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Single step hydrothermal synthesis of mixed valent V\textsubscript{6}O\textsubscript{13} nano-architectures: A case study of the possible applications in electrochemical energy conversion

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Abstract

Availability of several stable vanadium oxidation states offers numerous advantages in terms of applications but at the same time it poses great challenge to isolate them in single phase during their synthesis process. In this study, we developed a facile single step hydrothermal synthesis of V\textsubscript{6}O\textsubscript{13} nano-architectures using environmental friendly citric acid as a reducing agent. By means of time dependant hydrothermal conditions study, we observed evolution of several stable vanadium oxide phases. The as-synthesized powder samples phase confirmation was thoroughly studied by powder X-ray diffraction and transmission electron microscopy. The morphology of the products formed was investigated at each hydrothermal reaction time. Finally, these V\textsubscript{6}O\textsubscript{13} nano-architectures were employed as counter electrode (CE) in dye sensitized solar cells (DSSCs). The photovoltaic performance and the electrical impedance studies of the DSSC device made use of V\textsubscript{6}O\textsubscript{13} nano-architectures are reported here. It is believed that with further optimization, this relatively inexpensive material can act as efficient CE for DSSCs, which thereby open up a new avenue for vanadium oxides as a new class of materials for clean energy generation.

Keywords: Hydrothermal synthesis; V\textsubscript{6}O\textsubscript{13} nano-architectures; Counter electrode; DSSCs; Pt free; Chemical synthesis
1. Introduction

Over the past few decades, vanadium oxides have attracted much research attention due to existence of multiple valence states from two in VO, three in V₂O₃, four in VO₂ to five in V₂O₅.[1] Along with these multiple valence states, different co-ordination geometries and their layered structured nature made them promising candidates for potential energy related applications, such as cathode in lithium batteries, super capacitors.[2-7] The vanadium-oxygen (V-O) phase diagram is complex due to existence of a wide range of ordered and disordered defect structures with mixed valent compounds, so-called Magneli (VₙO₂ₙ₋₁) and Wadsley (V₂ₙO₅ₙ₋₂) phases.[8, 9] It is worth noting that the mixed-valence chemistry of these vanadium oxides is considerably less well established, especially in terms of solution based synthesis processes such as hydrothermal methods.[10]

V₆O₁₃ belongs to the Wadsley phase category taking the mixed valences of V⁴⁺ (d¹) and V⁵⁺ (d⁰) and has been considered as an excellent candidate for the battery cathode material due to its high electrochemical capacity.[11, 12] So far, numerous synthetic procedures are proposed to prepare the pristine V₆O₁₃ such as solid state reaction at elevated temperatures for few days, annealing the hydrated vanadium pentoxide aerogels under pure argon, thermal decomposition of NH₄VO₃ in a stream of high purity argon/nitrogen atmosphere, an electrodeposition thermal process, and a hydrothermal process.[13-19] In addition, often the V₆O₁₃ phase is formed as an intermediate during VO₂ synthesis under reducing conditions.[20, 21] Among these, solution-based hydrothermal synthesis has many advantages due to its selective nature, the number of adjustable parameters during reaction, low cost and suitability for large-scale synthesis, low temperature and no special equipments required. In general, the main strategy to prepare V₆O₁₃ under hydrothermal conditions is to reduce stable high oxidation
degree of vanadium ($V^{5+}$) using reducing agents. Some of the recent hydrothermally processed $V_6O_{13}$ results are summarized in Table 1, where in some cases four preparation steps are involved and even hydrogen peroxide ($H_2O_2$) is essential to obtain the desired $V_6O_{13}$ phase. Due to complex V-O phase diagram, isolation of one single phase compounds are often very challenging particularly mixed valent compositions. Hence, one needs to work out an elaborate synthesis protocol to ensure the formation of a pure phase and to avoid other undesirable vanadium oxides.

Dye sensitized solar cells (DSSCs) have evolved as commercially realistic generators of electric power from sunlight. Due to high electrocatalytic activity and excellent conductivity, platinum (Pt) is a conventional choice as a counter electrode (CE) which is an important component of DSSCs. Pt costs about 40% of the total manufacturing cost of DSSCs.[22] Hence there is an ongoing effort to discover alternative CEs. Since the vanadium oxides have both good catalytic activity and a significantly lower precursor price, we have selected and employed $V_6O_{13}$ nano-architectures as a CE in DSSCs. To the best of our knowledge, this is the first time $V_6O_{13}$ nano-architectures have been synthesized using $V_2O_5$ and citric acid as the starting materials by a facile single step hydrothermal process and explored as a CE for DSSCs.

2. Synthesis and characterization

2.1 Materials synthesis

$V_6O_{13}$ nano-architectures were synthesized by a single step hydrothermal synthesis. An aqueous solution of $V_2O_5$ (Sigma Aldrich analytical grade) was prepared by dissolving 2.6 mmol $V_2O_5$ in double distilled water under magnetic stirring. Later same molar quantity of citric acid monohydrate ($C_6H_8O_7\cdot H_2O$; Sigma Aldrich) was added into the above solution and
stirring was prolonged for 15 min. After complete dissolution, the resulting solution was transferred to a Teflon-lined stainless steel autoclave of 30 mL volume for thermal treatment at 180°C for different duration of reaction times. Once the reaction time was complete, the autoclaves were cooled down to ambient temperature naturally; the resultant powder samples were collected and rinsed with distilled water and then with ethanol several times; the products were finally dried in an oven at 50°C for 6 hrs.

2.2 Characterization

The phase purity and crystallographic structure of the as-synthesized powder specimens were confirmed by X-ray diffraction (XRD; PANalytical X’ Pert Diffractometer). Conventional transmission electron microscopy (CTEM) and as well as high resolution transmission electron microscopy (HRTEM) were carried out on V_6O_{13} nano-architectures in order to determine the local structure of the material. The followed procedures can be found in our previous reports.[23, 24] The surface morphology of powder specimens was investigated by scanning electron microscopy (Quanta 650 FEG SEM). The V_6O_{13} film was fabricated by doctor blade technique, as detailed in section 3.4.1, and then directly used as CE of DSSC. Photovoltaic performance and electrochemical impedance spectroscopy of these DSSCs were recorded on a Keithley 2400 source meter under AM1.5 Global solar simulator and with an Autolab electrochemical workstation.

3. Results and discussion

3.1. Phase formation studies using X-ray diffraction

Unless specified all the hydrothermal reactions were performed at 180°C. Fig. 1 represents typical XRD patterns of the samples prepared by the hydrothermal process at 180°C for different reaction durations. The dissolution of V_2O_5 in water gives rise to a yellow
coloured aqueous solution. The hydrothermal reaction for 5 hrs at this stage (absence of citric acid) results in yellowish $V_2O_5$ only and shows the phase stability of $V_2O_5$ under these hydrothermal conditions (Fig. 1a).[25] In the second step, by the addition of citric acid and prolongation of the stirring time, a light green/blue solution forms, which indicates that the valence state of vanadium in the solution was partly reduced from $V^{5+}$ to $V^{4+}$ ($V^{5+}$ and $V^{4+}$ solutions are yellow and blue colours, respectively). This indicated that citric acid acts as the reducing regent. It is noted that in this study only the duration of hydrothermal reaction was varied by keeping other parameters fixed. XRD studies after hydrothermal reaction for 1 hr shows a greenish coloured mixed valence hydrate $V_{10}O_{24}.9H_2O$ (Fig. 1b) (JCPDS card number 25-1006). This shows that $V_2O_5$ structure allows $H_2O$ molecules to be embedded in the intercalation sites without a far-reaching restructuring; in the same time the presence of a reducing agent as well as the increase in reaction duration promotes the reduction of $V^{5+}$ to $V^{4+}$ and accelerates the hydrate formation. Further increasing the duration to 5 hrs results in bluish coloured $V_6O_{13}$ and simulated pattern obtained using JCPDS card number 01-075-1140 (Fig. 1c). All the XRD reflections can be readily indexed as the monoclinic crystalline phase with space group: $C2/m$ (12) and lattice parameters of $a=11.934(2)$ Å, $b=3.6775(3)$ Å, $c=10.142(2)$ Å and $\beta = 100.81(1)^\circ$ of $V_6O_{13}$ and this is in agreement with the literature. [26] No peaks of any other phases are detected, indicating that the as-prepared $V_6O_{13}$ is phase-pure. In the final step, hydrothermal reaction for 7 hrs bluish-black coloured VO$_2$ (B) phases (Fig. 1d) (JCPDS card number 01-81-2392). These results express the conversions among vanadium oxides in these reducing hydrothermal conditions as follows: $V_2O_5 \rightarrow V_{10}O_{24}.9H_2O \rightarrow V_6O_{13} \rightarrow VO_2$(B). The $V_6O_{13}$ crystal structure contains slightly distorted VO$_6$ octahedra. These octahedra are joined by corner sharing single sheets and edge sharing
double sheets parallel to (010) plane. Corner share single sheets form a “V₂O₅-layer” of octahedra, and by contrast, edge share double sheets form a “VO₂(B)-layer” of octahedra. Obviously V₂O₅, VO₂(B) and V₆O₁₃ have a close resemblance among their crystal structures. They have similar polyhedral connectivity and a similar structural repeat unit along the a-b plane. It is expected from the adjacent area in V-O binary phase diagram that the free energy of V₆O₁₃ is close to that of V₂O₅ and VO₂(B), suggesting a rather facile inter-convertibility among V₂O₅, V₆O₁₃ and VO₂(B) through oxidation/reduction.

3.2 Morphological study by SEM

In order to investigate the morphology of the synthesized products of the time dependant hydrothermal reactions, SEM characterization was performed on samples at different reaction times. Fig. 2 shows the representative SEM images of the precursor (hydrothermally treated V₂O₅; without reducing agent), intermediate sample (V₁₀O₂₄.9H₂O), desired phase (V₆O₁₃) and the end product (VO₂(B)). The morphology of V₂O₅ precursor consists of rod-like structures shown in Fig. 2a whose size ranging from a few nm-1 μm. After 1 hr of reaction flower like particles (Fig. 2b) formed whose phase is confirmed as V₁₀O₂₄.9H₂O from XRD. When the reaction carried out to 5 hrs the desired V₆O₁₃ phase was formed which was confirmed by XRD and TEM in the next section. The morphology of V₆O₁₃ powder sample is predominantly consists of a large quantity of layered nano-structure stackings. These morphologies are consistent with the layered crystal structure nature of V₆O₁₃. It can be seen from the SEM micrograph in Fig. 2c that high density bundle-like V₆O₁₃ nano-architectures uniformly grow. Here each nano-architecture has a characteristic size of about 1-2 μm and consists of several thin nanosheets, which are stepwise stacked. A magnified view of these bundles can be seen in Fig. 2c inset, which shows the stacking of
these nanosheets. With further reaction upto 7 hrs, VO₂ (B) spherical particles with diameter range from ~1.5 to 4 µm were formed.

3.3 Phase confirmation of V₆O₁₃ by TEM

The phase confirmation of the as-synthesized V₆O₁₃ powder samples at 180°C/5 hr was further characterized by TEM. Fig. 3a shows a typical low resolution TEM image of an individual nanosheet which was scraped off the nano-architecture, which are made up of several nanosheets. The single nanosheet is of good transparency to the electron beam and is homogenous, which indicates that the nanosheets are very thin and their surfaces are very flat. On the other hand, a nano-architecture is not transparent. A set of well resolved parallel lattice fringes are observed in high resolution TEM, as shown in Fig. 3b. The interplanar spacing is measured to be 0.58 nm and corresponding to that of (200) planes of V₆O₁₃. This is confirmed in Fig. 3c which shows its corresponding diffraction pattern and exhibits visible bright spots corresponding to the crystal planes of the monoclinic V₆O₁₃ as imaged along the [001] zone axis, indicating the individual preferentially oriented grains are of good crystal quality.

3.4. DSSC device fabrication and characterization

3.4.1. DSSC electrodes preparation and device assembly

V₆O₁₃ films have been used as CEs. The detailed experimental procedures of CE preparation are described as follows. Initially fluorine doped tin oxide (FTO) coated glass substrates were cleaned with soapy water followed by deionised water and isopropyl alcohol. Adhesive tapes were stuck on the edges of the substrate to obtain an area of 1cm² shown in Fig. 4 step1. Later a smooth viscous paste was prepared by mixing V₆O₁₃ powder with ethyl cellulose and α-terpineol. A portion of this paste was applied near the top edge of the FTO glass and the paste spread across from one end to the other by sliding the microscopic glass
slide, as shown in step 2. The step 3 image shows that the area not covered by the adhesive tape has been coated by V\textsubscript{6}O\textsubscript{13}. Later the adhesive tapes were removed and the printed electrodes were sintered under inert atmosphere at 450ºC for 30 mins to remove the organic binders which ensure good electrical contact between the particles and good adhesion to the FTO substrate. The resulting sintered V\textsubscript{6}O\textsubscript{13} film (schematic of final CE is shown in step 4) was placed in a sealed environment to protect these films from absorbing moisture from ambient air.

The dye (N719) sensitized TiO\textsubscript{2} photo-electrode (PE) was prepared in the same way as reported elsewhere,[27] except the deposition method was doctor blade technique. Later a prototype DSSC was fabricated by assembling PE and CE into a sandwich type cell. Both the electrodes were fastened using paper binder clips and the liquid electrolyte (Iodine redox couple[28]) was drawn into the cell by capillary effect and the final device was set for characterization.

3.4.2. DSSC device characterization

Photovoltaic performances of DSSCs were tested at a light intensity of 100 W/m\textsuperscript{2} with an active cell area of 0.25 cm\textsuperscript{2}, which was defined by a mask. The photocurrent density–voltage (J-V) curve of DSSC is displayed in Fig. 5a and corresponding photovoltaic parameters are as follows: the short circuit current (J\textsubscript{sc}) is 1.83 mA/cm\textsuperscript{2}, open circuit voltage (V\textsubscript{oc}) is 0.55 V, fill factor (FF) is 0.57 and cell efficiency is 0.57\%. The lower power conversion efficiency of this DSSC compared with more conventional ones is attributed to the electro catalytic activity of the CEs.

Electrochemical impedance spectroscopy (EIS) measurements were performed to understand the electrocatalytic performance of the CE towards reduction of I\textsubscript{3}-. The impedance
spectra were collected under dark conditions by varying the frequency from 0.1 Hz to 1 MHz at AC amplitude of 10 mV. The obtained Nyquist plot of full cells at DC bias 0.9 V is shown in Fig. 5b. The charge transfer resistance at the CE/electrolyte interface ($R_{ct}$) in the Nyquist plots is our main focus since the CE used for DSSCs is responsible for this. The $R_{ct}$ value of DSSC at a bias of 0.9 V was found to be approximately 120 Ω. Furthermore, $R_{ct}$ is a measure of the catalytic activity of counter electrode for reducing I$_3^−$, therefore it is predicted that changing the morphology would increase the catalytic sites of the counter electrodes for reducing I$_3^−$ and hence improve the performance. Although the performance of V$_6$O$_{13}$ based DSSCs is presently inferior to that of conventional Pt based DSSCs, this material has great potential to be used as a CE in DSSCs due to its unique chemical stability, selectivity, good catalytic activity and electrical conductivity.

4. Conclusions and future directions

In summary, nano-architectures of pure phase V$_6$O$_{13}$ were successfully synthesized by a single step hydrothermal synthesis using citric acid as reducing agent for the first time. The phase formation and purity were confirmed by XRD and TEM and to the best of our knowledge; V$_6$O$_{13}$ has been implemented for the first time as a CE in DSSC devices. The photovoltaic performance of 0.57% is achieved with a fill factor of about 57%. As this device performance is far from being optimized, profound benefits would come with this inexpensive, facile synthesis and scalable materials, suggesting the potential of V$_6$O$_{13}$ as a candidate for alternative CEs in DSSCs. Further improvements can be expected by tuning the particle size, increasing electric conductivity by means of doping, making composites with graphene, and testing against alternative redox mediators and dyes.
5. Acknowledgements

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References


Table 1: V₆O₁₃ recent synthesis literature (LIBs: Li-ion batteries; NIBs: Na-ion batteries)

<table>
<thead>
<tr>
<th>Year</th>
<th>Precursors</th>
<th>Conditions</th>
<th>Morphology</th>
<th>Application</th>
<th>Reference</th>
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<tr>
<td>2011</td>
<td>V₂O₅, H₂O₂, Octylamine, Acetone, Absolute ethanol</td>
<td>160°C/48 hrs</td>
<td>Hollow-flowers</td>
<td>Super-capacitor</td>
<td>[13]</td>
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<tr>
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<td>V₂O₅, Ethanol</td>
<td>160°C/24 hrs Annealed at 350°C/2 hrs</td>
<td>Belt-like particles</td>
<td>LIB cathode</td>
<td>[14]</td>
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<tr>
<td>2014</td>
<td>V₂O₅, Ethanol</td>
<td>180/24 hrs</td>
<td>Nanosheets</td>
<td>LIB cathode</td>
<td>[15]</td>
</tr>
<tr>
<td>2014</td>
<td>NH₄VO₃, Oxalic acid</td>
<td>180°C/44 hrs 450°C/8 hrs</td>
<td>Nanosheets</td>
<td>LIB cathode</td>
<td>[16]</td>
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<td>2014</td>
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<td>Micro-flowers</td>
<td>Cathode in LIB and NIBs</td>
<td>[17]</td>
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<td>2015</td>
<td>V₂O₅, Oxalic acid</td>
<td>260°C/48 hrs</td>
<td>Nanobelts</td>
<td>Thermal decomposition of NH₄ClO₄</td>
<td>[18]</td>
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<td>2015</td>
<td>V₂O₅, H₂O₂, Absolute ethanol</td>
<td>250°C/48 hrs</td>
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<td>2016</td>
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<td>Nano-architectures</td>
<td>CE in DSSCs</td>
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Fig. 1. Room temperature powder XRD patterns of (a) V$_2$O$_3$ powder, (b) intermediate stage V$_{10}$O$_{24.9}$H$_2$O, (c) as-synthesized V$_6$O$_{13}$ powder and (d) VO$_2$ (B) powder. Here the XRD patterns are simulated using corresponding JCPDS data cards.
Fig. 2. SEM image of (a) $\text{V}_2\text{O}_3$ powder, (b) intermediate stage $\text{V}_{10}\text{O}_{24}.9\text{H}_2\text{O}$, (c) as-synthesized $\text{V}_6\text{O}_{13}$ powder, the inset figure shows the closer view and (d) $\text{VO}_2$ (B) powder.
Fig. 3. (a) TEM micrograph of $V_6O_{13}$ powder, (b) HRTEM micrograph of $V_6O_{13}$ powder, (c) diffraction pattern corresponding to micrograph (b) along the [001] zone axis.
Fig. 4. An illustration of fabrication steps of $V_6O_{13}$ counter electrode.
Fig. 5. (a) The J-V curves of the DSSCs fabricated with V$_6$O$_{13}$ as counter electrode. (b) Nyquist plots of full cells assembled DSSC with V$_6$O$_{13}$ counter electrode.
Highlights

1. Hierarchical nano-structures of $\text{V}_6\text{O}_{13}$ are synthesized by a facile one step hydrothermal process.
2. Phase formation mechanism investigated under hydrothermal conditions by using time dependant study.
3. For the first time, we show the feasibility of $\text{V}_6\text{O}_{13}$ in electrochemical energy conversion applications.