Close-packed storage of potassium metallic clusters achieved through nanostructure engineering of ultrafine hollow nanoparticles-based carbon nanoclusters

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Funding information
Education Department of Jilin Province “13th Five-Year” Science and Technology Research, Grant/Award Number: JJKH20201164KJ; Fundamental Research Funds for the Central Universities, Grant/Award Numbers: 2412018ZD009, 2412019FZ009; Jilin Provincial Research Foundation for Basic Research, Grant/Award Numbers: 20190303100SF, 20200201071JC; National Natural Science Foundation of China, Grant/Award Numbers: 21771035, 21872024

Abstract
Ultrafine hollow nanoparticles-based (7 nm) carbon nanoclusters (HNPCNCs) are developed by a facile and novel method. Benefiting from the ultrafine nanostructure, we have achieved close-packed storage of K metallic clusters and a close-packed K metallic clusters with a diameter of 7 nm has been observed for the first time through ex TEM. In K-ion batteries, HNPCNCs anodes deliver an ultrahigh capacity of 269.8 mA h g\(^{-1}\) at 0.5 A g\(^{-1}\) after 200 cycles, outstanding rate performance of 150.5 mA h g\(^{-1}\) after 5000 cycles at 5 A g\(^{-1}\). Moreover, an excellent electrochemical performance has been obtained by HNPCNCs/potassium Prussian blue potassium-ion full cells, highlighting the practicability of HNPCNCs. The unprecedented electrochemical performance is attributed to the close-packed K metallic clusters achieved by unique ultrafine hollow nanoparticles in the carbon nanoclusters.

KEYWORDS
close-packed storage, high rate, K metallic clusters, potassium-ion half/full batteries, ultrafine hollow carbon nanoclusters

1 INTRODUCTION

Currently, potassium-ion batteries (PIBs) come into our sight because of the closer redox potential of K/K\(^+\) (−2.93 V) to that of Li/Li\(^+\) (−3.04 V) and the abundant resource.\(^1\)-\(^7\) While rapid development has been made to produce excellent cathode materials, one of the major issues for PIBs is lack of suitable anode materials. Though a number of high capacity anode materials have been studied for PIBs, carbon is still the prime candidate with low cost and improved electronic conductivity.\(^8\)-\(^12\) Therefore, it is quite attractive to develop a versatile carbon material with high performances for PIBs.

Hard carbon exhibits better electrochemical performance than graphite for PIBs due to the low density and expanded interlayer spacing, however, it still suffers from low specific capacity, poor cycling stability, and rate performance.\(^13\)-\(^15\) Because the lack of long-range order in...
the amorphous structures of hard carbon would impact the electrical conductivity and thus influence the electron transport within the electrodes. For improving electrochemical performance, doping heteroatoms is considered a promising strategy because heteroatoms can introduce defects in carbon framework and thus provide more active sites.16-20 For example, Xie et al reported a high pyridinic N-content-doped porous carbon monolith that exhibits 152 mA h g⁻¹ at 1000 mA g⁻¹ after 3000 cycles.21 The nitrogen/oxygen co-doped carbon hollow multihole bowls reported by Zhang et al display a high capacity of 304 mA h g⁻¹ at 0.1 A g⁻¹.22 Nevertheless, because of the large radius of K⁺, the effect of either insertion/extraction or adsorption of potassium ions by doping heteroatoms cannot meet the application of PIBs. Moreover, conventionally doping heteroatoms is usually uncontrollable with tedious synthesis steps and limited doping amount.23 Optimization of electrolytes is another way to improve electrochemical property of carbon anode materials. Because either changing the carbonate electrolyte to ether-based electrolyte or changing the potassium bis(trifluoromethane)sulfonamide (KTFSI) or KPF₆ to potassium bis(fluorosulfonyl)imide (KFSI) in carbonate electrolyte could improve the electrochemical performance of anode material because of the more stable solid-electrolyte interphase (SEI) layer.24 However, when the voltage is higher than 4 V, the KFSI-based electrolyte will etch the aluminum foil (current collector) and decompose it, causing safety problems.25 In general, many strategies have been employed for hard carbon to handle these problems caused by the large K⁺, but they do not solve the problems well because the active sites for K⁺ storage provided by hard carbon are limited. However, every coin has two sides, although the intercalation and adsorption of K⁺ are limited because of the large radius of K⁺, large-sized K⁺ is more strongly affected by the volume restriction effect and more easily bound by carbon, which is like holding the sand with a hand, the sand will flow away through fingers, but holding the stone, the stone will be well bound. Inspire by this, we think whether we can utilize space effect to store more K⁺ to achieve close-packed storage of K metal through nanostructure engineering, and the capacity will be greatly improved.

Hollow carbon nanospheres (HCNSs) have been proved to be favorable in cycling stability.26-29 The inner cavity of HCNSs is benefit of buffering volume expand, providing a long cycle performance for PIBs.30-31 For example, Bin et al reported hollow interconnected neuron-like carbon architecture which delivers 340 mA h g⁻¹ at 0.1 C and superior cycling performance at 0.5 C for 150 cycles.26 Meanwhile, the inner cavity of the HCNSs can also provide the space for using space effect to achieve close-packed storage of K metal. Nevertheless, the reported HCNSs only adsorb K⁺ on the surface and cannot fill K metal in the inner cavity to achieve close-packed storage, which may be caused by the large size of the HCNSs. The large-sized HCNSs result in small curvature relative to the K⁺ and make them impossible to absorb more K⁺. Hence, the close-packed storage of K metal can be achieved only when the size of the HCNSs is small enough which leads to a large curvature. If the HCNSs can be filled with K⁺, the capacity will be greatly improved. Furthermore, the small-sized HCNSs can also provide a reduced ion/electron diffusion path, increase electrode-electrolyte contact area, enable high active material utilization and accommodate the volume change. Therefore, it is a great challenge to break through this super small scale HCNSs barrier to achieve close-packed storage of K metal.

To address these issues, we fabricate ultrafine hollow nanoparticle-based (7 nm) carbon nanoclusters (denoted as HNPCNCs) with a large scale production. To the best of our knowledge, the size of the hollow nanoparticle is the lowest uniform nanosize reported so far. The as-obtained HNPCNCs are organized by numbers of ultrafine hollow carbon nanoparticles and show ultrahigh specific capacity (269.8 mA h g⁻¹ after 200 cycles at 0.5 A g⁻¹), excellent rate performance (220.1 mA h g⁻¹ at 1 A g⁻¹ and 184.4 mA h g⁻¹ at 2 A g⁻¹ after 1000 cycles) and ultralong cycle life (150.4 mA h g⁻¹ after 5000 cycles at 5 A g⁻¹) for PIBs. Furthermore, HNPCNCs-800//potassium Prussian blue potassium-ion full batteries exhibit a high capacity of 317.7 mA h g⁻¹ at 0.1 A g⁻¹ and 187.7 mA h g⁻¹ at 0.5 A g⁻¹ after 200 cycles. The outstanding electrochemical performance for PIBs is much better than recently reported pure carbon materials. Binding K⁺ into the designed space to achieve close-packed storage of K metal will fill a large gap for K⁺ storage of carbon materials, opening up the opportunity of using carbon materials in the exciting area for PIBs.

2 RESULTS AND DISCUSSION

The synthetic process of HNPCNCs is schematically displayed in Scheme 1. Firstly, PAA-NH₄ nanospheres (NSs) were formed in an IPA/water system.32,33 Subsequently, MnO(OH)₂/PAA-NH₄ NS was obtained by Mn²⁺ hydrolysis on the PAA-NH₄ NS. After carbonization, the MnO(OH)₂/PAA-NH₄ NS was converted into MnO@C nanocluster (NC) due to the carbothermic reduction. The obtained MnO@C was subsequently referred to as MnO@C-700, 800, and 900, corresponding to the different pyrolysis temperatures of 700, 800, and 900°C. Finally, HNPCNCs were obtained after removing the MnO by acid treatment. The resulting HNPCNCs are subsequently referred to as HNPCNCs-700, HNPCNCs-800,
and HNPCNCs-900, corresponding to the different pyrolysis temperatures of 700, 800, and 900°C. As revealed by the transmission electronmicroscopy (TEM) observations (Figure 1A), the obtained PAA-NH₄ NSs are monodisperse and uniform with a diameter of ~180 nm. After adding Mn²⁺ to PAA-NH₄ NSs solution, the MnO(OH)₂/PAA-NH₄ NSs (180 nm) were shaped (Figure 1B). After the thermal treatment at 800°C in Ar gas, the obtained MnO@C-800 retains the pomegranate-like morphology without any obvious cracking (Figure 1C). The high-resolution TEM (HRTEM) images (Figure S1a,b) show that the single pomegranate-like MnO@C-800 NC is organized by many ultrafine MnO subunits with a size of 7 nm. Pomegranate-like MnO@C-800 NCs are shown in Figure 1D by scanning electron microscope (SEM), in which it can be seen that the NC is composed of lots of ultrafine subunits. The SEM image of HNPCNCs-800 after the acid treatment is shown in Figure 1G, and it is noted that the morphology of etched HNPCNCs-800 is unchanged, indicating the HNPCNCs-800 is organized by numbers of hollow carbon nanoparticles. As shown in Figure S2, the average size of the ultrafine hollow carbon nanoparticles is 7 nm. Figure 1E,H show TEM and SEM images of the HNPCNCs-800 which possess the uniform hollow nanospherical morphology with a diameter of 180 nm. Figure 1F and S1c exhibit that the HNPCNCs-800 are composed of a large amount of ultrafine hollow carbon subunits. The HRTEM image of the circle-marked area in Figure 1F can obviously find the ultrafine hollow carbon subunits (7 nm). To further confirm the inside structure of HNPCNCs, we find a cracked HNPCNC to see the inside structure directly, as shown in Figure S1d. It can be clearly seen that there are lots of ultrafine hollow nanospheres in the inside of the HNPCNCs, further indicating the pomegranate structure. The elemental mapping images of HNPCNC-800 reveal the co-existence of C (red) and O (purple) elements, and further demonstrate the uniform distribution of elemental in HNPCNCs-800 (Figure 1I-L). The morphologies of
HNPCNCs-700 and HNPCNCs-900 were also 180 nm. The HRTEM image displays the HNPCNCs-800 probed by SEM and TEM images which show similar structure to HNPCNCs-800 (Figure S3). In our case, about 1.0 g of HNPCNCs-800 can be fabricated (Figure S4), and the process is scalable which only depends on the volume of vessels.

Figure S5 displays XRD pattern of the pomegranate-like MnO@C NCs at different temperatures. All peaks can be indexed to MnO (JCPDS card no. 07-0230), demonstrating that MnO(OH)2/PAA-NH4 changes to MnO because of the carbothermic reduction between MnO(OH)2 and PAA-derived carbon. It can be seen that the intensity of all peaks is enhanced while annealing temperature is increased. The XRD patterns of HNPCNCs samples (HNPCNCs-700, HNPCNCs-800 and HNPCNCs-900) are displayed in Figure 2A. All identified peaks exhibit a broad and weak diffraction peak at about 24° and 43°, corresponding to (002) and (100) planes of carbon materials, respectively. No other diffraction peak is observed, revealing the complete etching of MnO nanoparticles in carbon networks. Comparing with HNPCNCs-700 and HNPCNCs-900, the diffraction peak of HNPCNCs-800 is more defined, suggesting its higher graphitization degree. The Raman spectra of HNPCNCs at different temperatures present a G-band at 1589 cm⁻¹ related to the E₂g mode and a D-band at 1346 cm⁻¹ attributed to disordered carbon, edges and other defects (Figure 2B). The intensity ratio of G band to D band (I_G/I_D) is usually employed to evaluate the degree of graphitic ordering in carbons. The I_G/I_D of HNPCNCs-800 (1.07) is slightly higher than those of other samples (1.03 for HNPCNCs-700 and 1.04 for HNPCNCs-900), suggesting the higher degree of graphitization, which is consistent with the XRD results. N2 adsorption–desorption technique was tested to investigate their pore-size distribution and surface area. As displayed in Figure 2C,D, the curves of MnO@C-800 and HNPCNCs-800 are all similar to the IV-type isotherm. The Brunauer-Emmett-Teller (BET) surface area of HNPCNCs decreases from 994.192 to 909.623 m² g⁻¹ with the increasing temperature from 700 to 800°C but increases to 1014.418 m² g⁻¹ at 900°C, which is because of the higher graphitization degree in HNPCNCs-800 (Figure S6). The pore size distributions of MnO@C-700, MnO@C-800 and MnO@C-900 are centered at 3.412, 3.828, and 3.832 nm and the pore size...
distributions of HNPCNCs-700, HNPCNCs-800 and HNPCNCs-900 are mainly focused on 3.627, 3.628, and 3.794 nm, indicating the mesoporous nanostructure. The pore channels are formed by piling up of ultrafine nanoparticles, and the similar pore size distributions of MnO@C and HNPCNCs indicate that the nanostructure remains well after etching the inner MnO and the surface of the ultrafine nanoparticles is almost no change. The BET surface areas of the three HNPCNCs samples are all about 10 times more than the MnO@C. Because the

**FIGURE 3** Potassium-ion half-cell performances of HNPCNCs. A, CV curves of the HNPCNCs-800, B, discharge/charge profiles of HNPCNCs-800 at 0.05 A g\(^{-1}\) in the voltage range of 0.01 to 3.0 V, C, Rate capability from 0.05 to 10 A g\(^{-1}\), D, cycling performance of HNPCNCs-700, HNPCNCs-800 and HNPCNCs-900 at 0.5 A g\(^{-1}\), E, Long cycling performances of HNPCNCs-800 at 1 and 2 A g\(^{-1}\) and, F, ultralong cycling performances of HNPCNCs-800 at 5 A g\(^{-1}\).
content of MnO is 80% (Figure S7a,b), the BET surface areas of the three samples are all twice than before, caused by the formation of ultrafine hollow carbon nanoparticles due to the etching the inner MnO, in accordance with the TEM images. A little weight loss after 700°C is caused by a small amount of residual polymer PAA in the sample (Figure S7a). The small amount of residue polymer PAA is due to the large production of samples prepared each time, which is maybe not completely calcined during the calcination process. Therefore, we reduce the amount of each calcination to ensure full calcination and retest the TGA with the heating temperature range of room temperature to 1000°C (Figure S7b). It can be seen that there is almost no weight loss after 600°C.

Cyclic voltammetry (CV) is displayed in Figure 3A at 0.1 mV s\(^{-1}\). During the first cathodic cycle, a peak at 0.58 V appears and disappears in the following cycles because of the formation of SEI film and decomposition of the electrolyte on the surfaces of HNPCNCs-800. Figure 3B displays the discharge/charge profiles of HNPCNCs-800 at 0.05 A g\(^{-1}\) for the initial three cycles. The HNPCNCs-800 delivers high charge capacities of 481.2, 445.5 and 417.1 mA h g\(^{-1}\) for the first three cycles, respectively. There is no clear voltage plateau can be observed during discharge/charge process which is attributed to the following reasons. The homogeneous chemical reaction with potential dependence leads to monotonic slope and numbers of K\(^+\) can be absorbed/desorbed on the electrode surface because of the large surface area, leading to unapparent plateau. Besides, the large size K\(^+\) with the sluggish kinetics can also cause the inconspicuous plateaus.\(^\text{16,36}\) We further test the rate performance of the HNPCNCs-700, HNPCNCs-800 and HNPCNCs-900 electrode (Figure 3C). The HNPCNCs-800 always deliver higher capacity than HNPCNCs-700 and HNPCNCs-900 with current density increasing from 0.1 to 50 A g\(^{-1}\), and the HNPCNCs-800 exhibit charge capacities of ca. 413.7, 356.8, 309.6, 282.4, 249.8, 218.4, and 191.7 mA h g\(^{-1}\) from 0.05 to 5 A g\(^{-1}\), respectively. Even at 10 A g\(^{-1}\), a reversible capacity of 168.7 mA h g\(^{-1}\) for HNPCNCs-800 is still maintained. After cycling at different rates, the capacity recovers to 365.4 mA h g\(^{-1}\) at 0.05 A g\(^{-1}\), revealing highly reversibility. The electrochemical impedance spectrum (EIS) was tested to study electrochemical interface in HNPCNCs. As shown in Figure S8, the HNPCNCs-800 electrode exhibits the lowest charge-transfer impedance, corresponding to
faster $K^+$ transportation. The cycling performances of the electrodes were tested under 0.5 A g$^{-1}$ (Figure 3D). Obviously, HNPCNCs-800 display higher capacity than the other two samples. The capacity fade during early cycling is because of the continuation of the irreversible potassiometric-induced changes which are described in respect to cycle 1 CV curves. The capacity of HNPCNCs-800 is 269.8 mA h g$^{-1}$ after 200 cycles with a high Coulombic efficiency (CE) retaining around 99.5%, far more than the capacity of HNPCNCs-700 (205.2 mA h g$^{-1}$) and HNPCNCs-900 (235.9 mA h g$^{-1}$). The capacity retention of HNPCNCs-800 anode can reach to 92.1% which is compared with the capacity of the 20th. Furthermore, long cycle performance was tested for 1000 cycles at 1 and 2 A g$^{-1}$ (Figure 3E). The capacity greatly decreases at the initial 15 cycles and gradually leveled off and eventually attains 220.1 mA h g$^{-1}$ (1 A g$^{-1}$) and 188.4 mA h g$^{-1}$ (2 A g$^{-1}$) after 1000 cycles with capacity retentions of 88.7% and 87.1%, respectively, revealing stable nanostructure of the HNPCNCs-800. To test the ultralong cycling performance of HNPCNCs-800 electrode, the anode was carried out upon 5000 cycles at 5 A g$^{-1}$ (Figure 3F). The capacity maintains stably at 150.5 mA h g$^{-1}$ with a capacity retention of 75.6% for 5000 cycles. The excellent electrochemical performance of HNPCNCs-800 is attributed to the unique nanostructure which can immobilize more $K^+$ and keep them stable in the ultrafine hollow carbon.

**FIGURE 5** Ex situ characterization of HNPCNCs-800 electrodes for potassium-ion batteries. TEM images of the HNPCNCs-800 sample A, after discharging to 0.01 V, G, after charging to 3 V. B, H, the magnified HRTEM images of the HNPCNC-800. The elemental mapping images of a single HNPCNCs-800 C, after discharging to 0.01 V, I, after charging to 3 V and corresponding elemental mapping D, J, overlap of C and K E, K, C and F, L, K. M, Schematic of potassium storage of HNPCNCs-800 and HCNSs.
nanoparticles. Outstanding cycling stability should be due to the unique structure that is piled up of numbers of ultrafine hollow carbon nanoparticles, which makes it possess both the rigidity of ultrafine hollow carbon nanoparticles and the elasticity of the whole structure. The result indicates the great cycling stability and quick discharge/charge performance of HNPCNCs-800 anode, which is much better than the reported carbon anodes for PIBs so far (Table S1). Figure S9 exhibits TEM image of HNPCNCs-800 after 5000 cycles at 5 A g\(^{-1}\). The pomegranate nanostructure can be well preserved without fracture after long cycling test.

To further prove the outstanding rate performance of the HNPCNCs-800, CV analysis was carried out from 0.1 to 20 mV s\(^{-1}\), as shown in Figure 4A. It can be seen that with the increasing scan rates, the anodic peak current expands to cover higher potential range. Moreover, the reaction kinetics are calculated by the formula:

\[ i = a \nu^b \]  

where \( a \) and \( b \) are adjustable parameters, \( i \) is the peak current and \( \nu \) is the scan rate. When \( b \) value approaches 1.0, a capacitive response tends to be indicated.\(^{37} \) The \( b \) value in our case is calculated to be 0.91, suggesting that HNPCNCs-800 is propitious to surface capacitive which results in splendid rate capability (Figure 4B). Moreover, the capacitive contribution can be investigated by the formula:

\[ i = k_1 \nu + k_2 \nu^{1/2} \]

and

\[ \frac{i}{\nu^{1/2}} = k_1 \nu^{1/2} + k_2 \]  

Herein, \( k_1 \) and \( k_2 \) are constants. Figure 4C exhibits the pseudocapacitive contribution at 2 mV s\(^{-1}\), where blue region occupies 81.6% of the total CV area. Figure 4D displays the contributions proportion and the percentages of pseudocapacitance at other scan rates, demonstrating the ultrafast potassisation/depotassisation.

To further explore the reason why HNPCNCs-800 can deliver ultrahigh capacities of K-ion batteries, Figure 5 shows TEM images of HNPCNCs-800 at the discharge and charge status in potassium-ion battery after 1000 cycles. As displayed in Figure 5b, the ultrafine
hollow carbon nanoparticles in the HNPCNCS-800 are filled with K metallic clusters (red solid circles) at the discharge status. The d spacing of two lattice planes is calculated to be 0.27 nm, which corresponds well to (200) lattice planes of metal K (Figure S10).38 This is the first-ever reported that close-packed of K metallic clusters (7 nm) has been observed. The elemental mapping images of HNPCNCS-800 at the discharge status displayed in Figure 5c-f also confirm that K metallic clusters fills in the whole NC. Compared with HNPCNCS-800 at the discharge status, HNPCNCS-800 at the charge status suggest that there are only a few K metal left on the NC, exhibiting excellent reversibility (Figure 5g-l). For deeply understanding the close-packed storage of K metallic clusters, we prepared 50 nm hollow carbon nanospheres (HCNSs) using SiO2 as the template. Detailed synthesis steps and characterization are presented in the Supporting Information. Ex TEM is also tested to probe the HCNSs at the discharge and charge status (Figure S12). It is clear that very few K+ can pass through the carbon shell via defects and be absorbed in the inner hollow nanoparticles.

Figure 5m shows the different K+ storage mechanisms of HNPCNCS-800 and HCNSs. The HCNSs store K+ only by adsorption and intercalation. The large inner cavity of HCNSs can only adsorb few K+ on the inner surface and cannot store K metal in the inner cavity because the surrounding carbon does nothing to immobilize the K+. By comparison, K metal can be stored into the inner cavity of the HNPCNCS-800 in addition to adsorption and intercalation. The reason is that the surface of the ultrafine hollow NSs is a curved sphere relative to the K+ compared with that of HCNSs which is similar to a flat surface because of the smaller radius of the ultrafine hollow carbon NSs, causing that all the surrounding carbon can immobilize K+ to achieve close-packed storage of K metallic clusters. Therefore, the ultrafine hollow NSs can immobilize more K+ and keep K+ more stable than HCNSs.

To investigate practical application of HNPCNCS-800, we fabricated full cells using HNPCNCS-800 as anode and potassium Prussian blue (KPB) as cathode which was synthesized by a facile method.39 XRD pattern and SEM image of KPB are displayed in Figure S13a,b, which consist with the previous report.37 Figure 6A shows the discharge/charge curves at 0.1 A g\(^{-1}\) in 2.0 to 4.0 V. The first discharge and charge capacity are 586.5 and 317.7 mA h g\(^{-1}\) (based on the active material mass of the anode). Impressively, HNPCNCS-800 display splendid rate performance of 350.8, 301.6, 264.1, 225.8, 191.1, and 155.5 mA h g\(^{-1}\) from 0.05 to 2 A g\(^{-1}\), respectively (Figure 6B). Figure 6C displays the cycling stability for 200 cycles at 0.5 A g\(^{-1}\). The HNPCNCS-800//KPB full cell maintains 155.1 mA h g\(^{-1}\) after 200 cycles. To further demonstrate the practical application of HNPCNCS-800, the soft-packaged of HNPCNCS-800//KPB full cell can light up a ‘‘NENU’’ light-emitting-diodes (LED) plate (Figure 6D). The outstanding full cell performance suggests the promising application of HNPCNCS-800 for PIBs.

3 | CONCLUSION

In summary, we report a facile and novel strategy to fabricate the HNPCNCS organized by numbers of ultrafine hollow carbon nanoparticles with a rather high yield to bind K+ into a space of carbon to achieve close-packed of K metallic clusters. This is the first-ever reported that close-packed of K metallic clusters (7 nm) has been observed. With this unique nanostructure, K+ can be adsorbed more and stored steadily in the ultrafine hollow carbon nanoparticles to achieve close-packed storage of K metallic clusters, and the HNPCNCS-800 has been evaluated as an excellent inserting host anode for PIBs. This ultrafine nanostructure will break people’s understanding of the low capacity of carbon materials, and open a new door for construction of high-performance carbon materials with wide applications in electrochemical energy storage, which have strategic guidance for the carbon electrode materials of the next generation potassium batteries.

ACKNOWLEDGMENTS

B. Q. L. and Q. Z. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Grant No. 21771035, 21872024), the Jilin Provincial Research Foundation for Basic Research (20200201071JC, 20190303100SF), the Fundamental Research Funds for the Central Universities (2412018ZD009, 2412019FZ009), the Education Department of Jilin Province “13th Five-Year” Science and Technology Research (JJKH20201164KJ) and Jilin Provincial Key Laboratory of Advanced Energy Materials.

CONFLICT OF INTEREST

The authors declare no conflict of interest. [Correction added on 10 June 2021, after first online publication: Conflict of Interest section has been added.]

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**SUPPORTING INFORMATION**
Additional supporting information may be found online in the Supporting Information section at the end of this article.

**How to cite this article:** Liu B, Zhang Q, Li L, et al. Close-packed storage of potassium metallic clusters achieved through nanostructure engineering of ultrafine hollow nanoparticles-based carbon nanoclusters. *EcoMat.* 2021;3:e12105. https://doi.org/10.1002/eom2.12105