

RAPID COMMUNICATION

V₂O₅ quantum dots/graphene hybrid nanocomposite with stable cyclability for advanced lithium batteries



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Abstract

High-speed electron transfer channels and short Li ion transport distance are beneficial to improvement of Li ion battery properties. Here, a two-step solution phase synthesis method is developed to construct the V₂O₅ quantum dots/graphene hybrid nanocomposite by controlling nucleation and growth processes. It is demonstrated that the V₂O₅ quantum dots with an average size of 2–3 nm are uniformly anchored on the graphene sheets. The specific capacity can achieve 212 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles. Significantly, the novel V₂O₅ quantum dots/graphene shows a stable cycling performance with 89% capacity retention after 300 cycles. The improvement in electrochemical properties could be attributed to the short Li ion transfer distance, two-dimensional electron channels, homogeneous dispersion and immobilization of V₂O₅ quantum dots. Meanwhile, it indicates that V₂O₅ quantum dots/graphene is promising cathode material for use in long-life rechargeable lithium batteries. This design conception and synthesis strategy for V₂O₅ could also be extended to other electrode material systems.

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Introduction

As energy demand increases, energy storage devices such as batteries can play a more important role in increasing the efficiency of energy utilization [1–3]. Recently, lithium-ion batteries have attracted wide attention for portable

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electronics, electric vehicles, and renewable energy storage because of their high energy density [4-6]. There are still significant challenges to develop new electrode materials with longer cycle life, higher reversible capacity and lower cost [7-9].

Vanadium pentoxide (V₂O₅) is considered to be one of the attractive cathode materials because of its high specific capacity, low cost and good safety [10,11]. However, the fast capacity fading, low electrical conductivity (10^{-5} - 10^{-3} S cm⁻¹) [12,13] and the low Li ion diffusion (10^{-13} - 10^{-12} cm² s⁻¹) [14,15] still limit its application as a Li battery cathode material. To improve the Li ion diffusion coefficient in V₂O₅, a large number of nano-structured V₂O₅ materials have been prepared, such as nanowires [16,17], nanorods [18] and nanosheets [19]. Carbonaceous materials were studied to improve the charge transfer of V₂O₅ by constructing the core-shell [20], tube-in-tube [21] and hollow microsphere structure [22]. Recently, graphene, a two-dimensional (2D) carbon atom monolayer structure, has become a desired substrate for V₂O₅ and other electrode materials due to its high surface area over 2600 m² g⁻¹, superior electric conductivity and excellent mechanical flexibility. In the past few years, a variety of hybrid nanomaterials consisting of graphene and active materials, such as TiO₂ [23], SnO₂ [24], LiFePO₄ [25], MoO₂ [26], Si [27] have been used as electrode for Li batteries. However, synthesis and lithium storage properties of quantum dots (QDs)/graphene are less investigated [28]. It is particularly worth noting that the QDs with high dispersion can provide a large space to buffer the volume change of the active materials and shorten the diffusion length of Li⁺, which are beneficial to longer life and higher capacity. To take the advantages of V₂O₅, QDs and graphene, we developed a two-step solution phase synthesis method to construct the V₂O₅ QD/graphene hybrid (VQDG) nanocomposite by controlling nucleation and growth processes. As expected, the as-prepared VQDG exhibit greatly enhanced lithium storage properties with stable cyclability and high reversible capacity.

Materials and methods

Preparation of V₂O₅ quantum dots/graphene hybrid nanocomposite

The reduced graphene oxide (rGO) was synthesized through a modified Hummer method [29-31]. A two-step solution-

phase method was used to synthesize the VQDG with the as-prepared rGO suspension (~0.1 mg ml⁻¹). The vanadium sol and aniline were mixed in a 100 ml beaker and stirred at room temperature for 30 min with the molar ratio of 1:0.03. Next, 13 ml rGO suspension was added into the mixture and stirred at 80 °C for 24 h. The sample was then transferred into a 100 ml autoclave and heated at 180 °C for 48 h. After washed and dried at 80 °C for 24 h, a blackish yellow powder was obtained.

Preparation of pure V₂O₅ nanowires

As a control experiment, the pure V₂O₅ NWs were prepared through a simple hydrothermal reaction without mixing with graphene and string at 80 °C/min. V₂O₅ powder was heated to 800 °C in a ceramic crucible. When the molten liquid was quickly poured into distilled water, a brownish V₂O₅ sol was formed. Then 1.3 mmol of the as-prepared V₂O₅ sol were dispersed in water and then transferred into a Teflon-lined stainless steel autoclave and kept at 180 °C for 2 days. Then the autoclave was allowed to cool down in air, and the yellow precipitate was obtained. The products were collected, washed repeatedly with distilled water, and finally dried at 80 °C in air for 12 h.

Result and discussion

To determine the crystalline structure of the products, X-ray diffractometry (XRD) measurements was conducted. The XRD patterns of the as-prepared VQDG and V₂O₅ nanowires were indexed to orthorhombic V₂O₅ (JCPDS No. 041-1426) (Fig. 1a). Differential thermal analysis (DTA) was used to further investigate the existence and content of graphene in VQDG (Fig. 1b and c). On the TG curve, a mass loss of about 1.46% was observed from 100 °C to 185.6 °C due to the oxidation of graphene surface and the loss of water. By combining differential scanning calorimetry (DSC) results, the detailed thermal reaction process is shown in Eqs. (1)-(3). Then the graphene was oxidized with a 7.14% mass loss from 185.6 °C to 320.9 °C in Eq. (4). The thermal gravimetry analysis (TGA) curves of Fig. 1b and c show a total mass loss of about 7.85% and 1.40%, respectively, below 400 °C, indicating that the content of graphene is 6.45%. Meanwhile, the heat absorption processes around 670 °C were

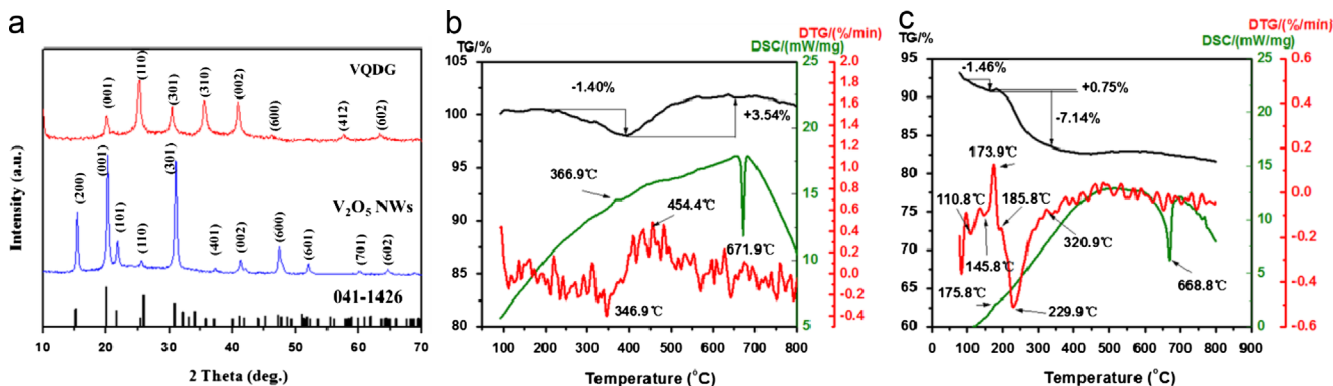


Fig. 1 (a) The XRD patterns of VQDG (red line), control sample V₂O₅ ultralong nanowires (blue line) and the standard sample orthorhombic V₂O₅ card (black line). (b,c) The TG (green line), DSC (blue line) and DTG (red line) curves of V₂O₅ nanowires and VQDG.

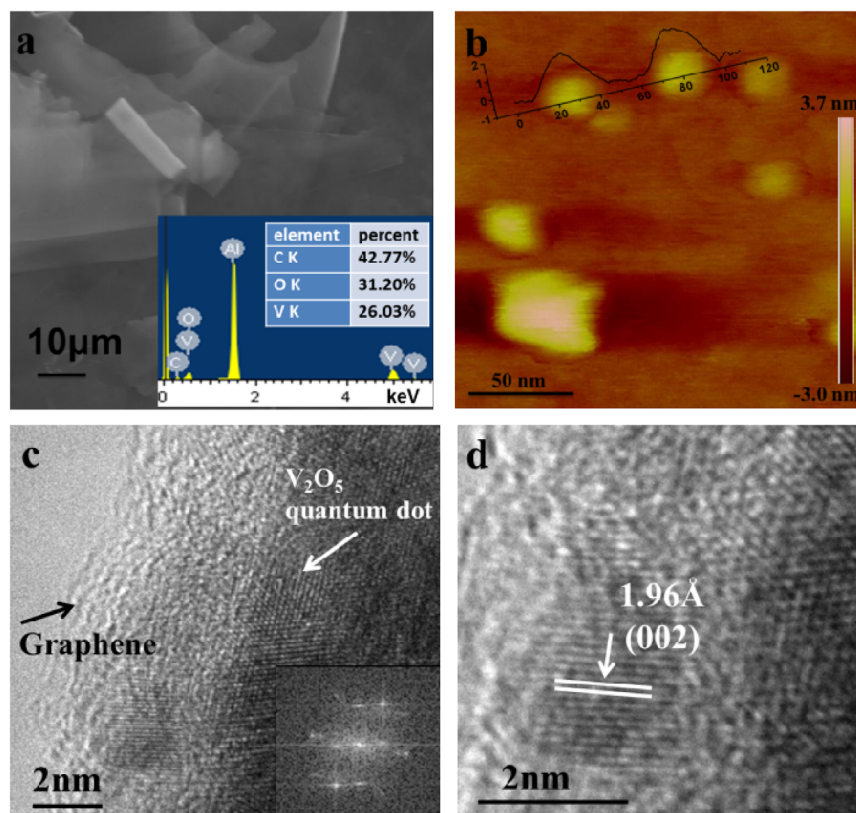


Fig. 2 (a) SEM image of VQDG. Inset image is the EDS microanalysis on selected area. (b) The section AFM image of VQDG. (c, d) TEM and high-resolution TEM images of VQDG.

both observed in these two samples, corresponding to the phase transition of V_2O_5 .

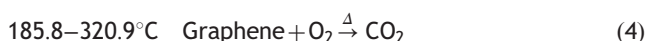
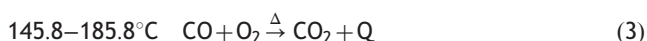
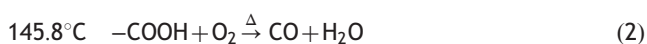


Fig. 2a shows the SEM image of VQDG. The VQDG aggregated to layer structure in microscale size. Atomic force microscope (AFM) was used to determine the exact size and thickness of rGO and VQDG. In **Fig. S1**, pure rGO with thickness of ~ 1 nm was used as the supporter of V_2O_5 . After supporting V_2O_5 , the thickness of VQDG changes to $\sim 2\text{--}3$ nm with a smaller size than pure rGO, indicating that the graphene was wrapped and folded while reacting with the vanadium sol. Further information about VQDG was obtained from transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). It is confirmed that large amount of V_2O_5 particles have dispersed on the graphene sheets surface (**Fig. 3b**, **Fig. S3**). This is beneficial to prevent the V_2O_5 QDs from agglomeration, and enables the good dispersion of V_2O_5 over the graphene support. Close inspection at the V_2O_5 particles shows that the V_2O_5 QDs with different lattice direction and crystal boundary are observed, confirming the crystal nature of V_2O_5 QDs. The size

of V_2O_5 QD is about 2 nm after statistically analyzing the TEM images (**Fig. 2c**). To further identify V_2O_5 distribution on graphene, the particle size distribution of V_2O_5 is obtained through statistically analyzing the dark field TEM image (**Fig. 3c**). **Fig. 3d** shows that over 60% of the quantum dots are in the size range of 2–3 nm, which is corresponding to the TEM results (**Fig. 2c**). The high-resolution TEM investigation (**Fig. 2d**) demonstrates that the V_2O_5 QD interlayer distances is consistent with the (002) interplanar distance of 0.196 nm.

In order to investigate the growth mechanism of VQDG, the SEM image and EDS pattern of VQDG precursor were obtained. The VQDG precursor (**Fig. S4a**) was collected by mixing graphene suspension and vanadium sol at 80°C for 24 h. EDS microanalysis on **Fig. S4a** is shown in **Fig. S4b**. Comparing with VQDG, the graphene sheets have not wrapped and folded with each other. The graphene surface consist of 16.22% V element, indicating that the vanadium sol has nucleated on the surface of graphene at 80°C . At such a relatively low temperature, the vanadium sol can attach to the functional groups on graphene to decrease surface energy [32]. Therefore, the oxygen-containing functional group bonded with the vanadium oxide to form the crystal nuclei. As is shown in **Fig. 2b**, the content of V on the graphene increased from 16.22% to 26.03% after the temperature increased to 180°C with a higher pressure in autoclave indicating that by consuming residual vanadium sol, resulting the formation of V_2O_5 QDs from nuclei (**Fig. 3a**).

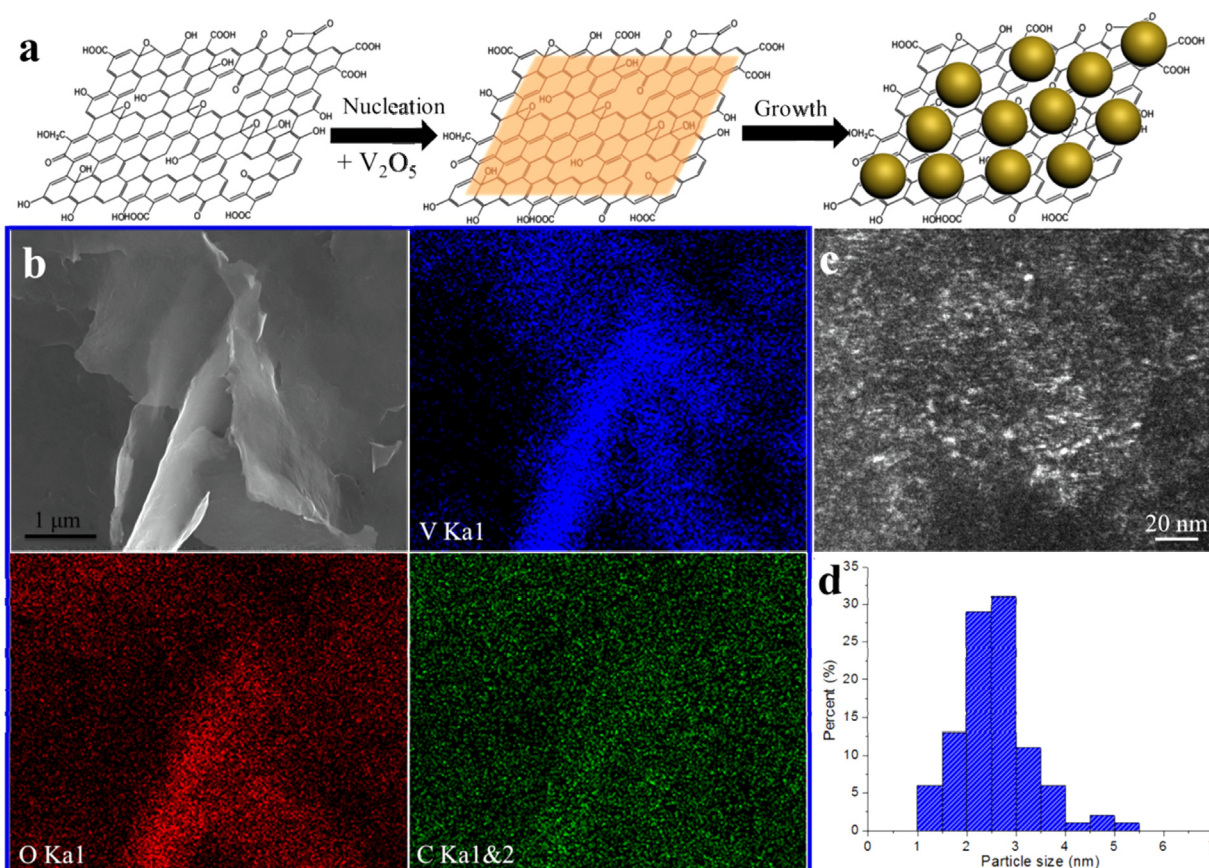


Fig. 3 (a) Schematic construction processes of VQDG. The black network represents the reduced graphene oxide, the orange transparent plate represents the V₂O₅ sol and the blackish yellow particles are V₂O₅ QD. (b) SEM image and the corresponding elemental mapping of C, Mo, and O of VQDG. (c) The dark field TEM image of VQDG. (d) Particle size distribution of V₂O₅ quantum dots on graphene.

Theoretically, the specific capacities of V₂O₅ as cathode is 290 mA h g⁻¹ in the voltage ranges from 2 to 4.0 V vs. Li/Li⁺. The chemical equation can be noted below:



The combination of the layered structure and the high reactivity with the Li ions in the conversion process is attractive for V₂O₅ in lithium batteries. In our experiments, V₂O₅ QD was loaded on graphene successfully with the nucleation and growth process. Herein, graphene provide electron transport pathways which is beneficial for high capacity [24]. Meanwhile, the construction of V₂O₅ QD shortens the Li-ion transfer distance and reduces the surface stress during charge and discharge [28]. Besides, as a control experiment, the pure V₂O₅ without adding graphene and nucleation process was also prepared through a simple hydrothermal reaction, leading to the formation of nanowires. The cycling performances of VQDG and V₂O₅ nanowires at 100 mA g⁻¹ were shown in Fig. 4a. Although the initial specific capacity of V₂O₅ nanowires can be up to 280 mA h g⁻¹, fast capacity fading for V₂O₅ is observed. Besides, for the VQDG with the similar V₂O₅ crystalline structure, capacity retention is significantly improved. At current density of 100 mA g⁻¹, the initial discharge capacities of VQDG and V₂O₅ nanowires are 288 and 245 mA h g⁻¹, respectively. The discharge capacities decreased to 126 mA h g⁻¹ and 212 mA h g⁻¹

after 100 cycles, corresponding to the capacity retention of 43.75% and 86.5%, respectively. Interestingly, during the first several cycles the capacity of V₂O₅ nanowires decreased rapidly, but the capacity of VQDG shows a slight increase during the first 20 cycles. It has been reported that, the initial capacity fading can come from the active material dissolution, passive SEI film formation and loss of electrical contact. In the first several cycles, graphene has wrapped the V₂O₅ QD which slows down the processes above. At the same time, the graphene will spread to decrease the surface stress during the intercalation and de-intercalation of Li⁺, resulting in a better electrolyte wetting and infiltration, which leads to first an increase and then a stabilization of the capacity. This behavior became more noticeable during the following tests at higher current densities.

Fig. 4b and the inset image displays the 1st, 10th, 50th and 100th charge-discharge curves of VQDG at 100 mA h g⁻¹ and the corresponding differential capacity plots of 1st charge-discharge curve, respectively. The discharge plateaus located at ~2.95 V and ~2.40 V can be identified as the two-phase transformation from V₂O₅ to LiV₂O₅ and from LiV₂O₅ to Li₂V₂O₅. The reduction peaks at 2.87 V and 2.39 V can be observed in cyclic voltammetry curve of Fig. S5 corresponding to the plateau of discharge in Fig. 4b.

The capacity retention of VQDG is shown in Fig. 4c. The capacity retention is 100%, 96.92%, 89.16% and 65.72% at

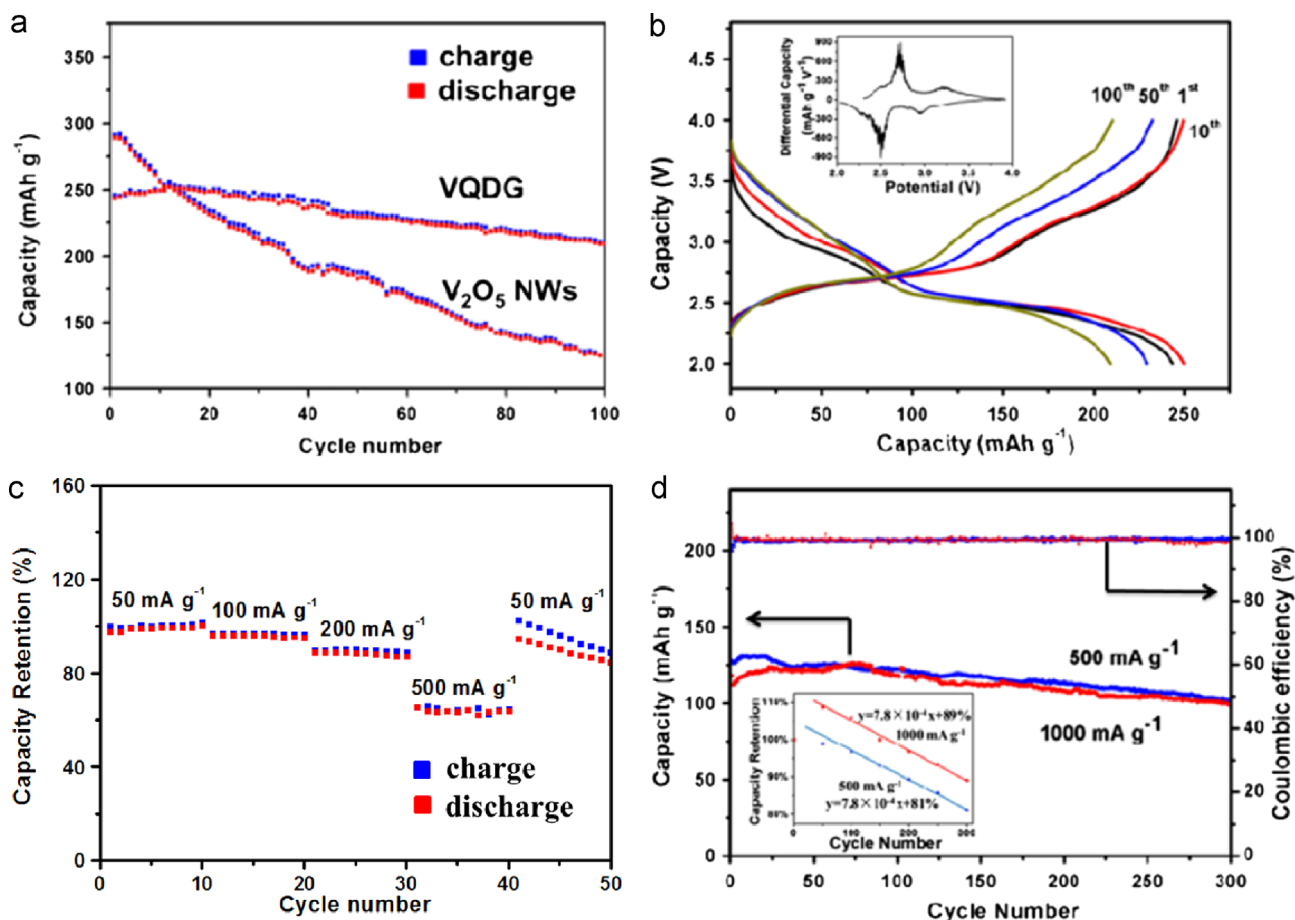


Fig. 4 (a) Cycling performance of VQDG and V₂O₅ nanowires at 100 mA g⁻¹. (b) Charge-discharge curves of VQDG in the voltage ranges of 2.0-4.0 V at 100 mA g⁻¹. Inset image is the corresponding differential capacity plots. (c) Capacity retention of VQDG at various current densities from 50 mA g⁻¹ to 500 mA g⁻¹. (d) Charge-discharge cycling performance of VQDG at high current densities of 500 mA g⁻¹ and 1000 mA g⁻¹. Inset image is the capacity retention plots.

current density of 50, 100, 200 and 500 mA g⁻¹, respectively. In addition, after the high-rate measurement, the battery with VQDG cathode was able to recover to high capacity retention of 94.73% at 50 mA g⁻¹. This indicates the excellent structural stability and reversibility of VQDG. The high-rate performance of VQDG was further investigated. At the current of 500 and 1000 mA g⁻¹ (Fig. 4d), the initial discharge capacities were 128 and 118 mA h g⁻¹, respectively. After 300 cycles, the capacity at 500 and 1000 mA g⁻¹ decreased to 102 and 100 mA h g⁻¹, corresponding to a capacity fading of 0.074% and 0.055% per cycle. Meanwhile, both the coulombic efficiencies stayed at ~100% in the overall battery test, which indicates the good reversibility of VQDG. Interestingly, V₂O₅ QD/graphene shows lengthy (over 50 cycles) activated process at 500 and 1000 mA g⁻¹ with almost the same fading rate (~0.085% per cycle) in the 100th to 300th cycles (inset image in Fig. 4d), which indicates that the spreading of graphene can effectively decrease the surface stress in the process of intercalation and deintercalation of Li⁺ and make more active sites thoroughly exposed in electrolyte. The higher the current density is, the more drastically the graphene spread. Such improvement in electrochemical properties is attributed to the short Li ion transfer distance, two-dimensional

electron channels, homogeneous dispersion and immobilization of V₂O₅ quantum dots.

Conclusion

In summary, we have successfully loaded the V₂O₅ QDs on the rGO by controlling nucleation and growth process. The V₂O₅ QDs have an average diameter of ~2 nm and are uniformly dispersed on the rGO. Such VQDG is ideal for lithium storage. First, the V₂O₅ QDs provide a great deal of active sites and a short Li⁺ transfer distance, which are beneficial to the high lithium storage capacity. Second, the V₂O₅ QDs that firmly anchored on the rGO could reduce the surface stress during charge and discharge; meanwhile, the rGO could provide the stable electron transfer pathways, both leading to the excellent cycling performance. As a result, the VQDG shows not only a high capacity of 245 mA h g⁻¹ at 100 mA g⁻¹, but also a stable cycling performance (300 cycles with 89% capacity retention). The VQDG with superior electrochemical performance is promising for rechargeable Li batteries with long-life and high-energy density. This design conception and synthesis strategy for V₂O₅ could also be extended to other electrode material systems.

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Appendix A. Supporting information

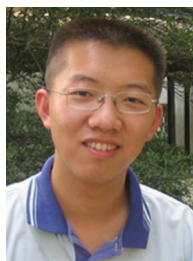
Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2013.03.012>.

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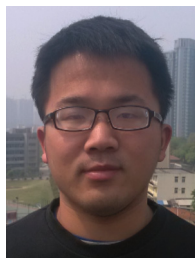
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