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Self-Assembled Vanadium Pentoxide (V_2O_5) Hollow Microspheres from Nanorods and Their Application in Lithium-Ion Batteries**

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Self-assembled structures with highly specific morphology and novel properties are of great interest to chemists and materials scientists. As a result of rapid advancements in synthetic strategies, highly organized building blocks of metals,[1] semiconductors,[2] copolymers,[3] organic–inorganic hybrid materials,[4] and biominerals[5] have been synthesized by using various methods. However, controlled organization into curved structures from rodlike building blocks remains a challenge. Such a capability is attractive to scientists not only because of its importance in understanding the concept of self-assembly with artifial building blocks but also for its great application potential.[6–9] Vanadium pentoxide (V_2O_5) has been extensively studied as a well-known transition-metal oxide. Various nanostructures of V_2O_5,[10] such as nanotubes, nanowires, nanofibers, nanobelts, nanorods, and mesoporous structures have already been synthesized by a variety of methods, including reverse-micelle transition, sol–gel process, hydrothermal treatment, and electrochemical deposition. Nanostructured V_2O_5 has potential application in the fields of lithium-ion batteries,[10c,d,11] actuators,[10f] catalysis,[12] and sensors.[13] To our knowledge, hollow microspherical V_2O_5 has not been reported until now although such a structure has long been a focus of research.[14]

Herein, we describe a facile method to self-assemble V_2O_5 nanorods into microspheres. A mediated polyol process was adopted to prepare hollow microspherical V_2O_5, in which ethylene glycol (EG) is treated with a metal salt in the presence of poly(vinylpyrrolidone) (PVP). Such a method was previously used to obtain metal nanoparticles, nanowires (EG as a reductant),[15] and oxide nanowires (EG as a ligand).[16] We now present its use, for the first time, to synthesize hollow microspheres of V_2O_5. Using vanadium(III) acetylacetonate (acac) as the metal-ion source, we have synthesized hollow microspheres with nanorods on their surface; moreover, the morphologies of such nanorods are

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readily tunable. The as-prepared vanadium hollow microspheres can be calcined into crystalline V_2O_5 without changing their morphologies. These V_2O_5 products exhibit improved electrochemical properties when they are used as cathode material in lithium-ion batteries and show good application potential.

Briefly, PVP was mixed with $[V(acac)_3]$ in a solution of EG at room temperature and normal pressure then heated at 140 °C for about 100 min, which led to the eventual formation of vanadium precursors with different structures. It is worth noting that PVP had a great influence on the morphologies of the synthesized vanadium precursors. In the absence of PVP, nanorods mainly form, the aspect ratios and diameters of which are tunable. Figure 1 a shows such nanorods with diameters of about 200 nm and lengths up to 2 µm at a concentration of 6 mM $[V(acac)_3]$. The energy-disperse X-ray (EDX) spectroscopic analysis (inset in Figure 1 a) of the nanorods shows their chemical composition correlating well to that of the vanadium precursor. Upon the introduction of 0.14 mM of PVP, uniform hollow microspheres formed in large quantity, the morphology of which could be readily regulated by changing the concentration of $[V(acac)_3]$. At a concentration of 6 mM $[V(acac)_3]$, the rods are relatively short and circle around to form the spherical shell just taking the shape of a nest (Figure 1 b). A broken sphere in the lower part of Figure 1 b clearly shows the hollow feature of the sphere. At a concentration of 18 mM $[V(acac)_3]$, these nanorods become longer and have a higher packing density as shown in Figure 1 c. At a concentration of 42 mM $[V(acac)_3]$, these nanorods eventually self-align perpendicular to the spherical surface and emanate from the center rather like the spines of a hedgehog (Figure 1 d).

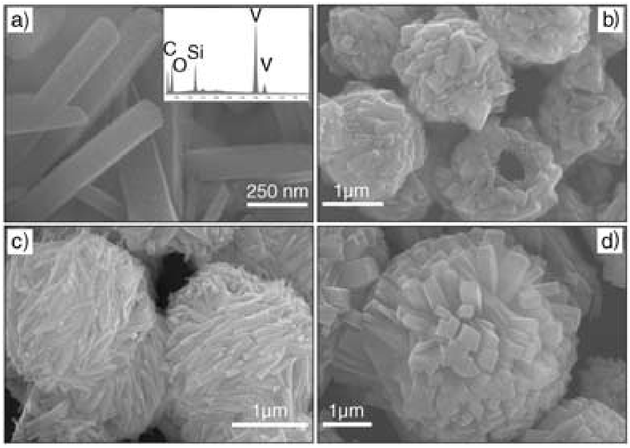

Figure 1. a) SEM image of the vanadium precursor prepared with 6 mM $[V(acac)_3]$ and no PVP. The inset shows the EDX pattern of the rod. b–d) SEM images of the microspheres synthesized with different concentrations of $[V(acac)_3]$ at 6 mM (b), 18 mM (c), and 42 mM (d), while the concentration of PVP was constant at 0.14 mM.

After the preparation of the precursors, we investigated the effect of calcination on the crystallization and morphology of the hollow microspheres. Subsequent calcination at 500 °C over 2 h did not change the individual morphologies of these vanadium precursors. Figure 2 a shows a representative SEM image of a calcined V_2O_5 sample, which shows that the structure of the hollow microspheres was preserved. The sample was prepared under the same conditions as those applied to generate the samples shown in Figure 1 c. The following characterizations are all based on this sample unless otherwise noted. Figure 2 b shows a wide-angle XRD pattern of this calcined sample, which can be indexed as the orthogonal symmetry of V_2O_5 (space group: *Pmmn* (59), $a = 11.516$, $b = 3.566$, $c = 3.777$ Å; JCPDS card no. 41–1426), thus demonstrating the presence of crystalline V_2O_5. The TEM image in Figure 2 c further affirms that the calcined V_2O_5 superstructures are indeed hollow microspheres with nanorods pointing out from the surface. The presence of nanorods can be clearly seen in Figure 2 d. In a high-resolution TEM (HRTEM) image taken from the edge of a nanorod (inset of Figure 2 d), the lattice fringes are clearly visible with a spacing of 0.581 nm, which is in good agreement with the spacing of the (200) planes of V_2O_5 (JCPDS card no. 41–1426).

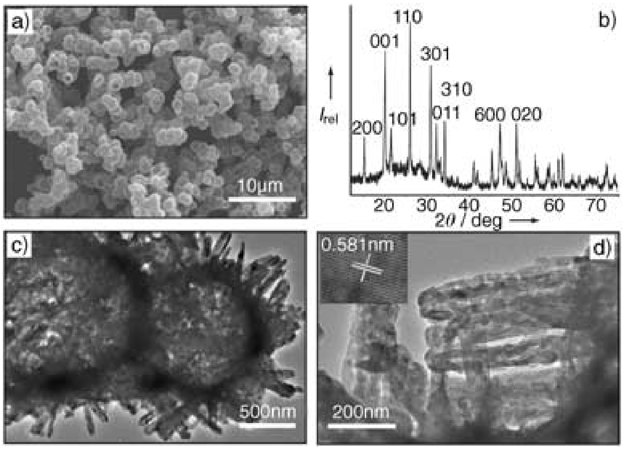

Figure 2. a) SEM image, b) XRD pattern, and c) low and d) high magnification TEM images of the calcinated V_2O_5 hollow microspheres. The inset in Figure 2 d is a high-resolution TEM (HRTEM) picture taken from the edge of a nanorod surface.

Time-dependent experiments were performed to gain insight into the formation process of such vanadium precursors. Products were collected at different stages from the reaction mixture once the precipitate had began to appear in solution, and their morphologies were subjected to SEM investigation. As shown in Figure 3, when a sample was taken immediately after the formation of precipitate ($t = 0$ min), the collected product comprised microspheres with smooth surfaces (Figure 3 a); after ten minutes, the surfaces of the samples were found to be rougher (Figure 3 b). Nanorods formed over the following 20 minutes (Figure 3 c), which were evidently very stable in solution as such their highly ordered superstructure remained unchanged with subsequent heating for over an hour (Figure 3 d).

Ethylene glycol has been established as a cross-linking reagent.[16,17] Xia and co-workers proposed that two key steps are involved in producing nanowires: 1) coordination of EG

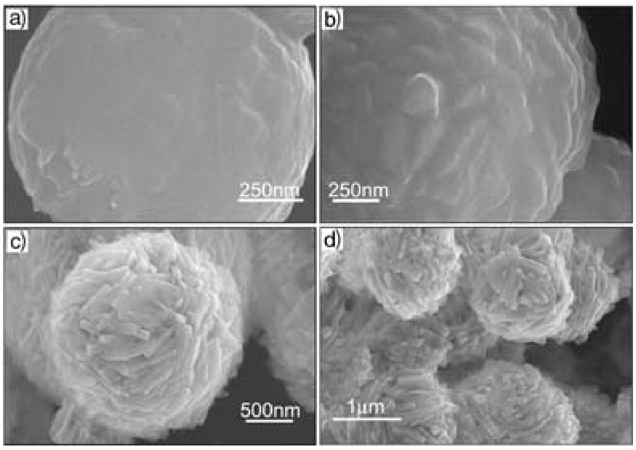

Figure 3. SEM images of the samples collected at different stages after the precipitate appeared in the clear solution: a) 0, b) 10, c) 30, and d) 90 min.

to the central metal ion to form a metal glycolate and 2) subsequent oligomerization.[16] Such a mechanism may be adapted to explain the formation of rodlike vanadium precursors. The XRD pattern (see the Supporting Information) of the vanadium precursor shows its crystalline nature with characteristically strong peaks around 10°, which is a feature of the coordination and oligomerization processes in EG.[16] FTIR spectra (see the Supporting Information) show the gradual displacement of the acac ligands with EG. The C–OH vibration at 1056 cm^{-1} together with the CH$_2$ band at 2939 and 2877 cm^{-1} in the final product increases at the expense of the characteristically strong bands of C=O in [V(acac)$_3$] at 1566 and 1527 cm^{-1}. This result indicates that EG has completely replaced acac in a similar way to that proposed by Xia and co-workers.[16]It is evident that PVP plays a completely different role to that reported in the polyol process.[15,16] The introduction of PVP is crucial in obtaining uniform hollow microspheres because of the template effect of the polymer. As the vinyl group is hydrophobic and carbonyl group is hydrophilic, PVP also functions as a surfactant in an EG solution. Indeed, hollow structures have already been synthesized with PVP as the template.[18] A probable mechanism for the evolution of such structures is presented in Figure 4. PVP forms spherical micelles in EG with the carbonyl groups on the outside. The acac ligand of [V(acac)$_3$] is gradually replaced by EG to form vanadium glycolates, which are easily adsorbed onto the micelle surface through their abundant hydroxy groups. Nanorods form and grow as the oligomerization of vanadium glycolates proceeds. These rods are flat on the surface at relatively low abundance but gradually turn and pack more tightly as the concentration of [V(acac)$_3$] increases. Finally, they are perpendicular to the surface because of a spherical hindrance effect. Hollow spheres retain their geometry even after PVP is removed. Considering the abundant carbonyl and hydroxy groups in the system and because PVP is known to be a hydrogen-bonding acceptor,[3a,19] we believe the key factors affecting this self-assembly process are hydrogen bonding and the requirement that the "grafted" nanorods pack effectively. The exact role of PVP in the polyol process has long been an issue of debate,[16,18] and extensive work is underway towards its further clarification.

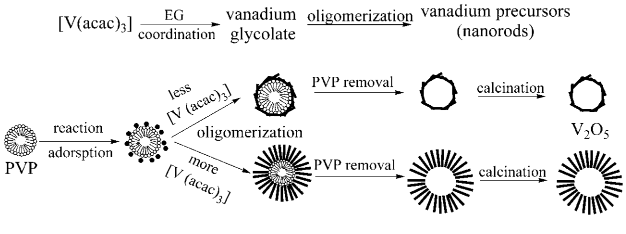

Figure 4. Schematic illustration of the evolution of V$_2$O$_5$ hollow microspheres.

Cyclic voltammetry was used to investigate the electrochemical behavior of the highly ordered superstructures. Figure 5a shows the cyclic voltammograms (CVs) of V$_2$O$_5$ hollow microspheres. Curve A (Figure 5a) is the first scan and B is the scan after 15 cycles. In the potential region from −400 to 600 mV, two sets of peaks can be seen at 80 and 270 mV. These peaks have been attributed to two successive electrochemical processes [Eq. (1) and (2)]:[11a–c]

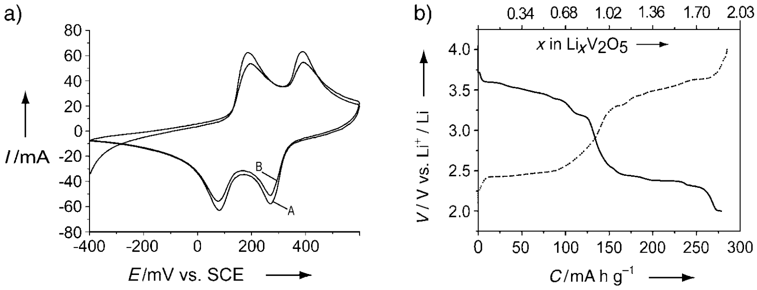

Figure 5. a) Cyclic voltammograms of V$_2$O$_5$ microspheres obtained at a scan rate of 10 mV s^{-1}. The first scan is indicated by curve A and after 15 cycles by curve B. b) The third charge(dash–dot line)–discharge(solid line) profile with a current rate of C/5.

$$V_2O_5 + \tfrac{1}{2}\,Li^+ + \tfrac{1}{2}\,e^- \rightleftharpoons Li_{0.5}V_2O_5 \quad (1)$$

$$Li_{0.5}V_2O_5 + \tfrac{1}{2}\,Li^+ + \tfrac{1}{2}\,e^- \rightleftharpoons LiV_2O_5 \quad (2)$$

In the first reduction peak at 270 mV, only a fraction of the V^{5+} ions is reduced to V^{4+} ions. The remaining V^{5+} ions are reduced to V^{4+} ions in the second peak at 80 mV.[11b] The reverse reactions take place as indicated by the two corresponding oxidation peaks. With the electrochemical reaction, different phases of Li$_x$V$_2$O$_5$ are formed. From the binary phase diagram of V$_2$O$_5$–Li$_x$V$_2$O$_5$, we determined that the cathodic peaks at 80 and 270 mV correspond to the phase transformations from α-V$_2$O$_5$ to ε-V$_2$O$_5$, and ε-V$_2$O$_5$ to δ-V$_2$O$_5$, respectively.[11d,e]

The charge–discharge capability of the microspheres was investigated by using V$_2$O$_5$ as the cathode in a lithium-ion battery. Figure 5b is the profile of a third charge–discharge cycle. The capacity was as high as 286.4 mA h g^{-1} while the charge–discharge efficiency was up to 97.2% in the potential range from 2.0 to 4.0 V. These results show that V_2O_5 might be very good cathode material.[10c,d,11] The V_2O_5 samples with different morphologies (from nest-shaped to hedgehog-shaped) were tested for their electrochemical performances; they exhibited similar CV characteristics and had a variation of capacity in the Li-ion battery of less than $7\,\mathrm{mA\,h\,g^{-1}}$ ($\approx$2%).

After the electrochemical investigation had been performed, the morphologies of the V_2O_5 samples were reinvestigated by TEM. The results showed that the structure of the hollow microspheres and nanorods remained unchanged.

The correlations among structure, composition, morphology of V_2O_5, and its electrochemical properties in the lithium-ion battery have been well studied by other researchers.[10c,d] In our system, the hollow microspheres together with the porous and rugged nanorods that have interconnected nanoparticles are favorable in reducing the diffusion distance of the solid-state lithium ion. Thus, the intercalation and extraction processes are of much higher efficiency, the kinetic performance of the lithium-ion battery is better, and therefore a higher capacity can be achieved.

In summary, we have developed a mediated polyol process to synthesize V_2O_5 with highly ordered superstructures, in which nanoparticles interconnect to form nanorods, and these rods circle around to form hollow microspheres. The protocol represents a substantial simplification over more conventional methods such as electrostatic spray or thermal evaporation. The physical state of the nanorods on the surface can be varied by changing the concentration of [V(acac)$_3$] and the formed microspheres can adopt different shapes that range from nest-like to hedgehog-like. The prepared V_2O_5 exhibits desirable electrochemical properties such as high capacity and remarkable reversibility when it is used as cathode material in a lithium-ion battery.

Experimental Section

Preparation of V_2O_5 hollow microspheres: In a typical synthesis, [V(acac)$_3$] (0.3 g, 18 mM; Aldrich) and PVP (0.4 g, 0.14 mM; $\bar{M}_w$ = 58000; ACROS Organics) were added to ethylene glycol (48 mL; Beijing Chemical Reagent Ltd.) to give a cloudy solution. The mixture was stirred with a magnetic stirrer bar and heated to 140°C. The cloudy mixture turned clear after 20 min and became opaque again after 70 min, indicating the formation of vanadium precursor. The solution was heated for another 30 min to ensure the formation of the composite structure before being allowed to cool to room temperature. The products were washed and separated by centrifugation–redispersion cycles with alcohol. These vanadium precursor was calcined at 500°C for 2 h to obtain crystalline orthogonal V_2O_5.

Characterization: Products were characterized by XRD, (Rigaku Dmax/rb diffractometer with $\mathrm{Cu_{K\alpha}}$ radiation, $\lambda = 0.1542$ nm, 40 kV, 100 mA), TEM (Philips TECNAI-20), SEM (Hitachi S-4300F), and by FTIR (Bruker Tensor 27).

CV measurements were conducted by using an electrochemical cell with a three-electrode configuration. The working electrode was a glassy carbon disk of 3 mm in diameter, polished with Al_2O_3 paste, and washed ultrasonically in Millipore water. The experiment was carried out in an $LiClO_4$–propylene carbonate (Li–PC, 1M) solution with a standard calomel electrode (SCE) as the reference electrode and a Pt counter electrode with an EG&G instrument (model 273, Princeton Applied Research). Electrochemical discharge–charge behavior was investigated directly in coin cells assembled in an argon-filled glove box. The cell was made from a lithium anode and a cathode that was a mixture of V_2O_5 (80%), graphite/carbon black (12%), and teflon (8%). The cathode was separated from the anode by an insulator sheet. The electrolyte reservoir was made from $LiPF_6$ (1M) in a mixture of ethylene carbonate/dimethyl carbonate/dimethoxy ethane 1:1:1 (w/w).

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