Conductive WO$_{3-x}@$CNT networks for efficient Li-S batteries

Bo Yu and Yuanfu Chen

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

Email: botonyyu@gmail.com

Abstract. Oxygen-vacancy-containing WO$_{3-x}$ nanodots homogeneously decorated on conductive CNT networks (WO$_{3-x}@$CNT) have been synthesized by a simple and industrial spray-drying approach followed by annealing. Benefiting from the enhanced conductivity of CNT networks and the effective absorption for polysulfides by ultra-small polar WO$_{3-x}$ nanodots, the designed WO$_{3-x}@$CNT/S cathode demonstrates excellent electrochemical performance, with an excellent rate capability (1000.1 and 518.2 mAh g$^{-1}$ at 0.2 and 3 C, respectively), a high reversible specific capacity of 754.1 mAh g$^{-1}$ at 1 C after 50 cycles.

1. Introduction

Lithium-sulfur (Li-S) battery has proved to be one of the most promising next-generation energy-storage devices [1, 2]. However, there continue to be many problems to limit its applications. The nature of inherently insulating of sulfur and Li$_2$S still limit the utilization of the active materials. It has been demonstrated that highly conductive materials such as carbon nanotubes (CNT) and graphene can be used as the electrode materials [3-5]. However, the severe shuttle effect of polar lithium polysulfides (LiPS) generated during cycling lead to the irreversible loss of active materials. To solve this problem, a large number of W-based polar compounds, such as WS$_2$ and W$_2$C, have been researched as sulfur hosts to provide active sites for the adsorption of LiPS [6, 7]. However, it has been noted that the previous synthesis methods of above materials are too complex. Although hydrothermal method can be used to synthesize nanosized compounds, it is not conducive to large-scale application. Direct annealing under high temperature is simple, but serious agglomeration is inevitable. So, previous methods usually need multistep process [8-11].

Herein, we put forward a facile strategy to synthesize porous conductive WO$_{3-x}@$CNT networks by using industrial spray-drying approach followed by annealing to achieve a large-scale production. The WO$_{3-x}@$CNT/S cathode displays excellent electrochemical performance with an outstanding reversible capacity for Li-S batteries. The excellent performance can be attributed as follows: (1) The existence of oxygen vacancy in WO$_{3-x}$ can efficiently facilitate the charge transfer to improve the conductivity of host materials compared with pure WO$_3$ [12, 13]. (2) The porous architecture is fabricated by WO$_{3-x}$ nanodots homogeneously grown on the highly conductive CNT networks, which provides efficient electron transfer pathway [14, 15]. (3) Ultrasmall polar WO$_{3-x}$ nanodots can offer many heterogeneous adsorption sites for LiPS, which can restrain the shuttle effect [6]. Because of such advantages, WO$_3$. $x_0@$CNT/S cathode delivers excellent electrochemical performances with the rate capability of 1000.1 and 518.2 mAh g$^{-1}$ at 0.2 and 3 C, respectively, a high reversible capacity of 754.1 mAh g$^{-1}$ at 1 C after 50 cycles.
2. Experimental

2.1. Synthesis of CNT and WO$_3$-x@CNT

The WO$_3$-x@CNT was prepared by a facile spray-drying method followed by annealing. Briefly, 10 g of 5 wt% commercial CNT conductive paste (LB200-54, Cnano Technology Ltd.), and then 1.87 g (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O) were dissolved in 500 mL DI water and the solution was stirred well for 6 h. Then, the above suspension was ultrasonicated for 1 h. Subsequently, the above solution was treated with a commercial spray-drying procedure (SUNYI Spray Dryer SP-1500). Finally, the black product was collected and annealing under Argon gas (150 sccm) at 500 °C for 3 h with a heating speed of 5 °C min$^{-1}$ to get the WO$_3$-x@CNT. The CNT was synthesized by the similar process except that (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O) is not added.

2.2. Synthesis of CNT/S and WO$_3$-x@CNT/S

The CNT or WO$_3$-x@CNT and sublimed sulfur powder in a 1:4 mass ratio was mixed and then the samples were put in argon filled stainless steel autoclave and sealed at 155 °C for 12 h, and then the CNT/S and WO$_3$-x@CNT/S were obtained.

2.3. Characterizations

The phases of as prepared CNT and WO$_3$-x@CNT were performed by XRD (Rigaku D/MAX-rA diffractometer). The surface morphologies, microstructure and elemental compositions of the samples were characterized using scanning electron microscopy (SEM, JSM-7000F, JEOL), transmission electron microscope (TEM, Tecnai F20) and X-ray photoelectron spectroscopy (XPS, Kratos XSAM800).

2.4. Electrochemical Measurements

The cathode slurry was prepared by mixing 80 wt% active materials (CNT/S and WO$_3$-x@CNT/S), 10 wt% polyvinylidene fluoride binder (PVDF) and 10 w% carbon black (super P Timcal) in N-methyl-2-pyrrolidone (NMP), and then uniformly painted the slurry onto aluminum foil, subsequently dried at 60 °C in vacuum for 12 h. Lithium foil was used as counter electrode, Celgard 2400 was used as membranes. 1 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) and 0.1 M LiNO$_3$ additive dissolved in 1,3-dioxolane (DOL)/1,2-dimethoxy-ethane (DME) (1:1, v/v) was used as the electrolyte. The specific capacity of mAh g$^{-1}$ was calculated based on the mass of sulfur, and the active material loading is ~1.5 mg cm$^{-2}$.

3. Results and Discussion

Scanning electron microscopy (SEM) images of WO$_3$-x/CNT are shown in Figure 1a-b. One can be clearly observed is the porous structure constructed by CNT conductive networks, which can accommodate more electrolyte and LIPS. Moreover, from the transmission electron microscopy (TEM) images shown in Figure 2a-b, the ultrasmall WO$_3$-x nanodots are evenly distributed on the CNT networks, and no obvious particles can be seen. As can be observed in the inset of Figure 2b, interestingly, there are no large-sized particles or aggregation can be seen. These results highlighted the advantages of spray-drying method in controllable synthesizing ultra-small nanocomposites. As shown in Figure 2c, HAADF and corresponding EDS element mappings of C, W and O indicate the evenly distribution of WO$_3$-x on the conductive CNT networks.
Figure 1. (a-b) SEM images of WO$_3$-x/CNT.

Figure 2. (a-b) TEM images and (c) EDS spectra of WO$_3$-x/CNT.

Figure 3a displays the XRD patterns of CNT and WO$_3$-x@CNT. As shown in Figure 3a, CNT displays typical peaks at 26.2° and 44.4°, which can be indexed to the (002) and (100) (JCPDS 75-1621) diffractions. The characteristic peaks observed at 23.6°, 33.6°, 41.5°, 48.4°, 54.6° and 60.3° correspond to the (200), (220), (222), (400), (420), and (422) planes of the tetragonal phase of WO$_3$ (JCPDS 46-1096), respectively. The full width at half maxima (FWHM) of WO$_3$-x is much larger than that of previous literature, which demonstrates the ultrasmall size of WO$_3$-x [13, 16-18]. The XPS was carried out to study the chemical environment and valence state in the WO$_3$-x@CNT. Figure 3b displays the XPS survey spectrum of the WO$_3$-x@CNT proves the existence of C, O and W elements. Figure 3c shows the W 4f spectra of WO$_3$-x@CNT, the strong peaks at ~38.2 (W 4f$_{5/2}$) and ~36.1 eV (W 4f$_{7/2}$) were attributed to W$^{6+}$ oxidation state. The binding energy at around 34.1 eV is ascribed to W$^{5+}$ (4$<$&$<$6), which is in agreement with previously reported reports [17, 19]. The presence of W$^{5+}$ on the surface is advantageous to increase the conductivity of electrodes, making for the enhancement of rate performance. Moreover, the wide peak located at around ~41.9 eV is corresponding to the W 5p$_{3/2}$ [20]. The high-resolution C 1s spectra of WO$_3$-x@CNT is shown in Figure 3d, one strong peak at 284.8 eV is corresponding to C-C species, and three weak component peaks located at 285.7 and 287.1, C=O, C=O, respectively [21]. From XPS data, we can conclude that there are many functional groups in CNT generated during the annealing process. These functional groups can further enhance the adsorption of polysulfides [22].
To evaluate the electrochemical properties of WO$_{3-x}$/CNT cathode, CR2025 coin cells are assembled with lithium foil as the anode. Figure 4a shows the cyclic voltammogram of the WO$_{3-x}$/CNT/S cathode at 0.1 mV s$^{-1}$. In the first cathodic scan, the peaks at 2.34 V (Peak A) and 2.04 V (peak B) are assigned to the reduction of sulfur from S$_8$ to the soluble lithium polysulfides (Li$_2$S$_{2x}$; 4<x<8) followed by reduction to insoluble Li$_2$S. Correspondingly, the anodic peaks located at around 2.4 V (peak C) is attributed to the conversion from Li$_2$S to lithium polysulfides (Li$_2$S$_{2x}$; 4<x<8) and finally to the sulfur. Figure 4b displays the charge/discharge curves of WO$_{3-x}$/CNT/S cathode at first 0.1 C cycle. WO$_{3-x}$/CNT/S cathode plays high initial discharge capacities of 1143.5 mAh g$^{-1}$. The discharge plateaus at around 2.3 V and 2.1 V are corresponding to the formation of long-chain lithium polysulfides (Li$_2$S$_{8}$ (4<x<8)) and short-chain Li$_2$S$_2$ and Li$_2$S. Figure 4c shows the cycling performance of WO$_{3-x}$/CNT/S cathode. After two cycles at 0.1 C, a capacity of WO$_{3-x}$/CNT/S is maintained at ~754.1 mAh g$^{-1}$ after 50 cycles at 1 C, the capacity retention is calculated to be 96.6 %, corresponding to a low capacity decay rate of 0.091 % per cycle. After cycling, the coulombic efficiency of the WO$_{3-x}$/CNT/S cathode is higher than 98 %, indicating that the shuttling phenomenon has been efficiently suppressed. Figure 4d illustrates the charge/discharge profiles of the WO$_{3-x}$/CNT/S cathode at 1 C rate. We can clearly find the voltage plateaus almost no change. As shown in Figure 4e, WO$_{3-x}$/CNT/S cathode also displays outstanding rate performance at different rates from 0.2 C to 3C. The WO$_{3-x}$/CNT/S electrode delivers high discharge capacities of 1000.1 mAh g$^{-1}$ at 0.2 C, 877.3 mAh g$^{-1}$ at 0.5 C, 788.7 mAh g$^{-1}$ at 1 C, 673.8 mAh g$^{-1}$ at 2 C, 518.2 mAh g$^{-1}$ at 3 C rate, corresponding charge/discharge profiles are shown in Figure 4f. The above results indicate that the porous conductive WO$_{3-x}$/CNT networks can effectively restrain the dissolution of LIPS [1].

Figure 3. (a) XRD image of CNT and WO$_{3-x}$/CNT, (b) XPS survey spectrum, (c) W 4f XPS spectrum, and (d) C 1s XPS spectrum of the WO$_{3-x}$/CNT.
4. Conclusions

In summary, we have rational designed WO$_{3-x}$/CNT networks by using industrial spray-drying method followed by annealing to realize a large-scale production. Due to polar and oxygen-vacancy-containing ultrasmall WO$_{3-x}$ nanodots and conductive and porous architecture of CNT networks, the as prepared WO$_{3-x}$/CNT can be used as sulfur host materials for Li-S batteries. The WO$_{3-x}$/CNT/S cathode exhibits excellent cycling performance and rate capability. These results offer a simple way to design and prepare ultrasmall nanodots on conductive porous networks for Li-S batteries.
Acknowledgments
The research was supported by the National Natural Science Foundation of China (Grant Nos. 21773024, 51372033), and National High Technology Research and Development Program of China (Grant No. 2015AA034202).

References
[1] Xue W, Shi Z, Suo L, Wang C, Wang Z, Wang H, So KP, Maurano A, Yu D, Chen Y, Qie L, Zhu Z, Xu G, Kong J, Li J 2019 Intercalation-conversion hybrid cathodes enabling Li–S full-cell architectures with jointly superior gravimetric and volumetric energy densities Nat. Energy 4 374
[2] Yu B, Chen Y, Wang Z, Chen D, Wang X, Zhang W, He J, He W 2020 1T-MoS2 nanotubes wrapped with N-doped graphene as highly-efficient absorbent and electrocatalyst for Li–S batteries J. Power Sources 447 227364
[3] Zhang X, Yu B, Wang X, Yang D, Chen Y 2019 Self-assembled globular clusters-like cobalt hexacyanoferrate/carbon nanotubes hybrid as efficient nonprecious electrocatalyst for oxygen evolution reaction J. Power Sources 434 126670
[4] Wu H, Li Y, Ren J, Rao D, Zheng Q, Zhou L, Lin D 2019 CNT-assembled dodecahedra core@nickel hydroxide nanosheet shell enabled sulfur cathode for high-performance lithium-sulfur batteries Nano Energy 55 82
[5] Hu Y, Yu B, Li W, Ramadoss M, Chen Y 2019 W2C nanodot-decorated CNT networks as a highly efficient and stable electrocatalyst for hydrogen evolution in acidic and alkaline media Nanoscale 11 4876
[6] Zhou F, Li Z, Luo X, Wu T, Jiang B, Lu L, Yao H, Antonietti M, Yu S 2018 Low cost metal carbide nanocrystals as binding and electrocatalytic sites for high performance Li–S batteries Nano Lett. 18 1035
[7] Park J, Yu B, Park JS, Choi JW, Kim C, Sung Y, Goodenough JB 2017 Tungsten disulfide catalysts supported on a carbon cloth interlayer for high performance Li–S battery Adv. Energy Mater. 1602567
[8] Jin Z, Hu P, Xu W, Zhou J, Guo W, Chen Y, Qiu C 2019 Hydrothermal synthesis and gas sensing properties of hybrid WO3 nano-materials using octadecylamine J. Alloy. Compd. 785 1047
[9] Mojaddami M, Simchi A 2020 First demonstration of photoelectrochemical water splitting by commercial W-Cu powder metallurgy parts converted to highly porous 3D WO3/W skeletons Int. J. Hydrogen Energ. 45 6369
[10] Li N, Chang T, Gao H, Gao X, Ge L 2019 Morphology-controlled WO3-x homojunction: hydrothermal synthesis, adsorption properties, visible-light-driven photocatalytic and chromic properties Nanotechnology 30 415601
[11] Covei M, Bogatu C, Periu D, Duta A, Visa I 2019 Self-cleaning thin films with controlled optical properties based on WO3-rGO Ceram. Int. 45 9157
[12] Koo B, Kim K, Ahn H 2018 Switching electrochromic performance improvement enabled by highly developed mesopores and oxygen vacancy defects of Fe-doped WO3 films Appl. Surf. Sci. 453 238
[13] Zheng XD 2019 The influence of ion implantation-induced oxygen vacancy on electrical conductivity of WO3 thin films Vacuum 165 46
[14] Yu B, Qi F, Zheng B, Hou W, Zhang W, Li Y, Chen Y 2018 Self-assembled pearl-bracelet-like CoSe2–SnSe2/CNT hollow architecture as highly efficient electrocatalysts for hydrogen evolution reaction J. Mater. Chem. A 6 1655
[15] Li W, Chen Y, Yu B, Hu Y, Wang X, Yang D 2019 3D hollow Co–Fe–P nanoframes immobilized on N, P-doped CNT as an efficient electrocatalyst for overall water splitting Nanoscale 11 17031
[16] Shinde PA, Lokhande AC, Patil AM, Lokhande CD 2019 Facile synthesis of self-assembled WO$_3$ nanorods for high-performance electrochemical capacitor J. Alloy. Compd. 770 1130

[17] Li Y, Chang K, Tang H, Li B, Qin Y, Hou Y, Chang Z 2019 Preparation of oxygen-deficient WO$_3$-nanosheets and their characterization as anode materials for high-performance Li-ion batteries Electrochim. Acta 298 640

[18] Chen Y, Wang L, Gao R, Zhang Y, Pan L, Huang C, Liu K, Chang X, Zhang X, Zou J 2019 Polarization-Enhanced direct Z-scheme ZnO-WO$_3$$_x$ nanorod arrays for efficient piezoelectric-photoelectrochemical water splitting Applied Catalysis B: Environmental 259 118079

[19] Okada M, Ono K, Yoshio S, Fukuyama H, Adachi K 2019 Oxygen vacancies and pseudo Jahn–Teller destabilization in cesium–doped hexagonal tungsten bronzes J. Am. Ceram. Soc. 102 5386

[20] Hu Y, Yu B, Ramadoss M, Li W, Yang D, Wang B, Chen Y 2019 Scalable synthesis of heterogeneous W–W$_2$C nanoparticle-embedded CNT networks for boosted hydrogen evolution reaction in both acidic and alkaline media ACS Sustain. Chem. Eng. 7 10016

[21] Li W, Yu B, Hu Y, Wang X, Yang D, Chen Y 2019 Core–Shell Structure of NiSe$_2$ Nanoparticles@Nitrogen-Doped Graphene for hydrogen evolution reaction in both acidic and alkaline media ACS Sustain. Chem. Eng. 7 4351

[22] Lin W, Chen Y, Li P, He J, Zhao Y, Wang Z, Liu J, Qi F, Zheng B, Zhou J, Xu C, Fu F 2015 Enhanced performance of lithium sulfur battery with a reduced graphene oxide coating separator J. Electrochem. Soc. 162 A1624