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 $Ni_3Si_2O_5(OH)_4$ nanotubes. Figure S1 shows TEM images of the β-$Ni(OH)_2$ particles along with EDX data.

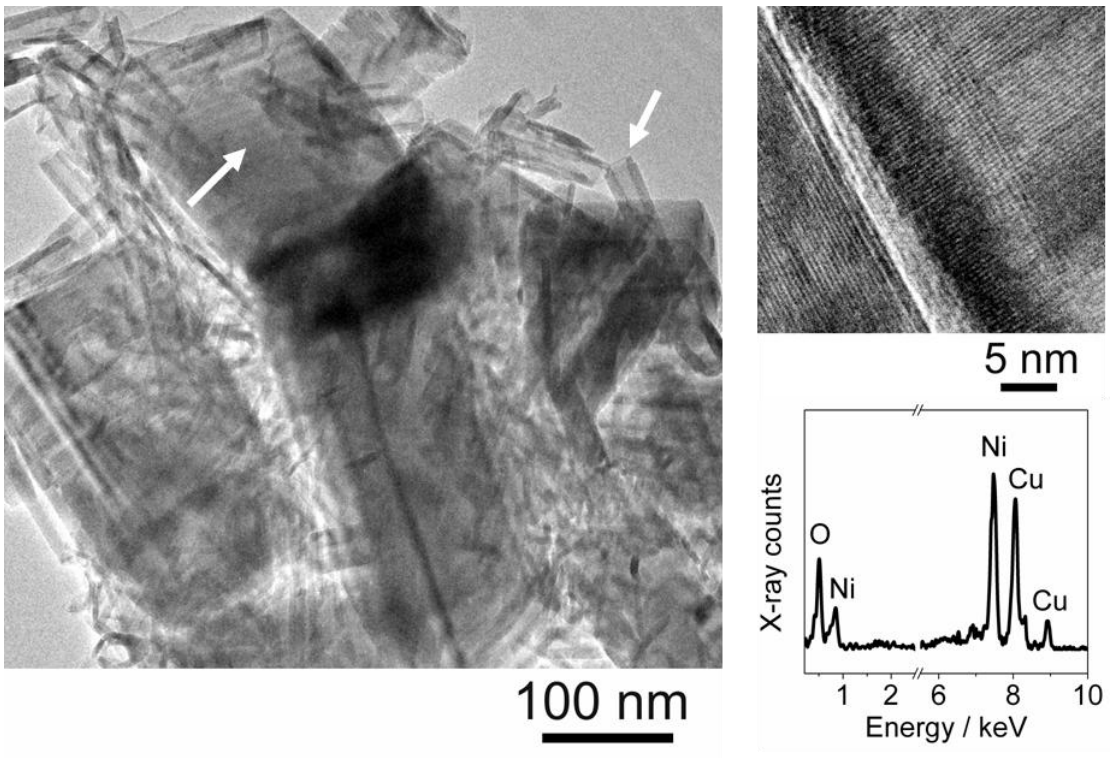

Figure S1. TEM image of β-$Ni(OH)_2$ particles formed at Ni/Si = 3, together with HRTEM and EDX images. The arrow on the left indicates a β-$Ni(OH)_2$ particle and the arrow on the right indicates a $Ni_3Si_2O_5(OH)_4$ nanotube.

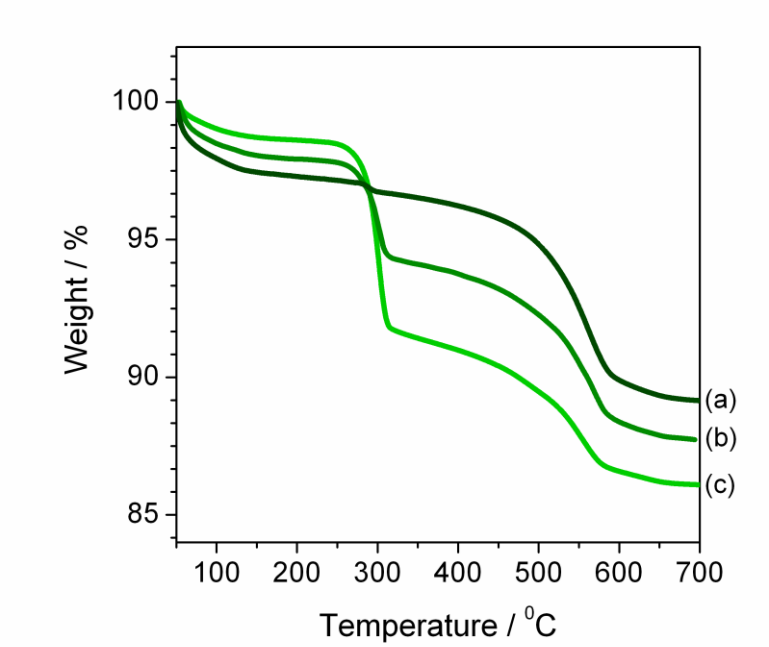

Figure S2. Thermogravimetric data for products with molar Ni/Si ratio (a) 1.5, (b) 2 and (c) 3 in the starting materials. The weight loss at 230-330 ºC corresponds to the dehydroxylation of β-$Ni(OH)_2$.

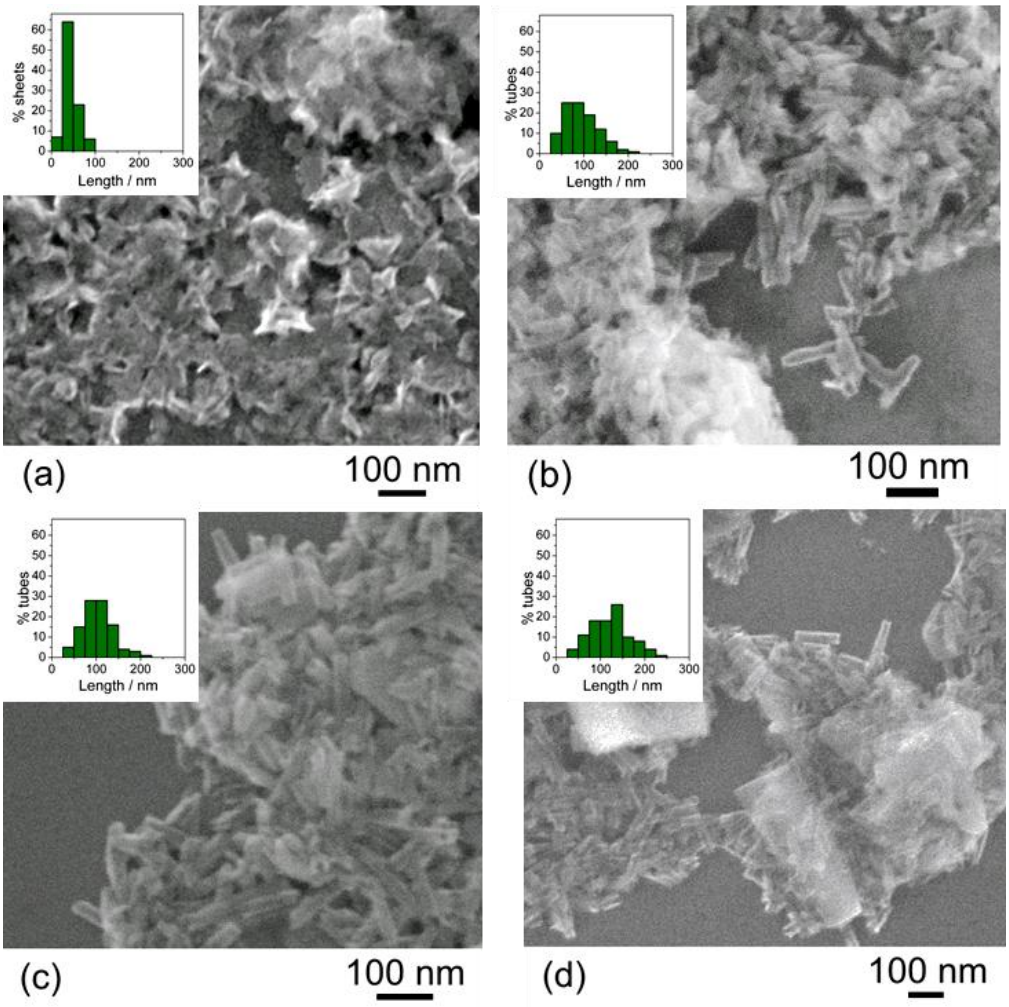

Figure S3. SEM images of products at (a) 1, (b) 1.5, (c) 2 and (d) 3 Ni/Si ratios with corresponding percentage length distributions of nanotubes.

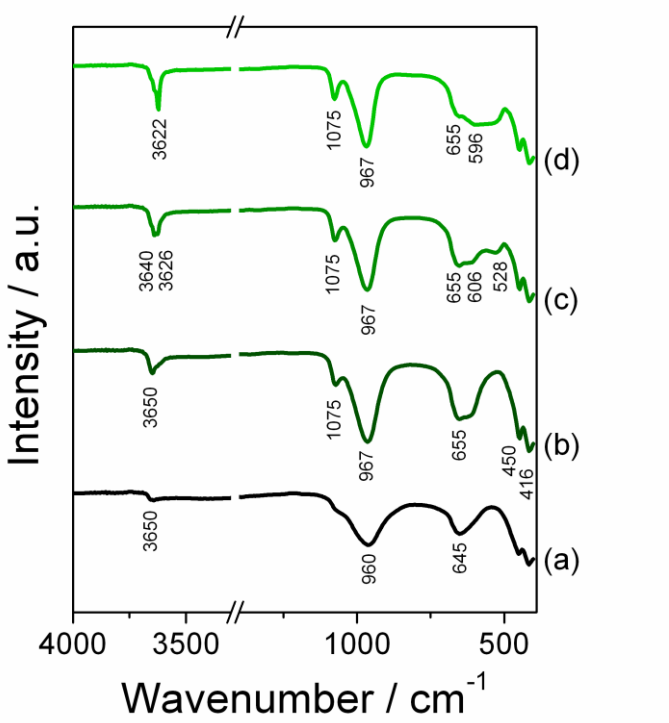

Figure S4. FTIR spectra of nickel silicates synthesised at controlled Ni/Si ratios (a) 1, (b) 1.5, (c) 2 and (d) 3.

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:

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

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

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

$$\beta\text{-}Ni(OH)_{2\,(s)} \overset{K_2}{=} Ni(OH)_{2\,(aq)} \quad \text{(S.3)}$$

The species $Ni(OH)^{+}_{(aq)}$ and $Ni(OH)_3^{-}{}_{(aq)}$ are thought to only exist in negligible amounts, [1] so are not included here. Thus the expression for the variation in Ni(II) concentration with pH is given by:

$$C_{Ni(II)} = 10^{(\log K_1 - 2pH)} + 10^{(\log K_2)} \quad \text{(S.4)}$$

The temperature dependence equation derived by Palmer et al. [1] states that

$$\log_{10} K_1 = -2.71 + (4228.48/T) \quad \text{(S.5)}$$

where T is measured in degrees Kelvin. Hence the values of log K_1 and can be derived at 25 ºC and 195 ºC, which was the synthesis temperature of $Ni_3Si_2O_5(OH)_4$ nanotubes used in this thesis. To calculate log K_2, the second hydrolysis constant K_{H2} for the reaction $Ni^{2+}_{(aq)} + 2H_2O = Ni(OH)_{2\,(aq)} + 2H^{+}$ was used in conjunction with log K_1 according to the formula

$$\log K_2 = \log K_1 + \log K_{H2} \quad \text{(S.6)}$$

Where log K_{H2} was calculated using the temperature dependence formula [2]

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

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.

Temperature/ ºC	log K_1	log K_2
195	6.34	-13.91

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 [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

$$C_{\mathrm{Si(IV)}} = C_{\mathrm{H_4SiO_4}} + C_{\mathrm{H_3SiO_4^-}} + C_{\mathrm{H_2SiO_4^{2-}}} \quad \text{(S.8)}$$

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

$$\mathrm{SiO_{2\,(s)}} + 2\mathrm{H_2O} \overset{K_1}{=} \mathrm{H_4SiO_{4\,(aq)}} \quad \text{(S.9)}$$

$$\mathrm{SiO_{2\,(s)}} + 2\mathrm{H_2O} \overset{K_2}{=} \mathrm{H_3SiO_4^-{}_{(aq)}} + \mathrm{H^+} \quad \text{(S.10)}$$

$$\mathrm{SiO_{2\,(s)}} + 2\mathrm{H_2O} \overset{K_3}{=} \mathrm{H_2SiO_4^{2-}{}_{(aq)}} + \mathrm{H^+} \quad \text{(S.11)}$$

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

$$C_{\mathrm{Si(IV)}} = 10^{(\log K_1)} + 10^{(\log K_2 + \mathrm{pH})} + 10^{(\log K_3 + 2\,\mathrm{pH})}$$

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

$$\mathrm{Log}\ K_1 = -8.476 - (485.24/T) - (2.268 \times 10^{-6} \times T^2) + 3.068(\log T) \quad \text{(S.12)}$$

where T is in degrees Kelvin. A value for the first acid dissociation constant, K_{H1} at 195 ºC 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_{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.

Temperature/ ºC	log K_1	log K_2	log K_3
195	-1.76	-10.60	-21.49

Table S.2. Logarithmic solubility constants for SiO_2.

[1]. D.A. Palmer and Gamsjäger, H., *J.Coord. Chem.*, 2010, **63**, 14-16, 2888-2908.

[2]. D.A. Palmer, P. Benezeth, C. Xia, D.J. Wesolowski and L.M.Anovitz, , *J. Sol. Chem.*, 2011, **40**, 680-702.

[3]. J.D. Hunt, A. Kavner, E.A. Schauble, D. Snyder and C.E. Manning, *Chemical Geology*, 2011, **283**, 161-170.

[4]. I.Gunnarson and S. Arnosson, *Geochim. et Cosmochim. Acta*, **64**, 13, 2295-2307.

[5]. R.H Busey and R.E. Mesmer, *Inorg. Chem.*, 1977, **16**, 10, 2444-2450.

[6]. R.A Robbie, B.S. Hemingway and J.R. Fisher, *U.S. Geological Survey Bulletin* **1979**, 1452, p456.