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One-step preparation of carbon nanotubes doped mesoporous birnessite $K_2Mn_4O_9$ achieving 77% of theoretical capacitance by a facile redox reaction

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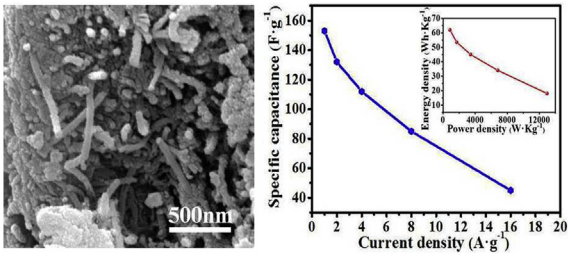
HIGHLIGHTS

- Mesoporous birnessite-type $K_2Mn_4O_9$ was prepared by a facile redox reaction.
- $K_2Mn_4O_9$/CNTs nano-composite was manufactured on the basis of $K_2Mn_4O_9$.
- They show capacitances up to 754 and 1055 F g^{-1} at 1A g^{-1}, respectively.
- $K_2Mn_4O_9$/CNTs//AC asymmetric supercapacitor achieves an energy density of 62 Wh kg^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile, scalable and cost-efficient redox reaction is developed to prepare micro-powders of a quasi-crystallised, mesoporous birnessite-type manganese oxide, $K_2Mn_4O_9$. In 1 M KOH electrolyte, the $K_2Mn_4O_9$ powder shows a high specific capacitance of 754 F g^{-1} at 1 A g^{-1} (calculated with the net weight of $K_2Mn_4O_9$ micro-powder only). Meanwhile, the electrode retains 91% of its initial capacitance after 5000 cycles at a high current density of 5 A g^{-1}. By simply adding carbon nanotubes (CNTs) into the reaction system, the specific capacitances of as-prepared $K_2Mn_4O_9$/CNTs composites are further increased to 929 and 1055 F g^{-1} at 1 A g^{-1} in 1 and 6 M KOH electrolyte (corresponding to 69 and 77% of the theoretical capacitance of MnO_2), or 600 and 674 F g^{-1} at 5 A g^{-1}, respectively. Significantly, a maximum energy density of 62 Wh kg^{-1} at a power density of 852 W kg^{-1} could be achieved based on a $K_2Mn_4O_9$/CNTs//activated carbon asymmetric supercapacitor (ASC). At the same time, the ASC device

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exhibits a decent long cycle life with 85% specific capacitance retained after 1000 cycles, suggesting its wide application potential in low-cost high energy density storage systems.

1. Introduction

Increasing global energy consumption coupled with the critical issue of climate change has made the need for efficient energy storage and delivery systems more urgent. Such systems should harvest and utilize in the best manner possible the energy that is generated by intermittent, renewable sources (e.g., solar and wind) or that promises to power hybrid/electrical vehicles [1]. The two major players that impact the growth in the field of energy storage and delivery are Li-ion batteries (LIBs) and supercapacitors (SCs). In particular, SCs have attracted considerable attention because of their fast charge/discharge rates (within a time frame of seconds), high power density (10^2 ~ 10^4 W kg^{-1}), excellent cycling lifetimes (up to ~ 10^6) and reliable safety performance [2]. However, the specific energy-storage density of existing supercapacitors is limited (~10^1 Wh kg^{-1}), generally an order of magnitude lower than that of batteries (~10^2 Wh kg^{-1}) [3,4]. Therefore, improving the energy density while maintaining the high power density and cycling stability of SCs remains a primary research focus in the field [5].

Compared to carbon electrode materials for electrochemical double-layer capacitors [6], pseudocapacitive electrode materials, including transition-metal oxides (such as RuO_2 [7], NiO [8], Co_3O_4 [9]) and conductive polymers (such as polyaniline [10], polypyrrole [11], polythiophene [12]), have larger electrochemical capacitances and energy densities due to their electrochemical redox charge storage mechanism and could therefore satisfy the potential needs of high-performance supercapacitors [13]. Among the various possible metal oxides, MnO_2 exhibits many intriguing characteristics, such as low cost, long cycling lifetimes, environmental compatibility, and a large theoretical specific capacitance (1370 F g^{-1} [14]), which makes it one of the most promising electrode materials for supercapacitors [15–19]. However, this material suffers from inherent drawbacks, mainly because of its low electrical conductivity (10^{-5}–10^{-6} S/cm) [4] and the cycling crystal shrinkage/expansion, which induces exfoliation from current collectors during charge/discharge cycling, thereby resulting in low utilisation of pseudocapacitive MnO_2 materials and thus poor rate capability, cycling stability and especially inferior practical specific capacitances far below theoretical values (e.g., 401, 328 and 299 F g^{-1} for MnO_2 nanoparticles [16], MnO_2 nanoflakes [5], amorphous MnO_2 [20] in aqueous KOH electrolyte, or 270 and 251.3 F g^{-1} for MnO_2 nanorods [21] and MnO_2 nanoflowers [22] in neutral Na_2SO_4 aqueous electrolyte, respectively).

To solve this problem, numerous types of nanostructures have been synthesized with the aim of facilitating electron/ion transport and thus electrochemical kinetics and performance. One of the effective, general approaches involves the growth of MnO_2 nanostructured arrays directly onto current collectors (e.g., Ni [23], graphene [24], Au [25] foams). In these nano-arrays, electrons and ions can easily move from current collectors and electrolyte into pseudocapacitive MnO_2, effectively promoting the electrochemical performance. For instance, Zhang et al. electrochemically deposited MnO_2 nanowires onto flexible graphene foams and achieved a specific capacitance of 422.5 F g^{-1} at a current density of 1 A g^{-1} in aqueous Na_2SO_4 electrolyte [24]. Lang et al. electrodeposited MnO_2 onto a nanoporous gold substrate (pore size: ~40 nm), resulting in a very high specific capacitance of ~1145 F g^{-1}, close to the theoretical value [25].

Rational design of hybrid composite structures of MnO_2 nanostructures and conductive materials (such as carbon nanomaterials, metal nanostructures, and conducting polymers) has proven to be another promising approach to improve the electrocapacitive performance [4]. Outstanding examples of this strategy include the uniform sputtering of Au atoms onto MnO_2 nanostructures [26] or mixing PEDOT:PSS conducting polymer [17] with MnO_2 nanostructures, which increases the specific capacitances by ~65% and ~45% (626 *vs.* 380 F g^{-1}, or 380 *vs.* 260 F g^{-1}, in aqueous Li_2SO_4 electrolyte), respectively. Loading of MnO_2 nanoparticles into mesoporous carbon microspheres also results in high specific capacitances of 459 and 354 F g^{-1} at current densities of 1 and 20 A g^{-1} in 6 M KOH electrolyte [27]. These excellent results confirm the great potential of this material in practical applications such as SCs.

Nevertheless, to achieve rationally controlled nanocomposite structures, all these works employed time-consuming synthesis procedures (5-step treatments [27]), complex instruments (vacuum PVD systems [26]) or high-cost materials (e.g., Au [25,26], graphene [17,24], or PEDOT:PSS [17]), thus making production scale up of these materials difficult. Therefore, a facile, low-cost, and environmentally friendly method to synthesize well-performing, MnO_2-based electrodes for electrochemical capacitors is still a substantial challenge.

MnO_2 possesses a wealth of crystallographic polymorphs, such as α-, β-, γ-, δ-, λ- and ε-types, made of [MnO_6] octahedra with very different connectivities [28]. However, almost all of current studies focus on nanostructure design and implementation in MnO_2 systems. The exploration and selection of well-performing manganese oxides from their various derivatives, in contrast, are rarely conducted. A outstanding work by Ghodbane et al. indicates that increasing the size and connectivity of cavities between [MnO_6] octahedra results in the improvement of the electrochemical performance [29]. Among these polymorphs, birnessite-type MnO_2 (δ-MnO_2) possesses a layered structure that hosts interstitial cations [30,31]. The relatively free interstitial cations in the lattice render this oxide highly electronic and ionic conductive compared with pure MnO_2. At the same time, birnessite-type MnO_2 also exhibits excellent ion-sieve properties for the adsorption of cations due to its 2D cavities [30]. Considering these features together, we believe that a birnessite-type MnO_2 system could be a potentially promising candidate for SC applications.

In this article, we report a facile, cost-efficient approach to fabricating low-crystallized and mesoporous birnessite-type manganese oxide ($K_2Mn_4O_9$) micro-powder by means of a simple redox reaction between inexpensive and common agents, namely $KMnO_4$ and citric acid, at only 250 °C in air. Without any further structural/surface modification, the as-obtained $K_2Mn_4O_9$ micro-powder exhibited high specific capacitances of ~754 F g^{-1} at 1 A g^{-1} or ~379 F g^{-1} at 5 A g^{-1} (calculated from the net weight of the $K_2Mn_4O_9$ micro-powder only) in 1 M KOH electrolyte, along with an excellent cycling stability of 90.1% of the initial capacity retained after 5000 cycles at 5 A g^{-1}. Furthermore, by simply adding highly conductive carbon nanotubes (CNTs) into the reaction system, the specific capacitances were further improved up to 1055 and 674 F g^{-1} at 1 and 5 A g^{-1} in 6 M KOH electrolyte, respectively, for