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Mesoporous cobalt 2,5-thiophenedicarboxylic coordination polymer for high performance Na-ion batteries

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ABSTRACT

Mesoporous flower-like Co-TDC coordination polymer was synthesized through a solvothermal method and applied as anode materials in Na-ion batteries for the first time. It delivers outstanding capacities of 328 mAh g^{-1} after 100 cycles, thus outperforms many of the carbon-based materials for SIBs.

1. Introduction

In recent years, the limited abundance and increasing price of lithium have triggered much interest on sodium-ion batteries (SIBs) as an alternative for both electric vehicles and large-scale grid-based electrical energy storage [1]. It is believed that SIBs offer great advantages over LIBs in cost, nature abundance, security, and environmental benignity [2,3]. Substantial efforts have been made to exploit suitable materials for SIBs [4], covering metal oxides [5], carbonaceous materials [6] and so forth.

Coordination polymers (CPs), also known as metal organic frameworks (MOFs), are one, two or three-dimensional metal-ligand compounds assembled through covalent metal-ligand bonding [7]. These materials display open architectures resulting from the combining of multifunction organic molecules with transition metal ions [8,9]. Notably, MOFs and CPs have gradually gained momentum in the field of electrochemistry in lithium-ion batteries, including MOF-177, Mn-BTC [10], Co-BTC CP [11]. However, their application in sodium-ion batteries has not been reported. Herein, we report the synthesis of flower-like cobalt 2,5-thiophenedicarboxylic coordination polymer (Co-TDC) through a convenient hydrothermal method. Encouragingly, when applied in SIBs, it possesses a good cycling performance that outperforms of many state-of-the-art carbon-based materials.

2. Experimental section

2.1. Synthesis of Co-TDC

$Co(NO_3)_2 \cdot 6H_2O$ and 2,5-thiophenedicarboxylic acid with a molar ratio of 2:1 were dissolved in 40 mL *N,N*-dimethylformamide solvent and 30 mL methanol with polyvinylpyrrolidone (K-40, 0.5 g) under magnetic stirring. Subsequently, the solution was transferred into a stainless steel autoclave and heated at 120 °C in an oven for 24 h. The resultant production was collected by pumping filtration followed by spontaneously cooling to room temperature. Eventually, the final powder designated as Co-TDC was obtained after drying under vacuum at 110 °C for 12 h.

2.2. Characterization

X-ray powder diffraction (XRD) patterns was analyzed by employing a Holland Panalytical PRO PW3040/60 Diffractometer. Scanning electron microscope (SEM) images and energy-dispersive X-ray spectroscopy mapping were collected using an S-4800 (HITACHI, Japan). The transmission electron microscope (TEM) and the selected area electron diffraction (SAED) patterns were recorded using a JEM-2100F (JEOL Ltd., Japan). Thermogravimetric analysis (TGA) was carried on a STA 449 F3 Jupiter® simultaneous thermo-analyzer. The nitrogen adsorption isotherm was measured with an ASAP 2020 Accelerated Surface Area and Porosimetry System (Microeritics, Norcross, GA). X-ray

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photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA spectrometer. Soft X-ray absorption spectroscopy (sXAS) was performed at Shanghai Synchrotron Radiation Facility (SSRF, BL08U1A).

2.3. Electrochemical measurement

The electrochemical properties of the Co-TDC particles were examined by manufacturing CR2032 coin-type cells with sodium acting as the reference electrode and the counter electrode in a 1 M $NaClO_4$ electrolyte solution. The working electrode was prepared by mixing 70% of Co-TDC, 20% of Super-P carbon black and 10% of polyacrylic acid in *N*-methyl-2-pyrrolidone to produce slurry. Afterwards, the obtained slurry was coated on the surface of copper foil and then dried in vacuum at 110 °C for 12 h.

The coin-cells were assembled in an argon-filled glove box with above electrode laminates as working electrodes. After aging for 12 h, the electrode capacity was tested on a multi-channel battery system (LAND cycler, Wuhan Kingnuo Electronic Co., China) with a voltage range between 0.01 and 3.0 V. All the specific capacities were calculated based on the weight of practical Co-TDC material. Cyclic voltammetric measurement was performed using a CHI 660e electrochemical workstation (ChenHua Instruments Co., China).

3. Result and discussion

Co-TDC was structurally characterized by XRD studies. As displayed in Fig. 1a, there are three sharp diffraction peaks at $2\theta = 9.24°$, 14.69° and 18.42°, respectively. These peaks are coherent with the (200), (11 −1) and (400) planes of the $Co(TDC)(H_2O)_{1.5}$ crystal structure [12]. Therefore, the crystal structure of our product should be similar to $Co(TDC)(H_2O)_{1.5}$.

In addition, the TGA measurement was conducted as displayed in Fig. 1b. In the initial phase of temperature-rising process, the mass of the material is slowly descending, with a weight loss of approximately 5.6%, indicating the dissociation of coordinated H_2O molecules. The Co-TDC doesn't have an apparent decomposition until 350 °C, above which CPs skeleton is collapsed. The comparatively high decomposition temperature indicates good thermal stability of Co-TDC. According to the TGA data, the formula of Co-TDC can be expressed as $Co(TDC)(H_2O)_{0.75}$.

To further understand the porous structure, nitrogen adsorption–desorption isotherms was measured (Fig. 1c). This Co-TDC material shows typical type IV curves, indicating its mesoporous feature. The BET surface area of the Co-TDC is calculated to be $22\ m^2\ g^{-1}$.

High resolution XPS spectrum was performed to ascertain the electronic state of the central metal atom (Fig. 1d). Two symmetric peaks appear at 797.1 and 781.1 eV, together with conspicuous satellite features appearing at 803.17 and 786.27 eV, respectively, indicating the Co (II) state.

To acquire insights into the microstructure of the Co-TDC, SEM and TEM were employed. As shown in Fig. 2a, the Co-TDC possesses an ordered flower-like architecture which is composed of secondary flakes. Fig. 2b shows the high-magnification SEM. We explicitly observe the slightly rough flakes with thickness in the range of 100–110 nm. The layered structure of Co-TDC not only provides cavities for the diffusion and storage of electrolyte ions, but also shortens the Na^+ diffusion distances to the internal surface. The EDX results indicate that Co, C, S and O elements are homogenously distributed (Fig. 2c–f). Fig. 2g exhibits the TEM micrograph of Co-TDC, which demonstrates its flaky morphology. Besides, the selected area electron diffraction SAED pattern (Fig. 2h) exhibits rows of well-defined spots. To a certain degree, it is conceivable that the Co-TDC is crystallized in certain crystal planes.

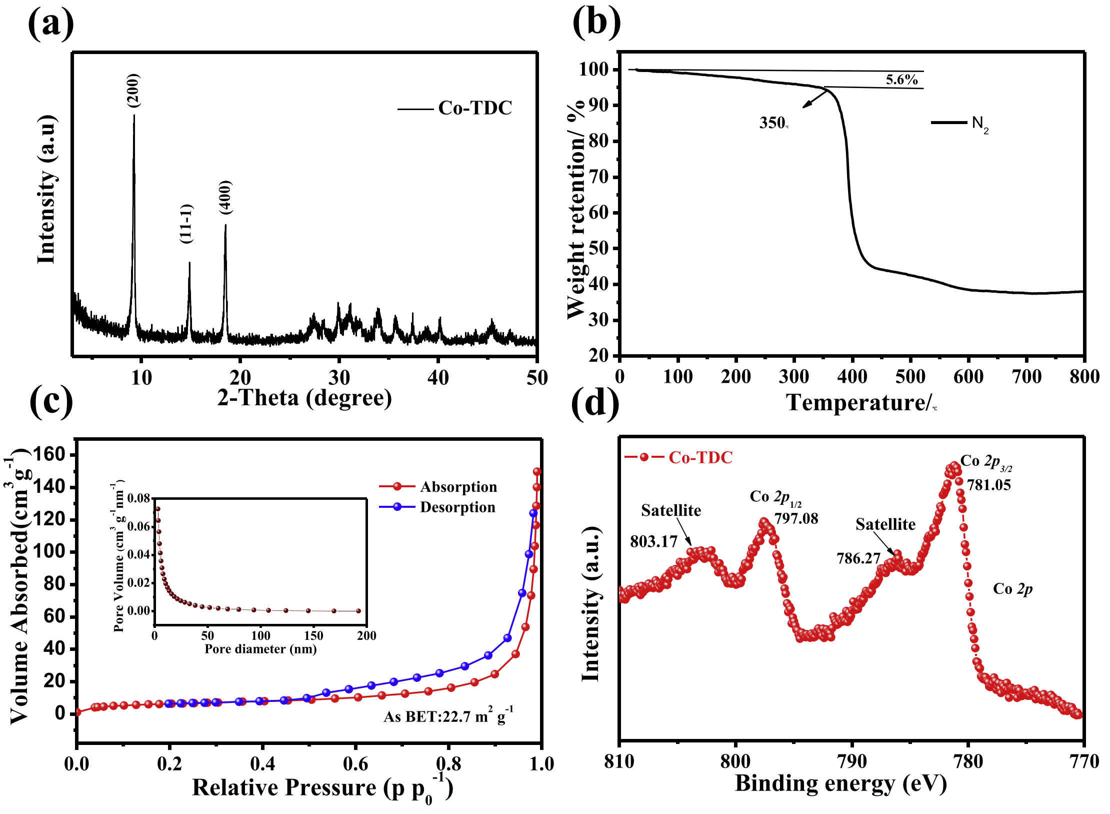

Fig. 1. (a) PXRD pattern, (b) TGA curve, (c) nitrogen adsorption-desorption isotherms, and (d) High resolution Co 2p XPS spectrum of Co-TDC material.

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