Mesoporous carbon matrix confinement synthesis of ultrasmall WO₃ nanocrystals for lithium ion batteries†

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Transition metal oxides (TMOs)/carbon nanocomposites are promising for high capacity long life lithium ion batteries (LIBs). Herein, we report a mesoporous carbon matrix confinement growth strategy to synthesize ultrasmall WO₃ nanocrystals for lithium storage. In this strategy, WCl₆ and phenolic resins (resol) are co-assembled with amphiphilic diblock copolymer PEO-b-PS into ordered mesostructures through an evaporation induced self-assembly (EISA) process. During the pyrolysis process, the resol molecules can be polymerized and carbonized into amorphous mesoporous carbon matrices, which lock the amorphous W species well. Then, WO₃ nanocrystals are formed and are uniformly distributed in the ordered mesoporous carbon matrix with the increased pyrolysis temperature; moreover, the particle size is well controlled to ~3 nm under the confinement effect of the carbon matrices. The resultant ordered mesoporous carbon/WO₃ composites show very large pore size (~11.3 nm), high surface area (~157 m² g⁻¹), high pore volume (~0.25 cm³ g⁻¹), and WO₃ content of 84%. As an anode material for LIBs, the obtained composites show excellent cycling stability and rate performance. A high specific capacity of 440 mA h g⁻¹ can be achieved after 100 cycles at a current density of 0.1 A g⁻¹. We believe that such a confinement synthesis strategy is versatile to create TMO-based nanocomposites for outstanding LIBs.

Introduction

Lithium ion batteries (LIBs) have been intensively investigated and widely used in electric vehicles and portable electronic fields.1–3 However, the low theoretical capacity (372 mA h g⁻¹) of commercial graphite anodes cannot satisfy the ever-increasing requirements.4–8 Recently, transition metal oxides (TMOs) have attracted much attention as promising anode materials because of their high theoretical capacities.9–13 Among them, tungsten oxide (WO₃) is of great interest for LIBs due to its low cost, high density and abundance. Nevertheless, the huge volume change during lithium ion insertion/exaction processes and the low electrical and ionic conductivities of bulk WO₃ greatly limit its application for high performance LIBs.14–18 Various nanostructured WO₃ anodes have been developed and show improved performances presumably due to their small sizes that enable fast Li⁺ diffusion and facile strain relaxation.19–23 However, it remains a challenge to facilely prepare ultrasmall WO₃ nanoparticles (<5 nm) for LIBs due to their easy crystallization nature.

Mesoporous carbon has recently gained enormous research interest in materials science owing to its high electrical conductivity, chemical stability, large surface area, uniform mesochannels, and nanosized pore walls.24–28 These features can not only facilitate the transport of electrolytes, ions and electrons, but also accommodate the strain relaxation during the charge/discharge process.29–34 Various mesoporous TMOs/carbon anode materials have been synthesized by confining the growth of TMO nanoparticles in the mesochannels and intensively investigated for LIBs.35–41 While this method can only be explored for loading a low content of TMOs,42–45 further increasing the active TMO content in mesoporous carbons would block the pore system and they severely aggregate into larger particles outside the mesopores, leading to a poor lithium storage performance.46–48

Herein, we report a mesoporous carbon matrix confinement growth strategy for the synthesis of ultrasmall WO₃ nanocrystals through an evaporation induced self-assembly (EISA) method by using poly(ethylene oxide)-block-polystyrene (PEO-b-PS) as a structure-directing agent, phenolic resins (resol) as a carbon...
precursor, and WCl₆ as a tungsten source. During the pyrolysis process, the resol molecules can be polymerized and carbonized into amorphous mesoporous carbon matrices, which lock the amorphous W species well. Then, WO₃ nanocrystals are formed and are uniformly distributed in the ordered mesoporous carbon matrices with the increased pyrolysis temperature; moreover, the particle size is well controlled to ~3 nm under the confinement effect of the carbon matrix. The resultant ordered mesoporous carbon/WO₃ (OMC–WO₃) composites exhibit a high surface area of ~157 m² g⁻¹, a large pore volume of ~0.25 cm³ g⁻¹, a uniform pore size of ~11.3 nm, and a high WO₃ content up to 84%. Owing to their unique mesostructures, the obtained OMC–WO₃ composites show remarkably high lithium storage of 440 mAh g⁻¹ at a current density of 0.1 A g⁻¹, excellent rate capacity, and superb cycling performance.

**Experimental section**

**Materials**

Monomethyl poly(ethylene oxide) (Mₜₙ : 5000 g mol⁻¹) (abbreviated as PEO-5000), 2-bromo-2-methylpropionyl bromide and N,N,N′,N′,N′-pentamethyl diethylenetriamine (PMDETA) were purchased from Aldrich. Phenol, sodium hydroxide, formaldehyde, hydrogen chloride (HCl), and 1,2-bromo-1,2-dimethyl propane were purchased from Aladdin. Styrene was purified as PEO-5000, 2-bromo-2-methylpropionyl bromide and WCl₆ as a tungsten source. During the pyrolysis process, the resol molecules can be polymerized and carbonized into amorphous mesoporous carbon matrices, which lock the amorphous W species well. Then, WO₃ nanocrystals are formed and are uniformly distributed in the ordered mesoporous carbon matrices with the increased pyrolysis temperature; moreover, the particle size is well controlled to ~3 nm under the confinement effect of the carbon matrix. The resultant ordered mesoporous carbon/WO₃ (OMC–WO₃) composites exhibit a high surface area of ~157 m² g⁻¹, a large pore volume of ~0.25 cm³ g⁻¹, a uniform pore size of ~11.3 nm, and a high WO₃ content up to 84%. Owing to their unique mesostructures, the obtained OMC–WO₃ composites show remarkably high lithium storage of 440 mAh g⁻¹ at a current density of 0.1 A g⁻¹, excellent rate capacity, and superb cycling performance.

**Synthesis of diblock copolymer poly(ethylene oxide)-block-poly(styrene) (PEO-b-PS)**

The diblock copolymer was prepared by a simple atom transfer radical polymerization (ATRP) method. The typical synthesis process was carried out as follows. The first step was the synthesis of PEO–Br. 20.0 g of monomethoxy PEO-5000 was dissolved in 120 mL of THF, and then 20 mL of pyridine was added to form a homogeneous solution at 40 °C. Next, the solution was cooled in an ice-water bath. After that, 6.00 g of 2-bromoisoobutyl bromide was added dropwise under stirring for 30 min. The solution was further stirred at 30 °C for 10 h. After cooling down to room temperature, 200 mL of cold ether was added into the solution. The white product of PEO–Br was precipitated from the reaction solution. It was washed with cold ether and further dried in a vacuum at 30 °C for 5 h. In the second step, 5.00 g of PEO–Br, 0.15 g of CuBr, 0.50 g of PMDETA and 35 mL of styrene were added into an ampoules bottle, which was degassed with three freeze–pump–thaw cycles and sealed under a vacuum. It was subsequently immersed in a thermostated oil bath at 110 °C under stirring. The reaction continued for 1.5 h, and then the system was cooled down to room temperature. The gel-like product was dissolved in 100 mL of THF and filtered through the Al₂O₃ column to remove the Cu complex. Petroleum ether (200 mL) was poured into the solution to precipitate the PEO-b-PS block copolymer. The copolymer was then dried in a vacuum at 30 °C for 5 h.

**Synthesis of resol precursor**

A resol was prepared in a base-catalyzed process from phenol and formaldehyde. In a typical preparation, phenol (0.80 g, 8.5 mmol) was melted at 45 °C in a round-bottomed flask and then 20% NaOH aqueous solution (0.17 g, 8.5 mmol) was added slowly over 5 min under stirring. Formalin (37 wt%, 1.45 g) containing formaldehyde (17.8 mmol) was added dropwise into this solution and the reaction mixture was further stirred at 70 °C for 1 h. After cooling the mixture to room temperature, the pH value was adjusted to neutral (~7.0) using a dilute HCl solution (2.0 M). Water in the resol was removed by vacuum evaporation at 50 °C. The final product was dissolved in ethanol (20 wt%) before use.

**Synthesis of OMC–WO₃ composites**

In a typical synthesis (Scheme 1), 0.10 g of PEO₁₁₋₁₇₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-1 the OMC–WO₃ composite exhibit a high surface area of ~157 m² g⁻¹, a large pore volume of ~0.25 cm³ g⁻¹, a uniform pore size of ~11.3 nm, and a high WO₃ content up to 84%. Owing to their unique mesostructures, the obtained OMC–WO₃ composites show remarkably high lithium storage of 440 mAh g⁻¹ at a current density of 0.1 A g⁻¹, excellent rate capacity, and superb cycling performance.
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Pisotherms, and the total pore volumes were estimated from the adsorption branches of the BJH model, the pore volumes and pore size distributions were derived from the adsorption branches of the Brunauer–Emmett–Teller (BET) method. The total pore volumes were estimated from the adsorbed amount at a relative pressure $P/P_0$ of 0.992. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851 analyzer from 50 to 900 °C in air (20 mL min$^{-1}$) with a ramp rate of 5 °C min$^{-1}$. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Field-emission scanning electron microscopy (FESEM) images were taken using a Hitachi S-4800 microscope. The dried samples were directly used for the observation without any treatment.

The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms, and the total pore volumes were estimated from the adsorbed amount at a relative pressure $P/P_0$ of 0.992. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851 analyzer from 50 to 900 °C in air (20 mL min$^{-1}$) with a ramp rate of 5 °C min$^{-1}$. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Field-emission scanning electron microscopy (FESEM) images were taken using a Hitachi S-4800 microscope. The dried samples were directly used for the observation without any treatment.

Field-emission scanning electron microscopy (FESEM) images were taken using a Hitachi S-4800 microscope. The dried samples were directly used for the observation without any treatment. Raman spectra were recorded with a Dilor LabRam-1 B microscopic Raman spectrometer, using a He–Ne laser with an excitation wavelength of 632.8 nm. X-ray photoelectron spectroscopy (XPS) was performed on a AXIS ULTRA DLD XPS system with a MONO Al source (Shimadzu Corp). Photoelectron spectroscopy was performed using monochromatic Al KR radiation under vacuum at $5 \times 10^{-9}$ Pa. All calibrations were referenced to the surface adventitious carbon (C 1s = 284.6 eV).

The synthesis process of ordered mesoporous carbon/WO3 composites (OMC–WO3 composites) is shown in Scheme 1. The OMC–WO3 composites display sequential mesostructure growth strategy. The SAXS pattern (Fig. 1a) of the as-made mesoporous W/resol composite sample prepared by the confinement growth strategy shows three scattering peaks $q$ values of 0.172, 0.334, and 0.576 nm$^{-1}$, which can be indexed to the 100, 200, and 300 reflections of the ordered primitive cubic mesostructure. The cell parameter ($a_0$) is calculated to be ~36.5 nm. After the pyrolysis of the as-made sample at 550 °C under N$_2$, the SAXS pattern (Fig. 1a) of the obtained product (denoted as OMC–WO3) still shows three scattering peaks at 0.339, 0.675, and 1.011 nm$^{-1}$ with a cell parameter $a_0$ value of ~18.5 nm, which suggests a large shrinkage percentage (49.3%) but still a highly ordered primitive cubic mesostructure. The XRD pattern of the as-made sample only exhibits one broadening peak at around 20°, attributed to the existence of an amorphous framework (Fig. 1b). After this pyrolysis, the OMC–WO3 composites display six broadening diffraction peaks at 23.9, 34.0, 42.1, 49.0, 55.2, and 61.0°, which are indexed to the 100, 110, 111, 200, 210, and 211 reflections of a cubic phase of WO3 with a $Pm3m$ space group.

Results and discussion

The SAXS pattern (Fig. 1a) of the as-made mesoporous W/resol composite sample prepared by the confinement growth strategy shows three scattering peaks at $q$ values of 0.172, 0.334, and 0.576 nm$^{-1}$, which can be indexed to the 100, 200, and 300 reflections of the ordered primitive cubic mesostructure. The cell parameter ($a_0$) is calculated to be ~36.5 nm. After the pyrolysis of the as-made sample at 550 °C under N$_2$, the SAXS pattern (Fig. 1a) of the obtained product (denoted as OMC–WO3) still shows three scattering peaks at 0.339, 0.675, and 1.011 nm$^{-1}$ with a cell parameter $a_0$ value of ~18.5 nm, which suggests a large shrinkage percentage (49.3%) but still a highly ordered primitive cubic mesostructure. The XRD pattern of the as-made sample only exhibits one broadening peak at around 20°, attributed to the existence of an amorphous framework (Fig. 1b). After this pyrolysis, the OMC–WO3 composites display six broadening diffraction peaks at 23.9, 34.0, 42.1, 49.0, 55.2, and 61.0°, which are indexed to the 100, 110, 111, 200, 210, and 211 reflections of a cubic phase of WO3 with a $Pm3m$ space group.

Cell assembly and electrochemical measurements

The anode electrodes were fabricated by mixing the active material, conductive agent Super P, and polymer binder (carboxymethylcellulose sodium, CMC) at a weight ratio of 8 : 1 : 1. This mixture was dispersed in deionized water to form a slurry and then cast on the Al foil. Then, the electrodes were dried at 80 °C in a vacuum oven overnight. A 2025 coin-type lithium ion cell was assembled in an argon-filled glovebox with moisture and oxygen concentration below 1.0 ppm for electrochemical characterization. 1.0 M LiPF$_6$ in a 1 : 1 : 1 volume ratio of diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethylene carbonate (EC) was used as the electrolyte. Li metal foils were used as counter electrodes for electrochemical measurements. Cyclic voltamograms (CVs) were obtained using a CHI660e electrochemical workstation at a scan rate of 0.1 mV s$^{-1}$ within a range from 0.01 to 3.0 V. The charge/discharge tests were performed on a LAND CT2001A multi-channel battery testing system within a voltage range of 0.05–3 V (vs. Li/Li$^+$) at room temperature. For the high rate testing, the charge/discharge currents were gradually increased from 0.1 to 0.2, 0.5, 1, and 2 A g$^{-1}$, and then decreased to 0.1 A g$^{-1}$. Electrochemical impedance spectroscopy (EIS) spectra were collected from 100 kHz to 100 mHz at room temperature (25 °C).

![Cell assembly and electrochemical measurements](image-url)
show representative type-IV curves with \( \text{H}_2 \) hysteresis loops, which is consistent with the SAXS results. The tiny \( \text{WO}_3 \) nanoparticles show a well-defined 3D primitive cubic mesostructure, which is consistent with the SAXS results. The tiny \( \text{WO}_3 \) nanoparticles embedded in the mesoporous carbon matrices can be clearly observed from the high-resolution TEM image (HRTEM; Fig. 2f). The particle size is estimated to be \( \sim 3 \) nm, which is in accordance with the XRD result. The corresponding selected area diffraction (SAED) exhibits the polycrystalline feature of \( \text{WO}_3 \) (Fig. 2f, inset). The periodic mesoporous structure can also be observed from the scanning TEM image (STEM; Fig. S3a†). Meanwhile, the corresponding elemental mapping images show that W, O, and C elements are uniformly distributed on the framework (Fig. S3b–f†), further indicating that the \( \text{WO}_3 \) nanoparticles are uniformly confined in the ordered mesoporous carbon matrices.

Nitrogen sorption isotherms of the OMC–\( \text{WO}_3 \) composites show representative type-IV curves with \( \text{H}_2 \) hysteresis loops (Fig. 1c). A sharp capillary condensation step at the relative pressure (\( P/P_0 \)) of 0.66–0.86 is observed, demonstrating a narrow pore size distribution. The BET surface area and pore volume of OMC–\( \text{WO}_3 \) composites are calculated to be \( \sim 157 \text{ m}^2 \text{ g}^{-1} \) and \( \sim 0.25 \text{ cm}^3 \text{ g}^{-1} \), respectively. The pore size distribution curve derived from the adsorption branch based on the BJH model shows an average pore size of \( \sim 11.3 \) nm (Fig. 1d), which is consistent with the TEM result. The Raman spectrum (Fig. S4†) shows two bands around 1325 and 1587 cm\(^{-1}\), demonstrating the amorphous nature of carbon frameworks.

The mass content of the carbon frameworks in the OMC–\( \text{WO}_3 \) composites is calculated to be 16% by TGA (Fig. S3†). XPS spectra also show the existence of only W, O, and C elements belonging to OMC–\( \text{WO}_3 \) composites (Fig. S6†), consistent with the EDX result.

To clearly distinguish the mesoporous carbon matrices from the composites, the tiny \( \text{WO}_3 \) nanoparticles were etched away by the HF solution. An ordered mesoporous carbon matrix (OMC) can be obtained after the HF treatment (Fig. 3a and b). The HRTEM image of the OMC shows the ordered mesopores connected by various micropores left by the \( \text{WO}_3 \) nanoparticles (Fig. 3c). No obvious nanoparticles can be observed, indicating the successful removal of \( \text{WO}_3 \) by HF, which can be further evidenced by the corresponding SAED pattern (Fig. 3d). These results further confirm the uniform distribution of the \( \text{WO}_3 \) nanoparticles in the ordered mesoporous carbon matrices. The XRD pattern of the OMC exhibits weak and broadening diffraction peaks of \( \text{WO}_3 \) due to the incomplete elimination as a result of carbon encapsulation effect (Fig. S7†). The corresponding EDX spectrum displays the existence of trace W elements (Fig. S8†). Moreover, the residual \( \text{WO}_3 \) nanoparticles can be observed through the corresponding STEM and elemental mapping images (Fig. 3e–h). Nitrogen sorption isotherms of the OMC show representative type-IV curves with \( \text{H}_2 \) hysteresis loops (Fig. S9a†). The BET surface area and pore volume increase to \( \sim 387 \text{ m}^2 \text{ g}^{-1} \) and \( \sim 0.84 \text{ cm}^3 \text{ g}^{-1} \), respectively (Fig. S9b†). The pore size distribution curve shows a new
additional pore size distribution located at ~3.2 nm, indicating the efficient removal of WO₃ by HF.

The effect of the pyrolysis temperature is explored to gain insight into the confinement synthesis process. When being pyrolyzed at 500 °C under N₂, no obvious WO₃ nanocrystals in the ordered mesoporous carbon matrices can be observed from the TEM image (Fig. 4a). However, large particles appear and the ordered mesostructure is broken partly (Fig. 4b) when the temperature is increased to 600 °C. The size of the WO₃ particles is estimated to be 16.6 ± 5.0 nm from the size statistics diagram (Fig. 4b, inset). On further increasing the temperature to 650 °C, WO₃ nanowires can be observed from the TEM image (Fig. 4c). The change of the mesostructure is mainly due to the increased particle size of WO₃ with increased temperature and can also be demonstrated by SAXS patterns (Fig. S10†). A number of diffraction peaks are obtained from the SAXS patterns with the increased pyrolysis temperature, demonstrating that the ordered mesostructure is broken. HRTEM images (Fig. 4d–f) and the corresponding SAED patterns (Fig. 4g–i) also demonstrate the transfer process from an amorphous tungsten precursor to highly crystallized WO₃ nanowires, which can also be evidenced by the XRD patterns (Fig. S11†). In addition, the decreased surface area and pore size can also be ascribed to the growth of WO₃ nanocrystals and the shrinkage of the mesopore framework with the increased pyrolysis temperature (Fig. S12†). Interestingly, ordered mesoporous WO₃ can also be obtained without using a carbon precursor, while larger nanocrystals would be formed at the same pyrolysis temperature, which can be observed from the HRTEM image (Fig. S13†).

Based on the above observations, we propose that the mesoporous carbon matrices play an important role in the confinement synthesis of ultrasmall WO₃ nanocrystals. With the evaporation of THF, the co-assembly process occurs between precursors and the PEO segment of PEO-b-PS via hydrogen bonds, which further induces the formation of spherical-like PEO-b-PS/WCl₆/resol composite micelles with a hydrophobic PS segment as the core. Subsequently, resols are further polymerized into 3D resol networks, in which the W species are uniformly distributed after thermosetting at 100 °C. Meanwhile, the formed spherical-like micelles assemble and pack into the highly ordered as-made mesoporous W/resol composites (as-made sample). After pyrolysis at 500 °C, the amphiphilic diblock copolymer PEO-b-PS templates can be decomposed, leading to uniform mesopores. Meanwhile, the resol molecules can be further polymerized and carbonized into amorphous mesoporous carbon matrices, which lock the amorphous W species well. Pyrolysis at 550 °C leads to the crystallization of the amorphous tungsten species into WO₃ nanocrystals. The particles can be limited to ~3 nm due to the confinement effect of carbon matrices. In contrast, larger WO₃ nanocrystals can be observed without the carbon matrix at the same temperature, further demonstrating that the confinement effect is effective. On increasing the pyrolysis temperature to 600 °C, the ultrasmall WO₃ nanocrystals aggregate into larger ones due to the oriented attachment growth mechanism.²¹ At this moment, the growth driving force shows a stronger impact on the sample than the confinement one by the carbon matrices. When the pyrolysis temperature is increased to 650 °C, the large nanocrystals further aggregate and grow into nanowires along the (100) direction, which cannot be covered in the carbon matrices anymore and appear in the external surface of the mesoporous carbon matrices. Meanwhile, the mesostructure is totally destroyed. The transition process from ultrasmall nanocrystals to nanowires demonstrates that the crystallization process is dominated by the balance between growth and the confinement force. Consequently, by controlling the addition of the resol precursor and the subsequent pyrolysis temperature, ultrasmall WO₃ nanocrystals (~3 nm) embedded in the ordered mesoporous carbon matrices can be obtained.

The resultant OMC-WO₃ composites were used as the anode materials for lithium-ion batteries. Cyclic voltammetry (CV) curves of the OMC-WO₃ composite electrode were recorded at a scan rate of 0.1 mV s⁻¹ in the voltage range of 0.01–3.0 V (Fig. 5a). During the first cycle, characteristic reduction peaks are measured at ~0.7 and ~0.4 V, corresponding to the decomposition of WO₃ to metal W and Li₂O and the formation of an irreversible solid electrolyte interphase (SEI) layer during the discharge process, respectively.²² In contrast, an oxidation peak at ~1.2 V can be observed during the charge process, corresponding to the decomposition reaction of Li₂O. The reduction peaks disappear in the subsequent cycles, which can be attributed to the formation of the SEI layer and irreversible electrochemical reactions between Li-ion and electrode materials. In addition, the CV curves tend to overlap after the second cycle, suggesting the excellent cycling stability of the electrode material.
The galvanostatic charge/discharge curves of the 1st, 2nd, 10th, 50th, and 100th cycles were recorded at a current density of 0.1 A g\(^{-1}\) between 0.01 and 3.0 V (Fig. 5b). A short plateau can be detected at \(0.7\) V (vs. Li/Li\(^+\)) from the discharge curve for the first cycle, corresponding to the formation of W and Li\(_2\)O. The short plateau disappears from the second cycle due to the formation of an SEI layer and irreversible electrochemical reactions, which is in good accordance with the CV results. The initial discharge and charge capacities are as high as 1275 and 717 mA h g\(^{-1}\), respectively, with an initial coulombic efficiency of 56.2%. The discharge capacity decreases to 712 mA h g\(^{-1}\) at the second cycle. Such an irreversible capacity loss can be attributed to the formation of the SEI layer and irreversible electrochemical reactions.

The rate capability of the OMC–WO\(_3\) composites was evaluated at various current densities varying from 0.1 to 2 A g\(^{-1}\) (Fig. 5c). The OMC, OMC–WO\(_3\)-70%, OMC–WO\(_3\)-40%, OM-WO\(_3\), MC-WO\(_3\) and WO\(_3\)-NW-C composites were used as control samples. The average specific capacities of the OMC–WO\(_3\) composites are 410, 301, 190, 128, and 68 mA h g\(^{-1}\) at current densities of 0.1, 0.2, 0.5, 1, and 2 A g\(^{-1}\), respectively. The capacity can quickly return to 420 mA h g\(^{-1}\) when the current density is turned back to 0.1 A g\(^{-1}\) after high current tests. In contrast, the rate capacities of control samples are
Conclusions

In summary, a facile mesoporous carbon matrix confinement growth strategy is developed to prepare ultrasmall WO3 nanocrystals through an EISA and subsequent precise pyrolysis method. In this case, the resol and WCl6 are co-assembled with PEO-b-PS into ordered mesostructures. The polymer/carbon frameworks direct the growth of tiny WO3 nanoparticles with a small size of ~3 nm during the high temperature treatment, most importantly, which are uniformly embedded in the carbon network. The obtained OMC–WO3 composites with a carbon content of 16% exhibit a high surface area of ~157 m² g⁻¹, a large pore volume of ~0.25 cm³ g⁻¹, and a uniform pore size of ~11.3 nm. Owing to their unique mesostructures, a high lithium storage of 440 mA h g⁻¹ can be obtained at a current density of 0.1 A g⁻¹ even after 100 cycles, showing superb stability when being used as anodes for lithium storage. We envisage that this strategy may provide a new opportunity to develop high capacity long life anodes for practical applications.

Conflicts of interest

There are no conflicts to declare.

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