Supporting Information

In the Ni/Si = 2 and Ni/Si = 3 samples approximately 6 and 10 wt % was composed of β-Ni(OH)₂ which was precipitated alongside the Ni₃Si₂O₅(OH)₄ nanotubes. Figure S1 shows TEM images of the β-Ni(OH)₂ particles along with EDX data.

Figure S1. TEM image of β-Ni(OH)₂ particles formed at Ni/Si = 3, together with HRTEM and EDX images. The arrow on the left indicates a β-Ni(OH)₂ particle and the arrow on the right indicates a Ni₃Si₂O₅(OH)₄ nanotube.
Figure S2. Thermogravimetric data for products with molar Ni/Si ratio (a) 1.5, (b) 2 and (c) 3 in the starting materials. The weight loss at 230-330 °C corresponds to the dehydroxylation of β-Ni(OH)$_2$. 
Figure S3. SEM images of products at (a) 1, (b) 1.5, (c) 2 and (d) 3 Ni/Si ratios with corresponding percentage length distributions of nanotubes.
**Figure S4.** FTIR spectra of nickel silicates synthesised at controlled Ni/Si ratios (a) 1, (b) 1.5, (c) 2 and (d) 3.

**Calculation of β-Ni(OH)$_2$ and SiO$_2$ solubility diagrams**

The total concentration of Ni(II) in aqueous solution is given by the sum of the concentrations of all hydrolysed species:

$$C_{\text{Ni(II)}} = C_{\text{Ni}^{2+}} + C_{\text{Ni(OH)}_2} \quad (S.1)$$

The concentration of the hydrolysed species can be calculated from the dissolution reactions

$$K_1 \quad \beta-\text{Ni(OH)}_2 (s) + 2\text{H}^+ = \text{Ni}^{2+} (aq) \quad (S.2)$$

$$K_2 \quad \beta-\text{Ni(OH)}_2 (s) = \text{Ni(OH)}_2 (aq) \quad (S.3)$$
The species Ni(OH)$_{3}^{+}$(aq) and Ni(OH)$_{3}^{-}$(aq) are thought to only exist in negligible amounts, so are not included here. Thus the expression for the variation in Ni(II) concentration with pH is given by:

$$C_{\text{Ni(II)}} = 10^{(\log K_{2} - 2pH)} + 10^{\log K_{2}} \quad (S.4)$$

The temperature dependence equation derived by Palmer et al.\textsuperscript{[1]} states that

$$\log_{10} K_{1} = -2.71 + (4228.48/T) \quad (S.5)$$

where T is measured in degrees Kelvin. Hence the values of log K\textsubscript{1} and can be derived at 25 ºC and 195 ºC, which was the synthesis temperature of Ni$_{3}$Si$_{2}$O$_{5}$(OH)$_{4}$ nanotubes used in this thesis. To calculate log K\textsubscript{2}, the second hydrolysis constant K$_{H2}$ for the reaction Ni$^{2+}$(aq) +2H$_{2}$O = Ni(OH)$_{2}$(aq) + 2H$^{+}$ was used in conjunction with log K\textsubscript{1} according to the formula

$$\log K_{2} = \log K_{1} + \log K_{H2} \quad (S.6)$$

Where log K$_{H2}$ was calculated using the temperature dependence formula\textsuperscript{[2]}

$$\log K_{H2} = 6.09 - (7282.7/T) - 0.009476T \quad (S.7)$$

The results of these calculations are presented below in table S.1. The values were substituted into equation S.4 to give the solubility plot.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>log K\textsubscript{1}</th>
<th>log K\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>6.34</td>
<td>-13.91</td>
</tr>
</tbody>
</table>

Table S.1. Logarithmic solubility constants for β-Ni(OH)$_{2}$. 

Amorphous silicon dioxide dissolves to produce mostly neutral or negatively charged monomeric species (under alkaline hydrothermal conditions > 100 ºC polymeric species are depolymerised\textsuperscript{[3]}). Therefore, amorphous SiO$_{2}$ has low solubility in acidic
solution and high solubility in strongly alkaline solution. The total Si(IV) concentration in solution is given by the formula

\[ C_{\text{Si(IV)}} = C_{\text{H}_4\text{SiO}_4} + C_{\text{H}_3\text{SiO}_4^-} + C_{\text{H}_2\text{SiO}_4^{2-}} \]  

(S.8)

The concentrations of the hydrolysed species can be derived from the equations

\[ K_1 \quad \text{SiO}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4(\text{aq}) \]  

(S.9)

\[ K_2 \quad \text{SiO}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{SiO}_4^{-}(\text{aq}) + \text{H}^+ \]  

(S.10)

\[ K_3 \quad \text{SiO}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SiO}_4^{2-}(\text{aq}) + \text{H}^+ \]  

(S.11)

Thus the expression for the variation in Si(IV) concentration with pH is given by:

\[ C_{\text{Si(IV)}} = 10^{(\log K_1)} + 10^{(\log K_2 + \text{pH})} + 10^{(\log K_3 + 2 \text{pH})} \]

The value of log \( K_1 \) could be calculated from the experimental results of Gunnarsson and Arnorsson [4] which relates \( K_1 \) to temperature:

\[ \text{Log } K_1 = -8.476 - (485.24/T) - (2.268 \times 10^{-6} \times T^2) + 3.068(\log T) \]  

(S.12)

where \( T \) is in degrees Kelvin. A value for the first acid dissociation constant, \( K_{\text{H1}} \) at 195 °C of -8.85 was obtained from the experimental results of Busey and Mesmer. [5]

The second acid dissociation constant has not yet been obtained experimentally, so a value of \( K_{\text{H2}} = -10.89 \) was calculated using the thermodynamic data of Robbie et al. [6]

These acid dissociation constants were used to calculate log \( K_2 \) and log \( K_3 \), using the method described by equation S.6. The values of all log \( K_n \) are shown below in table S.2.

<table>
<thead>
<tr>
<th>Temperature/ °C</th>
<th>log ( K_1 )</th>
<th>log ( K_2 )</th>
<th>log ( K_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>-1.76</td>
<td>-10.60</td>
<td>-21.49</td>
</tr>
</tbody>
</table>

Table S.2. Logarithmic solubility constants for SiO\(_2\).