A Bowknot-like RuO$_2$ quantum dots@V$_2$O$_5$ cathode with largely improved electrochemical performance†

Xiujuan Wei, Qinyou An, Qiulong Wei, Mengyu Yan, Xuanpeng Wang, Qidong Li, Pengfei Zhang, Bolun Wang and Liqiang Mai*

Bowknot-like RuO$_2$ quantum dots@V$_2$O$_5$ nanomaterials have been synthesized by a facile hydrothermal method followed by annealing treatment, which exhibit largely enhanced electrochemical performance. Especially, the RuO$_2$ quantum dots@V$_2$O$_5$ cathode delivers 160 mA h g$^{-1}$ at 1000 mA g$^{-1}$ after 100 cycles, which is much higher than 86 mA h g$^{-1}$ of the pure V$_2$O$_5$ cathode.

Introduction

With the global energy and environmental problems becoming more and more severe, the development of environmentally friendly and efficient energy storage systems are urgently required. Lithium-ion batteries (LIBs) play an important role as energy storage devices for use in portable electronic devices, electric vehicles and electric grid due to their high energy-density, high safety and environmentally benign nature. Among the potential cathode materials, vanadium pentoxide (V$_2$O$_5$) is one of the most promising materials for LIBs owing to its low cost, high energy density, easy synthesis, as well as a relatively high theoretical capacity of 294 mA h g$^{-1}$ in the voltage range of 4.0–2.0 V vs. Li$^+/Li$. Nevertheless, V$_2$O$_5$ suffers from poor diffusion coefficient of Li$^+$, poor electrical conductivities (10$^{-5}$–10$^{-3}$ S cm$^{-1}$) and poor structural stability, which limit the development of vanadium pentoxide electrode materials in LIBs.

In order to improve the electrochemical performances of V$_2$O$_5$ electrode materials, various nanostructures of V$_2$O$_5$ have been successfully synthesized, including nanowires, nanobelts, nanotubes and nanosheets. These nanostructures can shorten the diffusion distance of Li$^+$ and accommodate large volume change during the lithium intercalation and de-intercalation processes. Significant investigations have been carried out to develop unique nanostructured materials. For example, Shi et al. synthesized the LiV$_3$O$_8$ thin film with a mixed amorphous–nanocrystalline exhibiting high capacity and good capacity retention. Besides, the transportation of electrons within the electrode also exerts a significant impact on the rate capability of LIBs. The resistance arises from the low electronic conductivity of the electrode materials. Thus, it is required to use V$_2$O$_5$ in conjunction with another nanostructured material possessing higher electronic conductivity. For example, Chen et al. constructed the MWNT–V$_2$O$_5$ core–shell sponge for high power density. Zhang et al. fabricated carbon-coated V$_2$O$_5$ with high performance. RuO$_2$ exhibits high electronic conductivity (2.5 × 10$^4$ S cm$^{-1}$), fast Li$^+$ permeation and stable reaction interface (high coulombic efficiency above 98%), which has been extensively studied by many researchers. Maier and co-workers reported that using RuO$_2$ improved the electrode performance of porous LiFePO$_4$. RuO$_2$-containing composites reveal reversible capacities of 124 and 93 mA h g$^{-1}$ at rates of 2 C and 10 C, respectively. It is worth noting that quantum dots (QDs) with small size shorten the diffusion length for Li$^+$, which is beneficial to achieve cycling stability and rate capability. Han et al. constructed the V$_2$O$_5$ QDs–graphene hybrid nanocomposite exhibiting stable cycling ability and high reversible capacity. Mo et al. also synthesized the TiO$_2$ QDs–graphene nanosheets, which revealed enhanced electrochemical performance.

Herein, to take the advantages of RuO$_2$, QDs and V$_2$O$_5$, we designed and synthesized bowknot-like RuO$_2$ quantum dots@V$_2$O$_5$ (denoted as RQDV) nanomaterials via a facile and rapid hydrothermal synthesis method followed by annealing treatment. To our knowledge, the bowknot-like RQDV has not been reported before. As shown in Scheme 1, the RuO$_2$ QDs exhibit excellent electronic conductivity and fast Li$^+$ permeation. The RuO$_2$ QDs dispersed on the bowknot-like V$_2$O$_5$...
enhance the electronic conductivity of this material. The unique nanostructure with RuO₂ QDs dispersing on the V₂O₅ offers reaction sites for Li⁺ and short electron transport pathways. The RQDV cathode shows a higher rate capability and better cycling stability than the pure V₂O₅ cathode.

### Experimental section

#### Sample preparation

The RQDV was synthesized as follows: vanadium pentoxide (V₂O₅) powder (1 mmol) dispersed in deionized water (30 mL) and hydrogen peroxide solution (5 mL, 30%) was added under stirring until a clear orange solution formed. After that, ammonium dihydrogen phosphate (NH₄H₂PO₄) (1.5 mmol) was added in the solution. Then, 0.8 mL ruthenium chloride solution (0.1 mol L⁻¹) was added to the above solution. Finally, the resulting solution was transferred into a Teflon-lined stainless steel autoclave and kept at 180 °C for 3 h. The products were washed repeatedly with deionized water and ethanol, and finally dried at 70 °C for 12 h. The as-prepared samples were annealed at 450 °C for 3 h at a ramping rate of 3 °C min⁻¹.

The sample prepared by the hydrothermal process followed by annealing with RuCl₃ is noted as RQDV. The sample without RuCl₃ after annealing is noted as the pure V₂O₅. The sample without annealing is noted as the RQDV precursor.

#### Material characterization

X-ray diffraction (XRD) measurements were performed to obtain the crystallographic information using a D8 Advance X-ray diffractometer with a non-monochromated Cu Kα X-ray source. Field emission scanning electron microscopic (FESEM) images and energy dispersive spectra (EDS) were collected using a JEOL-7100F microscope. X-ray photoelectron spectroscopy (XPS) analysis was done on a VG Multilab 2000. Transmission electron microscopic (TEM) and high-resolution TEM (HRTEM) images were recorded using a JEOL JEM-2100F STEM/EDS microscope. X-Ray Fluorescence (XRF) analysis was conducted using an Axios advanced X-ray fluorescence spectrometer JY/T 016-1996.

### Results and discussion

Fig. 1a shows the XRD patterns of the pure V₂O₅ and RQDV. The pure V₂O₅ matches well with the orthorhombic V₂O₅ phase (JCPDS card No. 00-001-0359) with no impurity phase. The as-prepared RQDV is well crystallized and exhibits the standard diffraction peaks of the orthorhombic V₂O₅ phase. In addition, the standard diffraction peaks of RuO₂ also exist corresponding well to JCPDS card No. 00-050-1428, which reveals that RuO₂ is formed during the synthesis process. The formation of the RuO₂ QDs may be due to the hydrogen peroxide in the solution converting Ru(III) to RuO₂ nanoparticles in the hydrothermal process at 180 °C and subsequent crystallization in the annealing process.³⁸,³⁹ The XRD pattern of the RQDV precursor (ESI,† Fig. S1) was also measured. The peak intensity of the RQDV precursor is very weak, which indicates that the RQDV precursor has very low crystallinity. Fig. 1b shows the low-magnification FESEM image of the RQDV precursor, which exhibits uniform bowknot-like structure. The high-magnification FESEM image (Fig. 1c) shows that bowknot-like structure is composed of hierarchical assemblies of a single nanosheet with a transverse diameter of 50–200 nm. The EDS analysis of the bowknot-like nanomaterials indicates their chemical composition corresponding well to that of the RQDV (Fig. 1d). Fig. 1e and f present the low- and high-magnification FESEM images of the RQDV, respectively. It can be seen that the bowknot-like structure can be retained well after calcination. The low-magnification FESEM image of the pure V₂O₅ precursor shows that nanobelts extend continuously around a center (ESI,† Fig. S2a). The morphology of this sample can be further observed by the high-magnification FESEM image, which shows the structure of nanoribbons with an average diameter of ~100 nm (ESI,† Fig. S2b). After annealing, some nanobelts were damaged and aggregated (ESI,† Fig. S2c and d).

Time-dependent experiments were conducted to further understand the formation process of bowknot-like structure. The samples were collected at different stages during the synthesis process, and their morphologies were investigated by SEM (ESI,† Fig. S3). When the reaction time was 30 min,
some nanosheets were formed and aggregated (ESI,† Fig. S3a). As the reaction time increased to 1 h, more nanosheets were formed and constructed into bowknot-like structure (ESI,† Fig. S3b). With the reaction time prolonging to 2 h, some nanoflowers assembled by nanosheets through the Ostwald ripening process can be observed (ESI,† Fig. S3c). As the reaction time increased to 6 h, bowknot-like structure was formed, which was similar to that obtained at the initial stage (ESI,† Fig. S3d).

Fig. 2a shows the low magnification TEM image of the annealed RQDV, which further indicates the high thermal stability of the bowknot-like structure. The high magnification TEM image of annealed RQDV (Fig. 2b) exhibits nanometer-sized RuO₂ (0.5–3.5 nm) dispersed on the surface of V₂O₅. Fig. 2c shows the high resolution transmission electron microscopy (HRTEM) image of the annealed RQDV. The lattice spacing of 2.61 Å is indexed to the (013) set of planes of the orthorhombic V₂O₅ (JCPDS card No. 00-001-0359); it can be also observed that the lattice spacing of 2.79 Å indexed to the (111) set of planes of the RuO₂ (JCPDS card No. 00-050-1428) exists. The particle size distribution of RuO₂ is obtained through statistically analyzing the HRTEM of the RQDV (Fig. 2d). It exhibits that over 80% of the RuO₂ QDs are in the size range of 1–2.5 nm.

XRF analysis was performed to examine the composition of annealed RQDV. The XRF table shows that the as-obtained samples mainly contain V₂O₅ and RuO₂, which reveals that the mass percentage of RuO₂ is 2.56% in the composite (ESI,† Table S1). XPS measurements were conducted to further confirm the oxidation state of vanadium and ruthenium. Fig. 3a shows the binding energy for V 2p₃/₂ at 517.2 eV, which corresponds to V⁵⁺ in V₂O₅ according to the previous report. 40 Fig. 3b presents the spectra for Ru 3d₅/₂ and C 1s. The Ru 3d₅/₂ band was observed at 281.0 eV attributed to Ru⁴⁺ in RuO₂. 41 The C 1s band at 284.6 eV may be from the effect of the atmosphere. 42

Various electrochemical measurements were performed to contrast the electrochemical performances of the as-prepared samples (Fig. 4). The cyclic voltammetry (CV) curve of the RQDV electrode was tested at a scan rate of 0.1 mV s⁻¹ in the potential range from 2.0 to 4.0 V (Fig. 4a). It is clear that three pairs of redox peaks appear at 2.588/2.196, 3.291/3.118 and 3.493/3.323 V, which can be attributed to the Li-ion insertion and extraction processes, corresponding to the phase transitions from α-V₂O₅ to ε-Li₀.₅V₂O₅, ε-Li₀.₅V₂O₅ to δ-Li₂V₂O₅ and δ-Li₂V₂O₅ to γ-Li₂V₂O₅, respectively (eqn (1)–(3)).

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\begin{align*}
V₂O₅ + 0.5Li^+ + 0.5e^- &= ε-Li₀.₅V₂O₅ \\
ε-Li₀.₅V₂O₅ + 0.5Li^+ + 0.5e^- &= δ-Li₂V₂O₅ \\
δ-Li₂V₂O₅ + 0.5Li^+ + 0.5e^- &= γ-Li₂V₂O₅
\end{align*}
\]
The cyclic voltammetry curve of the pure V$_2$O$_5$ was also tested at a scan rate of 0.1 mV s$^{-1}$ in the potential range from 2.0 to 4.0 V (ESI† Fig. S4a). The three main cathodic and anodic peaks correspond to a series of phase transformation. The shape of the pure V$_2$O$_5$ is similar to that of the RQDV. However, there are some minor peaks, which may result from structural changes. Fig. 4b shows the charge–discharge voltage profiles for the 1st, 5th, 50th and 100th cycles of RQDV electrode at a current density of 100 mA g$^{-1}$. There are three voltage plateaus observed in the discharge process, which are in accordance with the redox peaks in CV curves. The charge–discharge voltage profiles for the 1st, 5th, 50th and 100th cycles of the pure V$_2$O$_5$ electrode were collected at a current density of 100 mA g$^{-1}$ (ESI† Fig. S4b). When the cycling numbers reach 50th and 100th cycles, the pure V$_2$O$_5$ shows poor reversibility.

Fig. 4c and d show the cycling performances of the pure V$_2$O$_5$ and RQDV tested via constant current charge–discharge in a voltage range of 2.0–4.0 V cycling up to 100 cycles, which demonstrate the superiority of the RQDV as a cathode material. Fig. 4c shows the comparison of the cycling ability of the pure V$_2$O$_5$ and RQDV at a current density of 100 mA g$^{-1}$. The capacity retentions of the pure V$_2$O$_5$ and RQDV after 100 cycles are 62% and 70%, respectively. RQDV reveals better cycling performance delivering relatively high capacity, which may be ascribed to its unique nanostructures with RuO$_2$ QDs dispersing on the V$_2$O$_5$. The cycling performances of the pure V$_2$O$_5$ and RQDV electrodes were also tested at a current density of 1 A g$^{-1}$ (Fig. 4d). Compared with RQDV, the pure V$_2$O$_5$ delivered a lower capacity of 86 mA h g$^{-1}$ after 100 cycles. The capacity retention of the pure V$_2$O$_5$ only remains 65% after 100 cycles, while the capacity retention of RQDV still remains 87%. The RQDV clearly exhibits excellent cycling performance. The capacity retention at 1 A g$^{-1}$ after 100 cycles was much higher than that at 100 mA g$^{-1}$. Such electrochemical performances may be caused by the following reasons: there are more Li$^+$ intercalation/de-intercalation in the internal structure of the RQDV electrode at a low current of 100 mA g$^{-1}$, the structure of the material may be more seriously damaged than that at a high current of 1 A g$^{-1}$ during the charge.

Fig. 3 The XPS spectra for annealed RQDV: (a) the V 2p$_{3/2}$ bands; (b) the Ru 3d$_{5/2}$ and C 1s bands.

\[ \text{δ-LiV}_2\text{O}_5 + \text{Li}^+ + e^- = \gamma\text{-Li}_2\text{V}_2\text{O}_5 \] (3)
Conclusions

In summary, we have successfully synthesized the bowknot-like RuO$_2$ quantum dots@V$_2$O$_5$ nanomaterials by a facile hydrothermal synthesis method followed by annealing treatment at 450 °C in air. The RuO$_2$ QDs have a diameter of 0.5–3.5 nm. The electrochemical tests demonstrate that the RQDV cathode exhibits enhanced electrochemical performance. Especially, it delivers a capacity of 160 mA h g$^{-1}$ at a high current density of 1000 mA g$^{-1}$ and improves the cycling stability (87% capacity retention after 100 cycles), whereas the capacity for the pure V$_2$O$_5$ is 86 mA h g$^{-1}$ (65% capacity retention after 100 cycles). The enhanced electrochemical performance can be ascribed to the unique nanostructure with RuO$_2$ QDs dispersed on the V$_2$O$_5$ surface. This strategy can be also used as an effective technique for improving the electrochemical performance of other electrodes especially at high rate.

Conflicts of interest

All authors discussed the results and commented on the manuscript. The authors declare no competing financial interest.

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Notes and references