A Facile Synthesis of A Novel Cu₂Se@CMK-3 Nanocomposite for Rechargeable Sodium Batteries

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Abstract. The rechargeable sodium-ion battery has become a research hotspot due to low cost and a large abundance of sodium resources. In this work, a novel nano-architecture of Cu₂Se nanoparticles imbedded in ordered mesoporous carbon (Cu₂Se@CMK-3) was synthesized. Benefiting from the high conductivity and special nano-architecture of CMK-3 matrix, the as-synthesized Cu₂Se@CMK-3 composite delivers a high specific discharge capacity (231 mA h g⁻¹) and superior cycling stability (a capacity decay of 0.33% per cycle during 100 cycles at 0.1 C) when used as cathode in sodium-ion batteries.

1. Introduction
The overexploitation and abuse of fossil fuels have caused irreversible damage to the ecological environment during the past few decades, including the greenhouse effect, air pollution, resource depletion, etc. [1]. Meanwhile, the ever-growing industrial demand has brought unprecedented challenges to efficient electrical-energy-storage technologies, especially for the rechargeable ion batteries [2]. The commercial lithium-ion batteries (LIBs) share the majority of the market due to their light weight, high operating voltage (≈ 3.2 ~ 3.8 V), high energy density (150-200 Wh kg⁻¹), and good cycle life [3]. Nevertheless, LIBs still cannot satisfy the drastic needs of the automotive power market. Furthermore, in view of the finite lithium mineral resources and intrinsic limits, the research on LIBs is reaching their boundaries [4, 5]. Since the element sodium is vaster and cheaper, sodium-ion batteries (SIBs) have gained more attention as the promising substitute for LIBs [6, 7]. Moreover, the physiochemical properties of sodium are analogous to lithium, so they share a similar electrochemical reaction mechanism. However, it is obviously unsuccessful to apply the electrode material of LIBs directly to SIBs [8-10]. Compared to lithium ion, sodium possesses a larger ionic radius (1.02 Å for Na⁺ vs. 0.76 Å for Li⁺), a higher standard electrode potential (-2.71 V for Na⁺ vs. -3.02 V for Li⁺) and a heavier molar mass, which may lead to a sluggish electrode reaction mechanism [11, 12]. For the sake of these discrepancies, it is crucial to select more suitable electrode materials, as well as designing rational electrode structure to accommodate the larger volume expansion and improve the
performances of SIBs. As the indispensable part of SIBs, cathode materials greatly affect the overall performance of sodium batteries. In recent years, researchers have put more effort into the cathode material of sodium batteries, and many cathode materials have been studied, such as layer and tunnel type transition metal oxides [13-15], transition metal sulfides [16, 17], fluorides [18], phosphates [19, 20], Prussian blue analogues [21, 22] and organic polymers [23, 24].

Copper selenide (Cu$_2$Se) is an outstanding superionic conductor [25], which means its electrical conductivity and electrochemical activity are quite high. Therefore, Cu$_2$Se is a perspective potential electrode material for SIBs, demonstrating a large reversible capacity when used as a positive electrode material for SIBs[26]. However, the cycle stability of Cu$_2$Se still needs to be improved. Herein, to further improve the cycle stability, we firstly designed a novel composite structure in which Cu$_2$Se nanoparticles were impregnated into CMK-3 (denoted as Cu$_2$Se@CMK-3) by a facile synthesis method. In addition, its application in rechargeable sodium-ion batteries has also been explored. As a kind of ordered mesoporous carbon, CMK-3 has been widely utilized in electrode materials thanks to its large specific surface, great pore volume, and the high conductivity. These features enable CMK-3 to provide faster ion transport and buffer volume expansion during cycling [27, 28]. As an innovative nanocomposite structure, Cu$_2$Se@CMK-3 cathode exhibits enhanced specific capacity and cycling stability.

2. Experimental details

1. Materials

Analytically copper nitrate (Cu(NO$_3$)$_2$, Macklin, AR), selenium powder(Se, Sigma, 99.99%), Carbon disulfide (CS$_2$, Aladdin, ≥99.9%), Molecular sieve (SBA-15, Aladdin). All reagents were used without further purification.

2. Preparation of Cu$_2$Se@CMK-3 nanocomposites

The Schematic illustration of the preparation process for Cu$_2$Se@CMK-3 nanocomposites is shown in Figure 1. The CMK-3 was prepared according to the previous reports [29]. Briefly, the template SBA-15 was dispersed in glucose solution and after calcination, CMK-3 is obtained by removing SBA-15 with NaOH aqueous solution. or synthesis of Cu$_2$Se@CMK-3 nanocomposites, Cu(NO$_3$)$_2$ was first dissolved in absolute ethanol to form a Cu(NO$_3$)$_2$ solution, which was added dropwise into a certain amount of CMK-3 to obtain Cu@CMK-3 precursor. The Cu@CMK-3 precursor was then dried and reduced at 200 °C for 1 h under argon mixed with 5% hydrogen environment to from Cu@CMK-3. Selenium powder was dissolved in carbon disulfide and added into the as-synthesized Cu@CMK-3. The resulting sample was annealed at 500 °C for 2 h in a vacuum to obtain Cu$_2$Se@CMK-3 nanocomposites. The mass ratio of generated Cu$_2$Se to CMK-3 is 7:3.

![Figure 1. Schematic illustration of the preparation process for Cu$_2$Se@CMK-3 nanocomposites.](image)

3. Materials characterization

X-ray powder diffraction patterns were measured in the 2-Theta range from 10~70°on D8-Advance diffractometer Bruker AXS (XRD, Germany, Cu-Kα radiation). The transmission electron images and selected area electron diffraction patterns were collected on a transmission electron microscope (TEM, JEOL 2011). X-ray photoelectron spectroscopy data were analyzed on Thermo Fisher Escalab 250Xi instrument using Al Kα X-ray radiation.
4. Electrochemical measurements
CR 2032 coin cells were assembled in an argon-filled glove box. The working electrode consisted of active material (Cu$_2$Se@CMK-3), conductive additive (Super P) and polymer binder (Polyvinylidene fluoride, PVDF) with a weight ratio of 8: 1: 1. The slurry was coated on aluminum foil current collector. The active material loading was around 1 mg cm$^{-2}$. Na foil was acted as counter and reference electrode and the separator was a Whatman GF/C glass fiber filter. The electrolyte was 1.0 M NaClO$_4$ in a mixture of ethylene carbonate and dimethyl carbonate (EC: DMC=1: 1, v:v). Galvanostatic charge-discharge experiments were conducted on a LAND CT2001 test system between 1.6 V and 2.5 V vs. Na/Na$^+$.

5. Results and discussion
The crystal structures and phase compositions of the CMK-3, the as-synthesized Cu@CMK-3 and Cu$_2$Se@CMK-3 are examined by X-ray diffraction (XRD), as indicated in Figure 2. The pattern of CMK-3 shows a widened peak at about 25°, which illustrates the graphitized structure and amorphous form of CMK-3. It can be seen that the copper nanoparticle was successfully deposited into the ordered mesoporous carbon from the diffraction pattern of Cu@CMK-3. For the Cu$_2$Se@CMK-3 composite, the characteristic peaks of Cu all disappear, while new peaks referring to Cu$_2$Se appear, indicating that all the copper nanoparticles were converted into Cu$_2$Se crystals after the annealing treatment.

Figure 3 manifests the TEM images of Cu@CMK-3 and Cu$_2$Se@CMK-3 to further investigate the microstructure of the as-prepared samples. It can be concluded that the CMK-3 still maintains a highly ordered pore structure after copper deposition and selenium impregnation from Figure 3(a) and (b), which confirms that the CMK-3 is a reliable carbon matrix. The average diameter of copper nanoparticles is about 6.61 nm and they are uniformly dispersed in the carbon matrix (Figure 3a, 3e). The HRTEM image and SAED pattern inserted show the clear copper lattice fringes (Figure 3c), while The HRTEM and SAED pattern in Figure 3d indicate the formation of cuprous selenide nanocrystallines. The sizes of the nanoparticles become slightly larger after copper is converted to Cu$_2$Se (~9.17 nm) and no agglomeration phenomenon was observed (Figure 3b, 3f).
Figure 3. TEM image (a), HRTEM image and SAED pattern (c), nanoparticulate size distribution histograms (e) of Cu@CMK-3; TEM image (b), HRTEM image and SAED pattern (d), nanoparticulate size distribution histograms (f) of Cu₂Se@CMK-3.

The X-ray photoelectron spectroscopy (XPS) was conducted to identify the element valence states in Cu₂Se@CMK-3, as shown in Figure 4. The high-resolution Cu 2p spectrum (Figure 4a) emerges two symmetrical and narrow main peaks at binding energies 932.3 eV (Cu 2p₃/₂) and 952.2 eV (Cu 2p₁/₂), respectively, which confirms the presence of Cu⁺. In addition, no satellite peaks were observed near the characteristic peak of Cu²⁺ (942 eV). Based on the above, we can determine that only Cu⁺ exists in the resulting sample [30]. The XPS spectrum of Se 3d suggests the -2 valence state of Se with the intense peak situated at the binding energy of 54.4 eV. Together with the results of the XRD, the pure Cu₂Se@CMK-3 composite was obtained.
To investigate the energy storage behavior of the Cu$_2$Se@CMK-3 nanocomposite, it is tested as cathode material for sodium-ion batteries. Figure 5a shows the cycling stability of the Cu$_2$Se@CMK-3 electrode at a current rate of 0.1 C, delivering initial capacity of 231 mA h g$^{-1}$ and retaining at 163 mA h g$^{-1}$ after 100 cycles with a capacity decay of 0.33% per cycle. Furthermore, the discharge/charge profiles of Cu$_2$Se@CMK-3 electrode at selected cycles are displayed in Figure 5b. In the initial discharging profile, one plateau at ~1.92 V was attributed to the conversion reaction of Cu$_2$Se, while the charge plateau is around 2.07 V. The first discharge/charge capacity is 231 mA h g$^{-1}$ and 221 mA h g$^{-1}$, respectively, with a quite high initial coulombic efficiency of 95.7%. After about 10 cycles,
the coulombic efficiency reached almost 100%, which indicates good electrochemical reversibility. Figure 5c shows the rate performance of Cu$_2$Se@CMK-3 electrode at various current densities. The Cu$_2$Se@CMK-3 electrode delivers capacities of 227, 177, 127, 108, 97 mAh g$^{-1}$ at rate of 0.1, 0.2, 0.5, 1, 2 C, respectively, indicating a good reaction kinetics of Cu$_2$Se@CMK-3 and sodium ion. Besides, the electrochemical impedance spectroscopy (EIS) of Cu$_2$Se@CMK-3 electrode was performed, as shown in Figure 5d. The value of semicircular loop standing for charge-transfer resistance of Cu$_2$Se@CMK-3 electrode is around 90 $\Omega$ cm$^2$, revealing a good charge-transfer kinetics after using conductive CMK-3 as Cu$_2$Se matrix.

The results above demonstrate that the Cu$_2$Se@CMK-3 nanocomposite can be utilized as a promising sodium storage material for sodium-ion batteries, and its good electrochemical performance can be attributed to: (i) the host CMK-3 improves the overall conductivity of the whole electrode. (ii) The nanoscale Cu$_2$Se shortens the diffusion distance of electrons and ions, which is beneficial to the electrochemical reaction kinetics; (iii) Ordered mesoporous carbon CMK-3 can buffer the volume change during charging and discharging and enhance structural stability.

6. Conclusions
In summary, a novel Cu$_2$Se@CMK-3 cathode material has been fabricated by a cheap and facile method. Benefiting from the inherent physicochemical properties of Cu$_2$Se and the structural specificity of the host material CMK-3, the obtained Cu$_2$Se@CMK-3 performs superior cycle stability with a capacity decay of 0.33% per cycle during 100 cycles at 0.1 C and good rate performance. This work proves that Cu$_2$Se@CMK-3 is a promising energy storage electrode material and provides a new idea for the study of transition metal selenide as cathode material for sodium-ion batteries.

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