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Low-cost and facile one-pot synthesis of pure single-crystalline ε-Cu$_{0.95}$V$_2$O$_5$ nanoribbons: high capacity cathode material for rechargeable Li-ion batteries†

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Pure single-crystalline ε-Cu$_{0.95}$V$_2$O$_5$ nanoribbons have been successfully synthesized *via* a facile one-pot solvothermal route using low-cost raw materials. The obtained materials can react electrochemically with 2.64 Li in a reversible fashion and thus greatly expands the range of cathode choices.

The growing demand for high-energy density applications such as for alternative energy and electric transportation has triggered significant research efforts on high-capacity lithium ion batteries (LIBs).[1] However, even after decades of intensive efforts, the low capacity of the cathode materials still limits its development.[2] Enhancements in capacity necessarily require passage from the present Li insertion/deinsertion compounds limited by 1e$^-$/formula unit to novel, advanced chemistries based on multi-electron reaction materials.[3]

Metal vanadates, as one of the most important family of functional inorganic materials, have numerous applications in the fields of catalysts,[4a] optical devices,[4b] and magnetic materials[4c] as well as battery materials.[4d–g] Intense interest has been focused on Ag–V–O and Cu–V–O systems because of their particular reactivity toward lithium by combination displacement/intercalation (CDI) electrode reactions, which enable multi-electron charge transfers, and thus could lead to impressive capacity gains.[3a,5] Among them, silver vanadium oxide (Ag$_2$V$_4$O$_{11}$, SVO) is of special interest because it can offer higher capacity.[5a,b] However, the silver displacement reaction shows lack of reversibility and thus SVO is restricted to primary lithium batteries. As for the rich family of copper vanadium oxides (CVOs),[3a,5e–f,6] Tarascon reported that Cu$_{2.33}$V$_4$O$_{11}$ can operate through a reversible process involving lithium insertion and metal extrusion.[3a] Unfortunately, up to now, these encouraging CVOs can only be synthesized by high-cost, energy consuming solid-state synthesis processes,

which casts a shadow over their application as high-capacity cathode materials in rechargeable LIBs.

One-dimensional (1D) structures such as nanowires and nanoribbons (NRs) have been receiving increased interest in energy-harvesting devices.[7] 1D material-based LIBs offer significant improvements in power and energy density over bulk electrodes because the 1D geometry enables benefits such as large surface to volume ratio to contact with electrolyte, continuous conducting pathways for electrons through the electrodes, facile strain relaxation during battery operation, and so on.[8] Although various methods have been developed for the synthesis of 1D nanostructures including vapor–liquid–solid process,[9a] solvothermal,[9b] template-assisted method,[9c] solution–liquid–solid route,[9d] and thermolysis,[9e] all these methods suffer from more or less severe drawbacks such as the requirement of special equipment, complicated time and energy consuming preparation process, and impossibility of large scale fabrication. Compared with the numerous publications on elemental and binary 1D materials, there are few reports on the controlled synthesis of ternary materials with 1D morphology. To the best of our knowledge, up to now pure single-crystalline ε-Cu$_{0.95}$V$_2$O$_5$ (ε-CVO) has rarely been synthesized, to say nothing of 1D structures. Therefore, developing new strategies to synthesize pure single-crystalline ε-CVO NRs and then exploring its electrochemical performance toward lithium are of great importance.

Herein, we present a methodology that affords the precipitation of pure single-crystalline ε-CVO NRs in a facile, time-efficient and low-cost one-pot fashion, wherein neither templates nor surfactants are employed. Unexpectedly, the obtained ε-CVO NRs can react electrochemically with lithium ions in a reversible way, leading to a capacity of 292 mA h g^{-1} above 2 V, which is almost twice the gravimetric capacity of the state-of-the-art cathode materials, and thus greatly expands the range of cathode choices.

A hydrothermal redox polymerization process is proposed to prepare ε-CVO NRs, wherein Cu(NO$_3$)$_2$·3H$_2$O and V$_2$O$_5$ are used as the metal precursors and acetophenone is employed as the reducing agent. It should be noted that although acetophenone was previously used as a ligand and/or stabilizer agent only,[10] we now utilize its potential reducibility for the first time, to effectively synthesize ε-CVO. Moreover, owing to its appropriate reducing strength, low-cost metal precursors in

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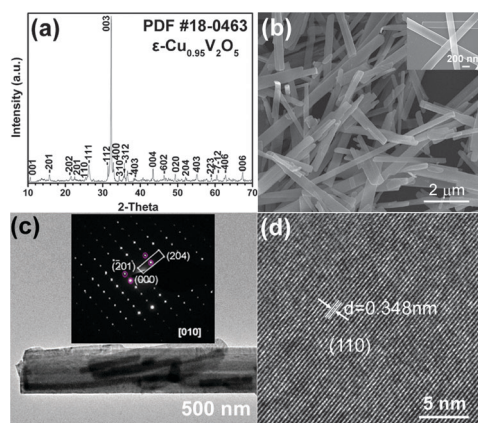
Fig. 1 (a) XRD, (b) SEM, (c) TEM and (d) HRTEM images of the as-synthesized ε-CVO nanoribbons. The inset in (b) is the magnified SEM image and the inset in (c) is the [010] zone SAED pattern. The regular appearance of some forbidden spots is marked with small red circles.

highest metal-valence can be employed, while expensive counterparts were necessary in previous synthesis route. Fig. S1 (ESI†) illustrates the reaction pathway toward ε-CVO NRs in the presence of acetophenone, in contrast to the formation of CuV_2O_6 NRs in its absence (Fig. S2†). The reaction with lithium of the obtained ε-CVO NRs is reversible, while CuV_2O_6 shows poor reversibility and is thus limited to primary lithium batteries.[4d,5e] It is found that noticeable amounts of benzaldehyde and benzoic acid are present in the final reaction solution (Fig. S3†). The oxidation of acetophenone to benzaldehyde and benzoic acid should be responsible for the formation of Cu^+, V^{4+} and V^{3+} in the ε-CVO product from the Cu^{2+} and V^{5+} precursors. Then, the obtained ε-CVO nuclei are aggregated and grow into lamellar microstructures in accordance with the well-known "Ostwald ripening mechanism". As reaction progresses, "a splitting process" occurs, during which the layered ε-CVO gradually split into nanoribbons (Fig. S4†).

Fig. 1a shows the X-ray diffraction (XRD) pattern for the product obtained with 150 μL acetophenone and reaction time of 15 h. All the diffraction peaks can be indexed to the monoclinic ε-CVO phase (space group $C2/m$, PDF #18-0463). It should be noted that, in order to obtain pure ε-CVO samples, the amount of acetophenone should be limited in the range of 120–200 μL. Beyond this range, either no ε-CVO phase or ε-CVO phase mixed with other impurities is formed (Fig. S5a†). This can be reasonably attributed to the fact that the reducing capacity of the present reaction system is highly dependent on the amount of acetophenone. XRD shows that a hydrated volborthite $Cu_3(OH)_2V_2O_7 \cdot 2H_2O$ crystalline intermediate phase is initially formed (Fig. S5b†) and then is gradually but completely transferred to ε-CVO with the help of acetophenone, provided the reaction time is prolonged to 15 h. In other words, the preparation of ε-CVO is controllable by the amount of reducing agent and dwell time. High-resolution photoelectron spectroscopy (XPS) spectra (Fig. S6†) reveals that the major copper species in the ε-CVO sample is Cu^+ together with a small amount of Cu^{2+}, and that V is mixed-valent between V^{3+}, V^{4+} and V^{5+}. This reduction of Cu^{2+}

and V^{5+} is consistent with the oxidation of acetophenone. The energy dispersive X-ray spectroscopy (EDS) pattern (Fig. S7†) shows that the as-synthesized NRs are composed of Cu, V and O, and the atomic ratio of Cu to V is 0.48, which is close to the nominal value in ε-CVO. Typical SEM (Fig. 1b) and TEM (Fig. 1c) images show 1D NRs morphology of the as-synthesized ε-CVO, which exhibits smooth side edges with length of several to tens of micrometres, a rectangular cross section on the tip surface with width of 200–500 nm, and thickness of 40–60 nm. The microstructure of the product is further studied by means of selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). The SAED pattern taken along [010] zone axis orientation was obtained (Fig. 1c inset). It should be noted that this [010] SAED pattern is unconventional since a regular appearance of some forbidden spots (marked with small red circles) is observed besides the allowed diffraction spots; detailed analysis is presented in Fig. S8†. Fig. 1d shows the HRTEM lattice image in which the clear lattice fringes display good crystallinity of the product. The planar spacing is measured to be about 0.348 nm, which is in good agreement with the (110) crystalline plane of ε-CVO, indicating that highly pure single-crystalline ε-CVO NRs (for crystal structure see Fig. S9†) is successfully synthesized.

The cathode performance of the ε-CVO NRs has been tested with respect to Li metal. Fig. 2 shows a typical galvanostatic signature for a ε-CVO/Li cell cycled between 2 and 3.6 V at 20 mA g^{-1}. During the first discharge, the potential drops noncontinuously in a stepwise fashion: initially the potential drops abruptly down to reach the first sloping potential plateau at 2.83–2.73 V having a capacity of about 0.79 Li, and then the potential drops smoothly and continuously down to the second inclined potential plateau at 2.6–2.55 V, whose length is about 0.84 Li, finally an extra 1.01 Li can be reacted as the potential reaches 2 V. Upon recharge, most of the 2.64 Li uptake lithium can be removed, leading to a reversible capacity up to 292 mA h g^{-1} (200 mA h g^{-1}, cut-off voltage: 2.4 V), which represents almost twice the gravimetric capacity of benchmark cathode materials such as $LiCoO_2$ or $LiFePO_4$. The subsequent charge/discharge curves show that ε-CVO electrode exhibits stable capacity for six cycles (Fig. 2 inset), indicating that it can react electrochemically with Li ion in a reversible way and thus greatly expands the range of cathode choices. The capacity gradually decreases and reaches
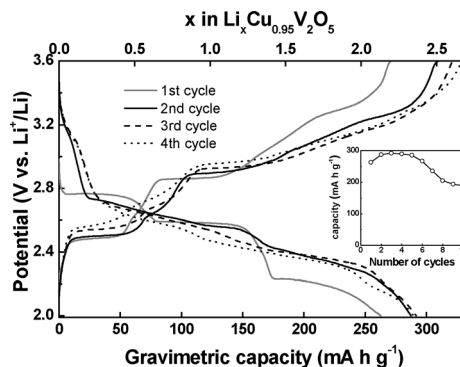

Fig. 2 Room-temperature potential composition–capacity profile for a ε-CVO/Li cell cycled in the 2–3.6 V voltage window at 20 mA g^{-1}.
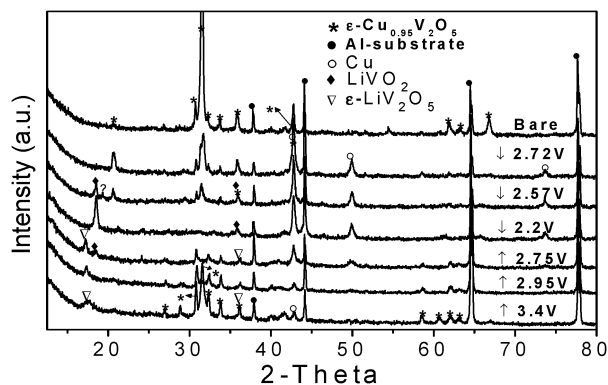
Fig. 3 (a) *Ex-situ* XRD patterns of ε-CVO electrode, as fabricated, discharged (↓) or charged (↑) to different voltages and charged to 3.6 V.

189 mA h g^{-1} at the 10th cycle. Although this value is not bad the capacity retention rate is lower than that of state-of-the-art electrode materials. Considering that the commercial electrodes have reached optimum performance, it is expected that improved capacity retention property can be accomplished in the future.

Fig. 3a shows *ex-situ* XRD patterns of ε-CVO electrodes recovered from multiple cells discharged or charged to selected voltages. As a ε-CVO/Li cell is discharged to 2.72 V, the rapid growth of Bragg peaks located at 42.7, 50, and 73.7° indicates the growth of metallic copper, meanwhile, a substantial decrease in peak intensity of the ε-CVO phase is observed. The extrusion of metallic copper is also confirmed by the SEM-EDS results shown in Fig. S10†. Several particles with greater contrast value in the electrode are separated out, and the atomic ratio of Cu to V for such a precipitate increases to 2.22, implying that the deposited metallic copper is likely to agglomerate, which is in accordance with the Cu dendrites reported in Cu$_{2.33}$V$_4$O$_{11}$[3a] and Cu$_{1.1}$V$_4$O$_{11}$[5f]. Afterwards, the addition of extra Li down to 2.2 V leads to the appearance of LiVO$_2$ phase peaks and the disappearance of peaks of the ε-CVO phase in the XRD pattern. The end result is a composite electrode made of an amorphous Li–V–O matrix containing a crystallized material and dispersed metallic copper. Upon recharge, we first note the related decreased intensity of metallic copper and LiVO$_2$ and new peak evolution of ε-LiV$_2$O$_5$ and Cu$_{0.95}$V$_2$O$_5$. When the cell is further recharged to 3.4 V, Bragg peaks of metallic copper together with LiVO$_2$ totally disappear, so that the structure of the initial structure of ε-CVO is regained. Therefore, the overall process is reversible and the underlying mechanism might constitute a delicate balance between three processes: ion diffusion (Cu-out/Li-in and *vice versa*), V reduction/oxidation, and rearrangement of the initial electrode material. Decreased crystallinity with cycling might be a consequence of the strong and rigid double (V$_2$O$_5$)$_n$ planes (Fig. S9†) which show lack of flexibility; the only way to minimize energy so as to accommodate guest species will be a gliding of the (V$_2$O$_5$)$_n$ planes. This inflexibility of the structure can not keep long-distance structure registry in the fully discharged state thus leading to a decrease in crystallinity of the regained ε-CVO.

In summary, we have developed a facile, time-efficient, and low-cost one-pot solution approach to the large-scale synthesis of pure single-crystalline ε-CVO NRs, wherein neither template nor surfactant is used and acetophenone as a reducing agent plays a decisive role. When employed as cathode material, ε-CVO can react with 2.64 Li (292 mA h g^{-1}) through a reversible process, during which Cu metal is extruded from the structure but is readmitted as cycling is reversed. Through a material survey, we deduce that due to the (V$_2$O$_5$)$_n$ framework inflexibility, the displacement reaction falls short of 100% efficiency. The obtained data for ε-CVO can provide helpful information for the operating mechanisms of cycle life of Li intercalation into transition metal vanadates based on CDI mechanism, which will greatly expand the range of cathode choices and could assist long-term endeavors in developing high capacity cathodes for rechargeable LIBs.

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