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Better Lithium-Ion Storage Materials Made through Hierarchical Assemblies of Active Nanorods and Nanocrystals

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Abstract

Lithium-ion storage materials with significantly improved performance were developed through hierarchical assemblies of vanadium-based oxide (V$_2$O$_5$ and LiV$_3$O$_8$) nanorods or iron oxide (Fe$_3$O$_4$) nanocrystals using an efficient, continuous aerosol-spray process. Such hierarchically porous spheres, which were made from networks of low-dimension building blocks, offer the materials with shorten ion-diffusion length, fast electrolyte diffusion, and structural robustness. Resulted from their unique hierarchical structure, these spheres exhibit high lithium storage capacity, excellent cycling stability and good rate capability. This work offers a novel synthesis approach towards better lithium-ion storage materials.

Keywords
hierarchical assembly, lithium-ion storage, aerosol-spray, vanadium oxide, iron oxide

Introduction

Lithium-ion batteries (LIBs) are important energy storage devices for broad uses in portable electronics, hybrid electric vehicles and many other devices [1]. Current lithium-ion electrodes are often made from micron-size particles of active materials, which may result in low rate-capability due to inefficient charge transport. To address this problem, active materials with low-dimension forms (e.g., nanoparticles, nanowires and nanorods) have been extensively explored [2-5]. While the use of low-dimension materials shortens the ion transport length, it also creates more interfaces between the active materials and the other electrode components (e.g., electrolyte, binder, and conductive agent), which may cause performance deterioration during electrode charge/discharge cycling. Materials with
hierarchical structures have shown great interest since they can provide both low-dimensional charge transport properties and better interfacial stability than their nanoscale building blocks. So far great effect has been devoted to design and synthesis of hierarchical electrode materials, such as $\text{V}_2\text{O}_5$[6], $\text{TiO}_2$[7], $\text{SnO}_2$[8], Si/Carbon[9] $\text{Li}_4\text{Ti}_5\text{O}_{12}$[10] and $\text{LiFePO}_4$[11]. However, making these materials is often based on batch-by-batch hydrothermal reaction with special structure directing agents or multi-step deposition/coating techniques, thus limiting the large scale application of such materials.

To address this challenge, we present herein a general structure design of electrode material based on a simple and continuous aerosol-spray synthesis, where nanorods or nanocrystals of the electrode active materials were assembled into robust network spheres. To demonstrate this concept, vanadium oxide ($\text{V}_2\text{O}_5$ and $\text{LiV}_3\text{O}_8$) and iron oxide ($\text{Fe}_3\text{O}_4$) were used respectively as the model cathode and anode materials. Both vanadium oxide and iron oxide are promising candidates for LIBs due to their high capacity, low cost and abundance. Although the average voltage of $\text{V}_2\text{O}_5$ and $\text{LiV}_3\text{O}_8$ is a little lower than that of $\text{LiCoO}_2$ and $\text{LiMn}_2\text{O}_4$, the capacity of $\text{V}_2\text{O}_5$ and $\text{LiV}_3\text{O}_8$ is about twice of these commercial cathode materials. For example, based on the intercalation of 2.5 lithium-ion (1.8-4.0 V) and 4 lithium-ion (2.0-4.0 V), a theoretical capacity of $\sim$350 and $\sim$372 mAh g$^{-1}$ may be achieved for $\text{V}_2\text{O}_5$ and $\text{LiV}_3\text{O}_8$, respectively [6,12-15]. Similarly, $\text{Fe}_3\text{O}_4$ holds a theoretical capacity of $\sim$926 mAh g$^{-1}$, which is significantly larger than that of the commercial graphite anode [16,17]. However, both vanadium oxide and iron oxide show low lithium-diffusion coefficient, poor electronic conductivity and structure instability during cycling [18-20]. Although various low-dimension vanadium oxide and iron oxide based structures (e.g.,
nanorods [21-23], nanowires [24-26], and nanoparticles [27-29]) have been developed with enhanced lithium intercalation kinetics, as explained above, such materials show rapid capacity decay due to structure failure.

Through a simple but efficient aerosol-spray synthesis, micron-size particles can be effectively formed in such a continuous process. These particles will be constructed by vanadium oxide nanorods or Fe$_3$O$_4$ nanocrystals, which are connected into robust porous networks through strong covalent, metallic or ionic bonds. Such micron-size particles, mesoscopically, still retain the low-dimension structure with shortened transport length ensuring better rate performance. Moreover, as-formed network structure provides the particles with mechanical robustness, which enables them to resist mechanical and chemical stress that may be generated during the charge/discharge process. Due to the unique structure, such a simple strategy provides the materials with significantly improved performance for lithium storage, shining light for their large-scale application. Note that aerosol- and ultrasonic-spray method has been used to make electrode materials (e.g., Sn/C[30], LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$[31], but few of them showed hierarchical structure (Si/C composite[32]). Our work provides a general approach that can use various precursors (either salt or colloidal particle solution) to make hierarchical structured electrode materials.

1. Experimental

1.1 Synthesis of V$_2$O$_5$ and LiV$_3$O$_8$ nanorod spheres

In a typical synthesis, 0.4 g of commercial V$_2$O$_5$ (98%, Aldrich) and 3.2 mL of nitric acid (HNO$_3$) (70%, Sigma-Aldrich) were dissolved in 40 mL of de-ionized water, forming a
homogenous light-yellow precursor solution. Then, 0.4 g of block copolymer F127 (EO$_{106}$PO$_{70}$EO$_{106}$, $M_w = 12600$ g mol$^{-1}$, where EO and PO represent ethylene oxide and propylene oxide, respectively) was added into the solutions after stirring for 6 h. The solutions were stirred vigorously for another 12 h before the aerosol-spray process. A homemade aerosol generator was employed to synthesize the nanorod spheres. During the aerosol-spray process, the solutions were delivered via the nitrogen carrier gas to the atomizer nozzle to generate micro-droplets. Then the aerosol droplets were passed through the heating zone set at 400 °C. The resultant powder product was collected on a 450 nm filter paper. The as-synthesized particles were then sintered at 400 °C in air for 6 h to obtain nanorod spheres.

The synthesis of LiV$_3$O$_8$ nanorod spheres was conducted using a similar process. In a typical preparation, 0.4 g of commercial V$_2$O$_5$ (98%, Aldrich) and 3.2 mL of HNO$_3$ (70%, Sigma-Aldrich) were dissolved in 40 mL of de-ionized water, forming a homogenous light-yellow precursor solution. Next, 0.054 g of Li$_2$CO$_3$ (99%, Sigma-Aldrich) was added, and the mixture was actively stirred for 6 h. Then, 0.42 g of F127 was added into the solutions. The solutions were stirred vigorously for 12 h before the aerosol-spray process.

### 1.2 Synthesis of Fe$_3$O$_4$ nanocrystal spheres

To make nanospheres, the Fe$_3$O$_4$ nanocrystals were first synthesized through a co-precipitation method reported by Chen et al.[33] Typically, 1.113 g of FeCl$_2$·4H$_2$O (99%, Aldrich) and 3.027 g of FeCl$_3$·6H$_2$O (97%, Sigma-Aldrich) were dissolved in 150 mL of de-ionized water in a 250 mL three-neck flask. The mixture solution was heated to 50 °C
and vigorously stirred under a nitrogen atmosphere. Then, 12.5 mL of aqueous ammonia solution (28%, Sigma-Aldrich) was rapidly poured into the solution with an immediate color change to black. After that, the reaction solution was cooled down to room temperature after reaction for 30 min. The Fe$_3$O$_4$ nanocrystals were collected by rinsing with de-ionized water for three times.

0.4 g of as-prepared Fe$_3$O$_4$ nanocrystals was dissolved in 40 mL of de-ionized water, sonicating for 2 h to form a homogenous precursor solution. A homemade aerosol generator was employed to synthesize the nanocrystal spheres. During the aerosol-spray process, the solutions were delivered via nitrogen carrier gas (40 psi) to the atomizer nozzle (TSI model 3076) to generate micro-droplets. Then the aerosol droplets were passed through the heating zone in a tube furnace set at 450 °C. The resultant powder product was collected at the end of the furnace and then sintered at 400 °C under an argon atmosphere for 4 h to obtain nanocrystal spheres.

1.3 Structural Characterization and Electrochemical Measurements

The x-ray diffraction (XRD) patterns were obtained with an X’Pert Pro X-ray powder diffractometer operating at 45 kV and 40 mA equipped with nickel-filtered Cu Kα radiation (λ = 1.5418 Å). The grain sizes of V$_2$O$_5$ sphere were calculated by JADE 5, determined by peaks of (110) reflection, using the Scherrer equation, $d = \frac{0.9 \cdot \lambda}{\beta \cos \theta}$, where the λ is the wavelength of the x-ray, β is the full width at half maximum (FWHM) corrected for instrumental broadening, and θ is the Bragg angle of the diffraction peak. Nitrogen adsorption/desorption isotherms were obtained using a Micromeritics ASAP 2020 analyzer.
The specific surface areas were calculated using N\textsubscript{2} adsorption branch at 77 K by the Brunauer–Emmett–Teller (BET) method. Pore size distributions (D\textsubscript{p}) were derived from the adsorption branches of isotherms. Prior to the measurement, all samples were degassed at 200 °C under vacuum for 4 h. The relative pressure of BET calculation is \( P/P_0 = 0.05 \sim 0.25 \). SEM and TEM were conducted on a JEOL JSM-6700 FE-SEM and Philips CM120 instrument, respectively.

The electrodes were fabricated by coating slurries containing 80 wt-% of active material, 10 wt-% of carbon black and 10 wt-% of PVDF binder dispersed in NMP (N-methylpyrrolidinone) on stainless substrates, and dried at 90 °C for 12 h under vacuum. Cell assembly was carried out in an argon-filled glovebox with moisture and oxygen below 1 ppm. 1.0 M LiPF\textsubscript{6} in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume ratio) was used as the electrolyte. For the V\textsubscript{2}O\textsubscript{5} nanorod spheres, the typical electrode loading was about 2.7 mg cm\textsuperscript{-2} (active material). The charge/discharge tests were performed over the potential region of 1.8–4.0 V with different rates on LAND CT2000 battery tester. Cyclic voltammetry (1.8–4.0 V, 1 mV s\textsuperscript{-1}) was conducted in a Bio-Logic VMP3 electrochemistry workstation. For the LiV\textsubscript{3}O\textsubscript{8} nanorod spheres, the typical electrode loading was about 3.0 mg cm\textsuperscript{-2}. The charge/discharge tests were performed over the potential region of 2.0–4.0 V with different current densities. For the Fe\textsubscript{3}O\textsubscript{4} nanocrystal spheres, the typical loading was about 2.9 mg cm\textsuperscript{-2}. The charge/discharge tests were performed over the potential region of 0.005–3.0 V with a current density of 100 mA g\textsuperscript{-1}.

2. Results and Discussion

2.1 V\textsubscript{2}O\textsubscript{5} nanorod spheres
Figure 1 illustrates our synthesis strategy based on a simple aerosol-spraying process. For example, we started with homogenous solutions prepared by dissolving commercial V$_2$O$_5$ powder in acidic surfactant solution. Atomization process using nitrogen as the carrier gas continuously generated aerosol droplets, which were passed through a heating zone and converted to homogenous V$_2$O$_5$ nanocomposite particles. Subsequent sintering process removed the surfactant, induced growth of V$_2$O$_5$ nanorods within the particles and resulted in the formation of porous spheres hierarchically constructed from networks of the nanorods.

![Figure 1](image)

**Figure 1.** Schematic illustration of the synthesis of V$_2$O$_5$ nanorod-spheres by aerosol spraying.

Figure 2a shows a scanning electron microscopy (SEM) image of the V$_2$O$_5$ particles with diameters ranging from 100 to 500 nm. Each particle is made from nanorods with diameters of about 20-40 nm and length of about 100 nm (inset of Figure 2a). Figure 2b shows transmission electron microscopy (TEM) images of the V$_2$O$_5$ particles, clearly confirming that
these nanorods are interweaved into porous networks. The inset of Figure 2b further confirms the small dimension of the nanorods with abundant mesopores with pore size of 20-30 nm. Figure S1 shows nitrogen adsorption/desorption isotherms and pore size distribution of V$_2$O$_5$ nanorod spheres and commercial V$_2$O$_5$ particles, both of which are similar in shape. Compared with commercial V$_2$O$_5$ particles, the V$_2$O$_5$ nanorod spheres exhibit higher surface area and larger pore volume, which is consistent with the SEM and TEM observations (Table S1). Although their average pore sizes are similar, the V$_2$O$_5$ nanorod spheres possess abundant mesopores, leading to the formation of a hierarchically porous structure that facilitates the transport of lithium ions.

![Figure 2: (a) SEM and (b) TEM images of the nanorod spheres.](image)

To understand the growth mechanism of the V$_2$O$_5$ nanorod spheres, we further investigated the morphological and structural evolution of the particles using electron microscopic and x-ray diffraction (XRD) techniques (Figure 3 and Figure 4). It was found that the as-synthesized particles (prior to the sintering process) show non-porous, smooth and uniform spherical structure (see the SEM image in Figure 3a and TEM image in Figure 3e);
XRD suggests an amorphous nature of such particles (Figure 4a). After sintering at 250 °C for 1 h, the surfaces of the particles became rough (Figure 3b, f) and the crystalline phase appeared (Figure 4a). The crystalline structure further developed with increasing temperature to 300 °C and 400 °C (Figure 4a); consistently, nanorods of the V$_2$O$_5$ were developed gradually leading to the formation of nanorod spheres at 400 °C.

Figure 3. SEM (a-d) and TEM (e-h) images of the V$_2$O$_5$ particles prior to and after sintering at 250 °C, 300 °C, and 400 °C for 1 h in air.
**Figure 4.** (a) XRD patterns of the V$_2$O$_5$ nanorod spheres sintered at different temperatures indicating their crystalline structure evolution and (b) XRD patterns of the V$_2$O$_5$ nanorod spheres and the commercial V$_2$O$_5$ particles.

The crystalline structure of the V$_2$O$_5$ nanorod spheres after sintering at 400 °C were further compared with that of the commercial one (Figure 4b). All the diffraction peaks of the nanorod spheres agree well with those of the commercial V$_2$O$_5$, which can be assigned to an orthorhombic phase with a space group of *Pmmn* (a = 11.516 Å, b = 3.5656 Å, c = 4.3727 Å). The diffraction peaks of the nanorod spheres show lower intensity and broader width, suggesting smaller crystallites. According to the Scherrer equation, the average grain size of the nanorod spheres is around 32.8 nm estimated from the (110) reflection, which is smaller than that of the commercial one (50.4 nm).

The lithium storage behavior of the V$_2$O$_5$ nanorod spheres was first characterized by cyclic voltammetry (CV) test in three-electrode cells using lithium foils as both the reference and counter electrodes. As shown in Figure 5a, in agreement with previous studies, two pairs of redox peaks can be observed in the high voltage window of 2.8–4.0 V, usually corresponding to lithium-ion intercalation into α-V$_2$O$_5$ to form ε-Li$_{0.5}$V$_2$O$_5$ and δ-LiV$_2$O$_5$, respectively. In the low voltage window of 1.8–2.8 V, another pair of redox peaks can be also noted, which is attributed to more lithium-ion intercalation into δ-LiV$_2$O$_5$ to form γ-Li$_2$V$_2$O$_5$ and ω-Li$_3$V$_2$O$_5$, respectively [34,35]. In comparison, a commercial V$_2$O$_5$-based electrode was also fabricated and tested at the same condition. It can be observed that the nanorod-spheres-based electrode has a larger CV area than that of the commercial V$_2$O$_5$-based
electrode, indicating a higher charge-storage capacity. In addition, the commercial V$_2$O$_5$ electrode presents similar intercalation/de-intercalation peaks, though the peak separation of the commercial-V$_2$O$_5$ electrode is significantly larger than that of the nanorod-sphere electrode, indicating a larger polarization due to inefficient ion transport [36].

Figure 5. (a) The CV curves of electrodes made from V$_2$O$_5$ nanorod spheres and commercial V$_2$O$_5$ particles cycled in a voltage range of 1.8 to 4.0 V (vs. Li/Li$^+$) at a scan rate of 1 mV s$^{-1}$. The peak currents were normalized to their active mass. (b) The charge/discharge curves of V$_2$O$_5$ nanorod spheres for the first three cycles between 1.8 and 4.0 V at a current density of 70 mA g$^{-1}$. (c) Comparison of the cycling stability of electrodes made from the nanorod spheres, crashed nanorod spheres, and commercial V$_2$O$_5$ particles cycled between 1.8 and 4.0 V at a current density of 70 mA g$^{-1}$. 
(d) Rate-capability of electrode made from V$_2$O$_5$ nanorod spheres cycled between 1.8 and 4.0 V at different current densities of 70, 140, 280, 1400 mA g$^{-1}$, respectively.

Galvanostatic charge/discharge experiments were further conducted to quantify the storage capacity of both electrodes. Figure 5b shows the charge/discharge curves of the nanorod-spheres-based electrode for the first three cycles in a voltage window of 1.8–4.0 V at a current density of 70 mA g$^{-1}$. On the first discharge, the electrode exhibited a typical voltage profile of lithium insertion into orthorhombic V$_2$O$_5$. After the cell was discharged to 1.8 V, a total capacity of 425 mAh g$^{-1}$ can be achieved, which is close to the theoretical capacity of V$_2$O$_5$ with intercalation of 2.5 lithium-ion (370 mAh g$^{-1}$), if considering some irreversible capacity contribution from proton replacement by lithium-ion or other surface reactions at the first cycle [37]. Three voltage plateaus due to the phase transitions (from $\alpha$-V$_2$O$_5$ to $\varepsilon$-Li$_{0.5}$V$_2$O$_5$, $\delta$-LiV$_2$O$_5$, $\gamma$-Li$_2$V$_2$O$_5$ and $\omega$-Li$_3$V$_2$O$_5$) associated with lithium-ion intercalation were observed on the first discharge curve. The multi-step voltage plateaus disappeared in the following cycles, which was in agreement with the CV test (Figure S2) and was consistent with previous reports [35,38]. In contrast, the commercial V$_2$O$_5$-based electrode showed similar phase transition behavior but with a much lower irreversible capacity of 228 mAh g$^{-1}$.

Note that for various V$_2$O$_5$-based lithium electrodes, a common issue is their rapid capacity decay due to structure and volume changes during cycling [18, 19]. Thus, improving the cycling stability of V$_2$O$_5$ electrode has been the main topic. Nevertheless, our unique nanorod-assembled sphere architecture does endow the V$_2$O$_5$ electrodes with excellent
cycling stability. Figure 5c shows cycling performance of the nanorod-sphere- and commercial V2O5-based electrodes cycled between 1.8 and 4.0 V at a current density of 70 mA g⁻¹. The nanorod spheres were able to deliver a discharge capacity of 306 mAh g⁻¹ at the 2nd cycle or a capacity of 232 mAh g⁻¹ and 201 mAh g⁻¹ at the 20th and 50th cycles, respectively. The average capacity fading rate was about 0.68 % per cycle, indicating a good cycling stability. By comparison, the commercial V2O5 exhibited a much lower capacity of only 146 mAh g⁻¹ at the 2nd cycle and 102 mAh g⁻¹ at the 50th cycle. Note that some other nanostructured V2O5 electrodes may show similar capacity at initial cycles, but with much faster capacity fading [39,40].

To further confirm that the nanorod-sphere structure is responsible for the outstanding cycling stability, we crashed the nanorod structure (see SEM image in Figure S3) and tested their lithium storage performance under the same condition. As shown in Figure 5c, the electrode made from the crashed sample still exhibited a high discharge capacity of 404 mAh g⁻¹ at the initial cycle, but showed a rapid capacity fading to a rather low value of 109 mAh g⁻¹ after 50 cycles. This study clearly demonstrates that the nanorod-sphere structure does significantly enhance the cycling stability.

Besides the improved capacity and stability, the nanorod-sphere electrodes also showed better rate-capability. Figure 5d shows the capacities of the nanorod-sphere electrodes at different charge/discharge current densities. These electrodes can deliver a reversible capacity of 306 mAh g⁻¹ at 70 mA g⁻¹, 211 mAh g⁻¹ at 140 mA g⁻¹ and 105 mAh g⁻¹ at 1400 mA g⁻¹. Moreover, after 40 cycles, a capacity of 225 mAh g⁻¹ was achieved when the charge/discharge current density was returned to 70 mA g⁻¹, further confirming the good
cycling stability. However, the commercial \( V_2O_5 \) can only deliver a capacity of 19 mAh g\(^{-1}\) at current of 1400 mA g\(^{-1}\) (Figure S4) due to slower lithium diffusion in the bulk electrodes. Such impressive rate performance is attributed to the low-dimension structure of the nanorods that enables fast lithium diffusion, as well as the porous channels that supports efficient electrolyte transport. Note that such rate capability is better than that of submicron spherical \( V_2O_5 \) reported in the literature [41,42]. Although electrospun-\( V_2O_5 \) electrode showed similar capacity but their rate capabilities were not reported [43].

2.2 LiV\(_3\)O\(_8\) nanorod spheres

Besides \( V_2O_5 \) nanorod spheres, nanorod-spheres of LiV\(_3\)O\(_8\) were also synthesized using a similar process. Figure 6a shows XRD of the LiV\(_3\)O\(_8\) nanorod spheres sintered at 400 °C, suggesting a layered-type LiV\(_3\)O\(_8\) (JCPDS 72-1193) structure of which the diffraction peaks can be assigned to a monoclinic phase with a space group of P2\(_1\)/m. Figure 6b displays the SEM image of the LiV\(_3\)O\(_8\) nanorod spheres, showing morphology similar to that of the \( V_2O_5 \) particles. The sizes of the spheres are ranged from 100 to 500 nm in diameter. Similarly, these spheres consist of nanorods with diameters of 10-30 nm and length of about 100 nm (inset of Figure 6b). Table S1 summarizes the surface area and the pore structure properties of LiV\(_3\)O\(_8\) nanorod spheres, revealing porous structure similar to that of the \( V_2O_5 \) nanorod spheres.

Similar to \( V_2O_5 \), previous LiV\(_3\)O\(_8\)-based electrodes also normally showed rapid capacity decay due to structure and volume changes during cycling [44,45]. Nevertheless, our unique nanorod sphere architecture could also endow the LiV\(_3\)O\(_8\) electrodes with excellent cycling
stability. Figure 6c shows the cycling performance of the LiV$_3$O$_8$ nanorod-sphere electrode cycled between 2.0 and 4.0 V at a current density of 100 mA g$^{-1}$. The nanorod-sphere electrodes presented an initial discharge capacity of 324 mAh g$^{-1}$. Hereafter, the discharge capacity decreased to 284 mAh g$^{-1}$ and 262 mAh g$^{-1}$ at the 20$^{th}$ and 50$^{th}$ cycles, respectively. The average capacity fading rate was about 0.38 % per cycle, which was lower than other nanostructured LiV$_3$O$_8$ electrodes with similar initial capacity at initial cycle [46,47].

![Figure 6](image_url)

**Figure 6.** (a) XRD patterns of the LiV$_3$O$_8$ nanorod spheres. (b) SEM image of the LiV$_3$O$_8$ nanorod spheres. (c) Comparison of the capacity retention of electrodes made from the LiV$_3$O$_8$ nanorod spheres and the crashed LiV$_3$O$_8$ nanorod spheres cycled between 2.0 and 4.0 V at a current density of 100 mA g$^{-1}$. (d) Rate-capability of electrode made from LiV$_3$O$_8$ nanorod spheres cycled between 2.0 and 4.0 V at different current densities of 100, 300, 500 and 1000 mA g$^{-1}$, respectively.
Similarly, we also crashed the LiV$_3$O$_8$ nanorod-sphere structure (see SEM image in Figure S5) and examined their lithium storage performance. As shown in Figure 6c, the electrodes made from the crashed sample still delivered a high discharge capacity of 323 mAh g$^{-1}$ at initial cycle, but it faded quickly to a rather low value of 122 mAh g$^{-1}$ at the 50$^{th}$ cycle. Therefore, the significantly enhanced cycling stability should be ascribed to the hierarchical nanorod-sphere structure.

In addition, the rate-capability was consistently improved. Figure 6d shows the capacities of the nanorod-sphere electrodes at various current densities. When operated at current density of 100 mA g$^{-1}$, 300 mA g$^{-1}$, 500 mA g$^{-1}$, and 1000 mA g$^{-1}$, these electrodes were able to deliver a reversible capacity of 324 mAh g$^{-1}$, 243 mAh g$^{-1}$, 187 mAh g$^{-1}$, and 133 mAh g$^{-1}$, respectively. Moreover, a capacity of 265 mAh g$^{-1}$ was achieved after 40 cycles at 100 mA g$^{-1}$, further confirming the good cycling stability. Such impressive rate performance is also attributed to the low-dimension structure of the nanorods and the porous channels. It should be mentioned that such rate capability is also better than that of micron-rod LiV$_3$O$_8$ reported in the literature [48].

### 2.3 Fe$_3$O$_4$ nanocrystal spheres

To further examine the superiority of hierarchical structure, iron oxide was used as a model material for anode application. Different from making V$_2$O$_5$ structures using molecular precursor solutions, Fe$_3$O$_4$ nanocrystal spheres was made by directly assembling Fe$_3$O$_4$ nanocrystals. The prepared Fe$_3$O$_4$ nanocrystal spheres were first examined by XRD. Figure S6 shows that the pattern of the annealed particles can be indexed as face-centered...
cubic Fe$_3$O$_4$ (JCPDS 65-3107, a = b = c = 8.390 Å). The size and morphology of the Fe$_3$O$_4$ particles were examined by SEM. Figure 7a shows that most of the Fe$_3$O$_4$ particles present spherical-shape with diameter of around 100-600 nm. It can be clearly seen that these spheres are composed of many nanocrystals with average size of about 8 nm; these nanocrystals are interconnected together forming a porous structure (inset of Figure 7a). Compared with the Fe$_3$O$_4$ nanocrystals, the Fe$_3$O$_4$ nanocrystal spheres exhibit lower surface area and smaller pore volume (Table S1). However, the Fe$_3$O$_4$ nanocrystal spheres possess larger average pore size than the Fe$_3$O$_4$ nanocrystals, which is expected to facilitate electrolyte penetration into the electrode particles, and provide favorable transport kinetics for lithium ions.

![Figure 7](image)

**Figure 7.** (a) SEM image of Fe$_3$O$_4$ nanocrystal spheres. (b) Comparison of the capacity retention of electrodes made from the Fe$_3$O$_4$ nanocrystal spheres and the Fe$_3$O$_4$ nanocrystals cycled between 0.005 and 3.0 V at a current density of 100 mA g$^{-1}$.

In order to examine the cycling stability of Fe$_3$O$_4$ nanocrystal spheres as lithium anode material, the capacity retention of Fe$_3$O$_4$ nanocrystal spheres and Fe$_3$O$_4$ nanocrystals is compared in Figure 7b. Compared with that of Fe$_3$O$_4$ nanocrystals, the specific capacity of
Fe$_3$O$_4$ nanocrystal spheres anode is greatly enhanced at a current density of 100 mA g$^{-1}$. The irreversible capacity loss in the first cycle can be attributed to the formation of a SEI layer. At the 2$^{nd}$ cycle, the Fe$_3$O$_4$ nanocrystal-sphere electrode exhibited a discharge capacity of 857 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$. The reversible capacity of Fe$_3$O$_4$ nanocrystal spheres remained to be approximately 511 mAh g$^{-1}$ at the end of 50$^{th}$ cycle, while it was better than those of the porous Fe$_3$O$_4$ spheres [49] and hollow Fe$_3$O$_4$ spheres synthesized via hydrothermal method [50]. This can be attributed to the structural robustness of the nanocrystal-sphere structure. Although the Fe$_3$O$_4$ nanocrystals electrode had a discharge capacity of 800 mAh g$^{-1}$ at the 2$^{nd}$ cycle, it faded quickly during the subsequent cycles: the electrode lost more than 80% of the initial capacity after 50 cycles.

The above results clearly demonstrate that nanorod/nanocrystal spheres have higher lithium ion storage capacity, better cycling stability, and better rate capability than native low-dimension nanorods or nanocrystals. The remarkable improvement of the electrochemical performance could be attributed to the following reasons: (a) the networks of interconnected nanoparticles could significantly facilitate the electrolyte to pass through the whole sphere structure, and therefore more surface sites are accessible when lithium ions react with the active materials; (b) hierarchical spheres have robust structures, which may greatly decrease the possible structural destruction induced by large lithium ion insertion, especially at high charge/discharge rates; (c) the porous structure keeps the electrode-electrolyte contact and shortens the lithium ions diffusion distance, which may improves the lithium ion transport [51-54]. In addition, we note that the electrochemical performance of such spheres could be further improved by introducing carbon matrices to facilitate electronic conductivity and
electron transport, which will be reported separately.

3. Conclusions

In summary, using an efficient aerosol-spraying process, we successfully demonstrated a class of high-performance lithium-storage architectures by constructing oxide-based hierarchical spheres. Such spheres are constructed from interconnected nanorod or nanocrystal networks with hierarchically porous structure, which simultaneously provides structure stability and fast lithium insertion/extraction kinetics. These properties endow the electrodes with high capacity, excellent cycling stability and good rate capability. Considering the generality of our method, we believe this materials strategy can be extended to synthesize many other metal oxides and composites for energy storage and other applications.

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Better lithium-storage architectures based on hierarchically assembled nanorods or nanocrystals were developed using an efficient aerosol-spraying process.

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