Supplementary Information for:

**Optimizing the Structure and Yield of Vanadium Oxide Nanotubes by Periodic 2D Layer Scrolling**

The degree of interdigitation can be estimated geometrically, and generalized for any bilayered system intercalated with long chain organic molecules. This approach assumes that the conformations of the alkyl chains are fully extended and that there is a maximum packing density on the substrate. Additionally, the chains are assumed to be free of gauche defects along their length, this would prevent variation in the defined length of each molecule and allow sufficient steric rigidity at maximal packing that would prevent bending which would otherwise cause entropic filling of free space in next-nearest neighbor chains in a sub-monolayer covered substrate.

**Figure S1** The geometrical arrangement which occurs when amine molecules aligned collinearly tail to tail at an angle $\alpha$ to the $V_2O_5$ layers

\[
\begin{align*}
  d &= 2l_{mol} \\
  d' &= \sqrt{4l_{mol}^2 - x^2} \\
  \tan \alpha &= \frac{d'}{x} \\
  \sin \alpha &= \frac{d'}{2l_{mol}} \\
  (d')^2 &= d^2 \left(1 - \frac{\sin^2 \alpha}{\tan^2 \alpha}\right) \\
  (d')^2 &= d^2 (\sin^2 \alpha)
\end{align*}
\]

Consider the case where amine chains are interdigitated tail on tail at an angle $\alpha$ with respect to the host layers of $V_2O_5$. The angle $\alpha$ refers to the angle subtended by the amine bilayer, where both molecules are collinear, as shown in Fig. 2(b) and in more detail in Fig. S1. The vertical distance in this case, i.e. the measured experimental interlayers spacing, is
defined as $d'$. The geometrical arrangement can be expressed in Fig. S1. This predicts the expected measured interlayer spacing, when the theoretical spacing as determined by $d = 2l_{mol}$ is known for each amine length used in the VONT synthesis. Alternatively, the angle subtended by a defect free amine molecule in bilayer configuration can be estimated if $d$ and $d'$ are known.

![Figure S2](image)

**Figure S2** Interlayer spacing as a function of the mixture ratio of amine to xerogel

**FTIR Spectra for Bulk V$_2$O$_5$, V$_2$O$_5$ Xerogel, Dodecylamine and VONTs**

FTIR spectra were also obtained to probe the structural changes associated with the various stages of the synthesis of the nanotubes. In order to do this, FTIR spectra of bulk V$_2$O$_5$, V$_2$O$_5$ xerogel, dodecylamine and VONTs synthesized with dodecylamine in a molar ratio of xerogel to amine of 1:2 were acquired, as shown in Fig. S3. The peak between 1610
and 1620 cm\(^{-1}\), associated with an O-H vibration, can be seen in the spectra for xerogel and the synthesized VONTs but not in the bulk V\(_2\)O\(_5\) spectra. This arises because the xerogel after distillation still retains some crystal water, which was added after heating under reflux with tert-butanol, having the form V\(_2\)O\(_5\).\(n\)(H\(_2\)O), with \(n\) ranging from 1.3-1.6 (74). Further evidence of this is the band above 3300 cm\(^{-1}\) associated with the stretching and bending modes of O-H vibrations which is also seen in the spectra for xerogel and as-synthesized VONTs, but not in the case of bulk V\(_2\)O\(_5\).

The peak associated with V=O bond at 1005 cm\(^{-1}\) for bulk V\(_2\)O\(_5\) is red-shifted to 982 cm\(^{-1}\) for xerogel and to 995 cm\(^{-1}\) for the VONTs. This shift in the wave number of the V=O peak shows the contribution of the addition of H\(_2\)O as well as the intercalated amines within the vanadium oxide layers, and is a fingerprint vibrational signature of multivalency in the resulting oxide. Typically, a red-shift in the vanadyl bond vibration to wavenumbers <1000 cm\(^{-1}\) implies a non-negligible (up to 40%) quantity of V\(^{4+}\) in addition to V\(^{5+}\), an effect that is only found when curved sheets of vanadium oxide are found in the structure. The reason for curvature development in a single crystal sheet(s) is a matter of debate still, but divalent vanadium species are characteristic, and organic species with self-assembled, packed structure within the gallery spacing of the oxide sheets are always required.

Several characteristics are evident from the IR spectra in Fig. S3. Firstly, the xerogel post reflux and distillation shows evidence or mixed valence where the V=O bond vibration is red shifted to a value below 1000 cm\(^{-1}\), but it retains the V–O vibrational structure of the orthorhombic V\(_2\)O\(_5\) as evidence in the V–O and V–O–V vibrations. The xerogel also contains the characteristic vibrational signature of water, which is also maintained in the final VONT. Analysis of the vibrational characteristics of dodecylamine on its own shows that the 4 primary C-H vibrations always found in the range 2700-3000 cm\(^{-1}\) are not shifted, and the N-H vibrations undergo no observable shifts (1465 cm\(^{-1}\)) confirming that the intercalated amines
retain their alkyl chain structure within the VONT. The V-O vibrations are also quite similar to the starting xerogel host, showing that the optimum ratio of amine to xerogel results in a high quality organic-inorganic interaction and structure.

Figure S3 FTIR spectra of bulk V$_2$O$_5$ powder, V$_2$O$_5$ xerogel, as-received dodecylamine, and VONTs synthesized with dodecylamine in a molar ratio of xerogel to amine of 1:2.