3D Urchin-shaped Ni$_3$(VO$_4$)$_2$ hollow nanospheres for high-performance asymmetric supercapacitor applications

Rudra Kumar, Prabhakar Rai*, Asutosh Sharma*

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

*Email: prkrai@iitk.ac.in, ashutos@iitk.ac.in

Figure S1. XRD pattern of Ni$_3$(VO$_4$)$_2$ precursors synthesized by hydrothermal method.
**Figure S2.** TGA-DTA curves of Ni$_3$(VO$_4$)$_2$ precursors synthesized by hydrothermal method using (a) NH$_4$OH and (b) NaOH.

**Figure S3.** SEM images of Ni$_3$(VO$_4$)$_2$ nanostructures after hydrothermal synthesis; (a) nanospheres and (b) nanoparticles at 180°C for 20 h, (c) nanospheres at 180°C for 10 h and (d) nanospheres at 120°C for 20 h.
Figure S4. EDS analysis and elemental mapping of Ni$_3$(VO$_4$)$_2$ nanospheres.

Figure S5. EDS analysis and elemental mapping of Ni$_3$(VO$_4$)$_2$ nanoparticles.
**Figure S6.** BET surface area and pore size distribution of Ni$_3$(VO$_4$)$_2$ nanostructures; (a) nanospheres and (b) nanoparticles.
**Figure S7.** Photograph showing the change in colour of (a) NiCl$_2·$6H$_2$O solution after (b) NH$_4$OH and (c) NaOH addition.
The formation of reaction intermediates has been confirmed by UV-visible and FTIR and spectroscopy. UV visible spectra of green \([\text{Ni(H}_2\text{O)}_6]^{2+}\) ions (hexaquonickel(II) ions) shows absorbance at 395 nm as shown in Fig. S8a.\(^1\) The addition of \(\text{NH}_4\text{OH}\) resulted in blue shift in peak position from 395 to 357 due to the \([\text{Ni(NH}_3)_6]^{2+}\) (hexamminenickel(II) ion) complex ions formation.\(^2\) The origin of UV visible absorbance in these complexes is related to crystal field splitting of d orbital of nickel.\(^3\) In an octahedral complex, the metal is at the centre of the octahedron and ligands are at the six corners. Thus under the influence of an octahedral ligand field the d orbitals split into two groups (\(e_g\) and \(t_{2g}\)) of different energies. The
difference in the energy between the two d levels is given by $\Delta o$ or 10Dq. The two e_g ($d_{x^2-y^2}$ and $d_{z^2}$) orbitals are 6Dq above the average level and three t_2g ($d_{xy}$, $d_{yz}$, $d_{zx}$) orbitals are 4Dq below the average. The magnitude of crystal field splitting depends on the nature of ligand. Since, NH$_3$ is stronger ligand than H$_2$O, hence it cause larger crystal field splitting and therefore absorption peak was blue-shifted. The formation of Ni(OH)$_2$ in NaOH medium was confirmed from absorption peak at 385 nm.

The formation of these intermediates has also been confirmed by FTIR spectra and shown in Fig. S8b. In Ni(OH)$_2$, the band at 3642 cm$^{-1}$ and a strong absorption at 1400-1600 cm$^{-1}$ can be ascribed to the stretching and bending modes of surface-adsorbed/trapped (hydrogen-bonded) water molecules, indicating the presence of water molecules in the structure. Ni–OH bending vibrations result in typical absorption bands at low wavenumbers, such as at 1071 cm$^{-1}$, in agreement with the previous reports. In [Ni(NH$_3$)$_6$]$^{2+}$ complex ions, NH$_3$ asymmetric and symmetric stretching vibrations were found at 3338 and 3180 cm$^{-1}$, respectively. In the bending region, the band at 1603 and 1172 cm$^{-1}$ was due to asymmetric and symmetric H-N-H deformation, respectively. The prominent bands at 2850–2950 are typical of C–H symmetric stretching and bending vibrations, respectively. This confirms incomplete removal of ethanol. Therefore, UV-visible and FTIR spectra confirmed the formation of two kinds of intermediates during Ni$_3$(VO$_4$)$_2$ nanostructures synthesis, which guided the growth process and resulted in the formation of different morphologies.
Figure S9. (a) CV and (b) GCD curve of Ni$_3$(VO$_4$)$_2$ nanoparticles.
Figure S10. (a) Rate capability and (b) long term stability of Ni$_3$(VO$_4$)$_2$ nanospheres.
Figure S11. (a) CV and (b) GCD curve of bare Ni foam and Ni$_3$(VO$_4$)$_2$ nanospheres.
Table S1. Comparison of asymmetric supercapacitor performance of our electrodes with others full cell device reported in literature.

<table>
<thead>
<tr>
<th>Asymmetric Supercapacitor</th>
<th>Voltage (V)</th>
<th>Energy Density (Wh kg⁻¹)</th>
<th>Power Density (W kg⁻¹)</th>
<th>Cyclic Stability</th>
<th>Ref. No</th>
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<tr>
<td>AC//Co(OH)₂/Ni foam</td>
<td>1.6</td>
<td>20.3</td>
<td>90.6</td>
<td>69% (1000)</td>
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<tr>
<td>3D rGO//Ni(OH)₂</td>
<td>1.7</td>
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<td>95% (3000)</td>
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<tr>
<td>AC//Ni(OH)₂@3D Ni</td>
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<td>660</td>
<td>96% (3000)</td>
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<td>AC//Ni(OH)₂/XC-72</td>
<td>1.6</td>
<td>36</td>
<td>490.7</td>
<td>85% (1000)</td>
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<tr>
<td>Ni₃S₂/MWCNT-NC//AC</td>
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<td>19.8</td>
<td>798</td>
<td>90% (5000)</td>
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<tr>
<td>AC//Co₃O₄NSs–rGO</td>
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<td>13.4</td>
<td>2166</td>
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<tr>
<td>VN//Co(OH)₂</td>
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<td>22</td>
<td>160</td>
<td>82% (1000)</td>
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<tr>
<td>Ni/VN//Ni₁₋ₓVₓO₂</td>
<td>1.6</td>
<td>23.3</td>
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<td>Material</td>
<td>Layer Thickness</td>
<td>Energy</td>
<td>Efficiency</td>
<td>Capacity</td>
<td>This Work</td>
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<td>AC//NiCo$_2$O$_4$NSs@HMRAs</td>
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<td>15.42</td>
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<tr>
<td>AC//CuO</td>
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<td>19.7</td>
<td>700</td>
<td>96% (3000)</td>
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<tr>
<td>Ni$_3$(VO$_4$)$_2$//AC</td>
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<td>25.3</td>
<td>240</td>
<td>92% (1000)</td>
<td>This work</td>
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References:


