDS spectrum. The performance of annealed composite catalysts analyzed in supercapacitor. The black slurry (see methodology section) contained catalysts N-Ni/PC, N-Co/PC, and N-NiCo/PC used as the working electrode. Cyclic voltammogram (CV) and galvanostatic charge-discharge characterization were carried out within -1.0 to 0 V potential window in 6M KOH solution. Figure 2a-c shows the CV curve of three annealed catalysts measured at various scan rates (mV/s) have an asymmetric shape which could be due to pseudocapacitance behavior. It can be seen from the CV profile that the area under the N-NiCo/PC CV curve is superior to that of N-Ni/PC and N-Co/PC nanostructures.
The specific capacitance calculated at different scan rates is present in figure 2d. Specific capacitance of the fabricated electrodes are based on the estimation equation $C_{sp} = \int \delta dV / S. \Delta V \cdot m$. Where, $C_{sp}$ is the specific capacitance (F/g), $\int \delta dV$ the area under the CV curve, $m$ is the active material mass, $S$ is the scan rate and $\Delta V$ is the potential window. The $C_{sp}$ of N-NiCo/PC is 410.21 and 329.26 (F/g), at the scan rates 10-100 mV/s, respectively. The improvement in the performance of N-NiCo/PC may be due to the reduction in crystal size, mesoporous structure, and high surface area allowing ions to rapidly enter the active site of the electrode [28]. The smaller the grain size, the larger the surface volume ratio, and the stronger the charge storage capacity of the electrode.

Figure 1: EDS spectra of N-NiCo/PC and surface morphology at 5µm resolution (Inset).
Figure 2: The cyclic voltammetry of three composite materials at various scan rates; (A) N-NiCo/PC; (B) N-Ni/PC; (C) N-Co/PC; and (D) specific capacitances of the above-mentioned electrodes

EIS was determined to demonstrate the excellent electrochemical performance of N-NiCo/PC supercapacitor electrode is shown in figure 3. $R_s$ electrodes are measured at 0.06429 $\Omega$, 0.0.0765 $\Omega$, and 0.7137 $\Omega$, respectively, indicating goodness of N-NiCo/PC electrodes Electrical conductivity. The semicircle is in the high-frequency range corresponds to $R_{ct}$ (charge transfer) resistance (Table1) caused by the Faraday reaction. The charge-transfer resistance of the N-NiCo/PC electrode is lower due to its higher surface area and uniform distribution of nickel nanoparticles providing a more active reaction site, indicating that the electrode material as a supercapacitor has a higher Electrochemical reactivity. Additionally, N-NiCo/PC has a relatively higher oxygen and nitride functional group that increased the electrode surface wettability resulted in a reduction in contact resistance [9]. The electrochemical properties of supercapacitor consistent with the fuel cell indicate that N-NiCo/PC is applicable in both energy conversion and energy storage systems.
Figure 3: Nyquist plot of N-Ni/PC, N-Co/PC, N-NiCo/PC electrodes fitted by an equivalent electrical circuit.

Table 1: Supercapacitor fitted EIS data for N-Ni/PC, N-Co/PC, N-NiCo/PC electrodes by an equivalent electrical circuit

| Supercapacitor electrode | $R_s$ (Ω) | $R_ct$ (Ω) | $R_d$ (Ω) | $R_t$ (Ω) |
|--------------------------|-----------|------------|-----------|-----------|
| N-NiCo/PC                | 0.0642    | 0.589      | 0.6223    | 1.2755    |
| N-Ni/PC                  | 0.0765    | 0.781      | 0.8351    | 1.6926    |
| N-Co/PC                  | 0.7137    | 0.838      | 0.7137    | 2.2651    |

The charge and discharge behavior of three synthesized catalysts was also determined at 0.5-10 A/g current density. The triangular charge/discharge curve with slight internal resistance ($IR$) is shown in figure 4a-c, which implies a high degree of symmetry of charge/discharge. In beginning, the $IR$ drop is usually associated with $ESR$ (equivalent series resistance) phenomenon. The specific capacitance of these catalysts calculated by the equation $C_{sp} = I\Delta t/m\Delta V$, Where, $C_{sp}$ is the specific-capacitance of charge and discharge, constant charge/discharge current (A) is $I$, discharging-time (s) is $\Delta t$, ($m$) mass of active material used and the potential window is $\Delta V$ [29]. The specific capacitance of N-NiCo/PC catalyst is 93.77% higher than N-Ni/PC while, 121.14% higher than N-Co/PC at a specific current 0.5 A/g. Further,
the charge and discharge behavior N-NiCo/PC was analyzed at current densities from 1 to 10 A/g figure 4d. The estimated specific capacitance is 895.5 and 865 F/g at current density 1 to 2 A/g, respectively. The specific capacitance obtained at 1 A/g is comparable to that of Partially graphitic-carbon with embedded Ni (886 F/g) [30] and much higher than many composite materials like nanosheets of Fe₃O₄/graphene (358 F/g) [31], N-doping of carbon fiber (202.0 F/g) [32] and hollow graphite N-doped [32] carbon spheres (260 F/g). The excellent capacitive performance of the N-NiCo/PC is mainly due to its unique structure. Moreover, there are many active reaction sites on the surface, which can carry out more Faraday reactions; N-doped sites act as heteroatom defects, resulting in good conductivity, wettability of both electrode and electrolyte, resulting in rapid electron transfer, diffusion, and absorption rates [33-35].

Figure 4: The charge-discharge behavior of composite catalysts at various current densities; (A) N-NiCo/PC; (B) N-Ni/PC; (C) N-Co/PC; and the specific capacitance charge-discharge comparison of N-NiCo/PC, N-Ni/PC, and N-Co/PC

The life cycle stability of the N-NiCo/PC electrode was evaluated by constant current charge and discharge at 2 A/g. Capacitance retention of N-NiCo/PC electrode during 900 charge/discharge cycles test shows in figure 5. The capacitance retention throughout the cycle test is calculated by (each cycle
ration/first cycle capacitance value), in the first 500 cycles, 8.5% capacitance retention of the N-NiCo/PC electrode is lost as increasing charge/discharge cycle and remains almost unchanged in begging 900 cycles. Outstanding life-cycle stability may result from a porous structure with least crystallographic changes during catalyst synthesis. Thus, good specific capacitance retention reflects the higher durability of N-NiCo/PC electrodes in excellent performance supercapacitor applications.

**Figure 5:** The 900 cycles stability of N-NiCo/PC composite material at 2 A/g current density.

**Conclusion**

In this paper, persimmon waste was used to synthesize an aerogel through the hydrothermal method. Then, nickel, cobalt, and nitride were introduced in aerogel and prepared N-NiCo/PC composite catalyst for supercapacitor electrode. The specific capacitance of N-NiCo/PC catalyst is 93.77% higher than N-Ni/PC while, 121.14% greater than N-Co/PC at a specific current 0.5 A/g. After, 900 cycles, our N-NiCo/PC electrode maintained 91.5% of its capacitance retention. Thus, this finding would promote cost-effective bimetallic nitride- electrode N-NiCo/PC has the potential for high-performance storage devices.

**Declarations**

**Funding**

This work was partially supported by the National Key R&D Program of China (Grant No. 2019YFC1407800) and the Natural Science Foundation of Tianjin City (Grant No. 19YFZCSN01130).
Conflicts of interest

There are no conflicts of interest to declare.

Availability of data and material

Not applicable

Code availability

Not applicable

Authors’ Contributions:

Investigation, Data curation, Writing -original draft: [Muhammad Irfan]; Conceptualization, Supervision, Writing-review and editing [Xianhua Liu]; Formal analysis and investigation [Suraya Mushtaq]; Formal analysis and investigation [Jonnathan Cabrera]; Conceptualization, Writing-review and editing [Pingping Zhang]

References

1. Afzal MM, Khan MA, Hassan MAS, Wadood A, Uddin W, Hussain S, Rhee SB (2020) A Comparative Study of Supercapacitor-Based STATCOM in a Grid-Connected Photovoltaic System for Regulating Power Quality Issues. Sustainability 12 (17):6781
2. Irfan M, Khan IU, Wang J, Li Y, Liu X (2020) 3D porous nanostructured Ni 3 N–Co 3 N as a robust electrode material for glucose fuel cell. RSC Advances 10 (11):6444-6451
3. Irfan M, Liu X, Li S, Khan IU, Li Y, Wang J, Wang X, Du X, Wang G, Zhang P (2020) High-performance glucose fuel cell with bimetallic Ni–Co composite anchored on reduced graphene oxide as anode catalyst. Renewable Energy
4. Gao M, Liu X, Irfan M, Shi J, Wang X, Zhang P (2018) Nickle-cobalt composite catalyst-modified activated carbon anode for direct glucose alkaline fuel cell. International Journal of Hydrogen Energy 43 (3):1805-1815
5. Dong F, Liu X, Irfan M, Yang L, Li S, Ding J, Li Y, Khan IU, Zhang P (2019) Macaroon-like FeCo2O4 modified activated carbon anode for enhancing power generation in direct glucose fuel cell. International Journal of Hydrogen Energy 44 (16):8178-8187
6. Javed MS, Zhong D, Ma T, Song A, Ahmed S (2020) Hybrid pumped hydro and battery storage for renewable energy based power supply system. Applied Energy 257:114026
7. Zhai S, Karahan HE, Wang C, Pei Z, Wei L, Chen Y (2020) 1D supercapacitors for emerging electronics: current status and future directions. Advanced Materials 32 (5):1902387
8. Okonkwo CA, Lv T, Hong W, Li G, Huang J, Deng J, Jia L, Wu M, Liu H, Guo M (2020) The synthesis of micromesoporous carbon derived from nitrogen-rich spirulina extract impregnated castor shell based on biomass self-doping for highly efficient supercapacitor electrodes. Journal of Alloys and Compounds 825:154009
9. Yang H, Sun X, Zhu H, Yu Y, Zhu Q, Fu Z, Ta S, Wang L, Zhu H, Zhang Q (2020) Nano-porous carbon materials derived from different biomasses for high performance supercapacitors. Ceramics International 46 (5):5811-5820
10. Gao Y, Zheng S, Fu H, Ma J, Xu X, Guan L, Wu H, Wu Z-S (2020) Three-dimensional nitrogen doped hierarchically porous carbon aerogels with ultrahigh specific surface area for high-performance supercapacitors and flexible micro-supercapacitors. Carbon 168:701-709
11. Al-Enizi AM, Ubaidullah M, Ahmed J, Ahamad T, Ahmad T, Shaikh SF, Naushad M (2020) Synthesis of NiOx@ NPC composite for high-performance supercapacitor via waste PET plastic-derived Ni-MOF. Composites Part B: Engineering 183:107655
12. Cheng F, Yang X, Zhang S, Ma J, Xu X, Guan L, Wu H, Wu Z (2020) Boosting the supercapacitor performances of activated carbon with carbon nanomaterials. Journal of Power Sources 450:227678
13. Krishnamoorthy K, Pazhamalai P, Mariappan VK, Manoharan S, Kesavan D, Kim SJ (2020) Two - Dimensional Siloxene – Graphene Heterostructure – Based High - Performance Supercapacitor for Capturing Regenerative Braking Energy in Electric Vehicles. Advanced Functional Materials:2008422
14. Han J, Wang H, Yue Y, Mei C, Chen J, Huang C, Wu Q, Xu X (2019) A self-healable and highly flexible supercapacitor integrated by dynamically cross-linked electro-conductive hydrogels based on nanocellulose-templated carbon nanotubes embedded in a viscoelastic polymer network. Carbon 149:1-18
15. Lin S, Wang F, Shao Z (2020) Biomass applied in supercapacitor energy storage devices. Journal of Materials Science 56:1943–1979
16. Reis GSd, Larsson SH, de Oliveira HPd, Thyrel M, Lima EC (2020) Sustainable Biomass Activated Carbons as Electrodes for Battery and Supercapacitors—A Mini-Review. Nanomaterials 10 (7):1398
17. Kobina Sam D, Kobina Sam E, Lv X (2020) Application of Biomass - Derived Nitrogen - Doped Carbon Aerogels in Electrocatalysis and Supercapacitors. ChemElectroChem 7 (18):3695-3712
18. Kim H, Surendran S, Chae Y, Lee HY, An T-Y, Han HS, Park W, Kim JK, Sim U (2020) Fabrication of an ingenious metallic asymmetric supercapacitor by the integration of anodic iron oxide and cathodic nickel phosphide. Applied Surface Science 511:145424
19. Zardkhoshoui AM, Davarani SSH (2020) Construction of complex copper-cobalt selenide hollow structures as an attractive battery-type electrode material for hybrid supercapacitors. Chemical Engineering Journal 402:126241
20. Mensah-Darkwa K, Zequine C, Kahol PK, Gupta RK (2019) Supercapacitor energy storage device using biowastes: a sustainable approach to green energy. Sustainability 11 (2):414
21. Gong Q, Lei J (2017) Design of a bidirectional energy storage system for a vanadium redox flow battery in a microgrid with SOC estimation. Sustainability 9 (3):441
22. Siwal SS, Zhang Q, Sun C, Thakur VK (2020) Graphitic carbon nitride doped copper–manganese alloy as high–performance electrode material in supercapacitor for energy storage. Nanomaterials 10 (1):2
23. Mohd Abdah MAA, Azman NHN, Kulandaivalu S, Sulaiman Y (2020) Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors. Materials & Design 186:108199
24. Yuan S, Pang S-Y, Hao J (2020) 2D transition metal dichalcogenides, carbides, nitrides, and their applications in supercapacitors and electrocatalytic hydrogen evolution reaction. Applied Physics Reviews 7 (2):021304
25. Liu Y, Zeng Z, Sharma RK, Gbewonyo S, Allado K, Zhang L, Wei J (2019) A bi-functional configuration for a metal-oxide film supercapacitor. Journal of Power Sources 409:1-5

26. Faber MS, Lukowski MA, Ding Q, Kaiser NS, Jin S (2014) Earth-abundant metal pyrites (FeS2, CoS2, NiS2, and their alloys) for highly efficient hydrogen evolution and polysulfide reduction electrocatalysis. The Journal of Physical Chemistry C 118 (37):21347-21356

27. Zhang M, Li X, Zhao J, Han X, Zhong C, Hu W, Deng Y (2020) Surface/interface engineering of noble-metals and transition metal-based compounds for electrocatalytic applications. Journal of Materials Science & Technology 38:221-236

28. Wang M, Du J, Zhou J, Ma C, Bao L, Li X, Li X (2019) Numerical evaluation of the effect of mesopore microstructure for carbon electrode in flow battery. Journal of Power Sources 424:27-34

29. Wang Z, Liu J, Hao X, Wang Y, Chen Y, Li P, Dong M (2020) Enhanced power density of a supercapacitor by introducing 3D-interfacial graphene. New Journal of Chemistry 44 (31):13377-13381

30. Wu M-S, Hsu W-H (2015) Nickel nanoparticles embedded in partially graphitic porous carbon fabricated by direct carbonization of nickel-organic framework for high-performance supercapacitors. Journal of Power Sources 274:1055-1062

31. Zhang W, Liu F, Li Q, Shou Q, Cheng J, Zhang L, Nelson BJ, Zhang X (2012) Transition metal oxide and graphene nanocomposites for high-performance electrochemical capacitors. Physical Chemistry Chemical Physics 14 (47):16331-16337

32. Chen L-F, Zhang X-D, Liang H-W, Kong M, Guan Q-F, Chen P, Wu Z-Y, Yu S-H (2012) Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors. ACS nano 6 (8):7092-7102

33. El Sharkawy HM, Dhmees AS, Tamman A, El Sabagh S, Aboushahba R, Allam NK (2020) N-doped carbon quantum dots boost the electrochemical supercapacitive performance and cyclic stability of MoS2. Journal of Energy Storage 27:101078

34. Wang B, Ye Y, Xu L, Quan Y, Wei W, Zhu W, Li H, Xia J (2020) Space-Confined Yolk-Shell Construction of Fe3O4 Nanoparticles Inside N-Doped Hollow Mesoporous Carbon Spheres as Bifunctional Electrocatalysts for Long-Term Rechargeable Zinc–Air Batteries. Advanced Functional Materials 30 (51):2005834

35. Zhou Y, Zhang M, Wang Q, Yang J, Luo X, Li Y, Du R, Yan X, Sun X, Dong C (2020) Pseudocapacitance boosted N-doped carbon coated Fe7S8 nanoaggregates as promising anode materials for lithium and sodium storage. Nano Research 13 (3):691–700