

## ABSTRACT

Using the Q500 Thermogravimetric Analyzer (TGA) it is demonstrated that it is possible to monitor the real time growth of Single Walled Carbon Nanotubes (SWCNTs) by Chemical Vapour Deposition (CVD) on SiO<sub>2</sub> supported Ni catalyst. The catalyst is made by first dissolving Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and SiO<sub>2</sub> in acetone and then allowing the acetone to evaporate. The resulting powder is then thermally decomposed in the Q500 TGA under an inert atmosphere of Ar(g) to generate SiO<sub>2</sub> supported NiO. The CH<sub>4</sub>(g) carbon precursor is then introduced, reducing the NiO to Ni and initiating the CVD growth of Carbon Nanotubes (CNTs). Thus both the formation of the catalyst and the growth of SWCNTs are monitored in real time by this method. The CVD grown carbon is confirmed as containing SWCNTs by Raman Spectroscopy. We believe this to be the first example of SWCNTs grown by CVD in a TGA.

## INTRODUCTION

Single Walled Carbon Nanotubes (SWCNTs) have over the years been synthesized via a variety of processes including Arc-discharge evaporation,<sup>1</sup> Laser vaporisation,<sup>2</sup> Thermal plasma<sup>3</sup> and Chemical Vapour Deposition (CVD)<sup>4</sup>. CVD is of great interest as it permits the growth of relatively well aligned arrays of SWCNTs whilst at the same time still generating relatively large quantities of material. The advantage of well aligned arrays of SWCNTs, as opposed to the disordered material that results from other syntheses, is that they enable easier characterization of the material generated and assessment of the potential applications.<sup>4</sup> It has been demonstrated previously that using a Thermogravimetric Analyser (TGA) the growth of Carbon Nanotubes (CNTs) can be monitored in real time<sup>5</sup> but this technique had not previously been used to generate and monitor the growth of SWCNTs.

We report that using the Q500 TGA the in situ CVD growth of SWCNTs can be monitored in real time using a SiO<sub>2</sub> supported Ni catalyst, where the catalyst is generated in the TGA just prior to CNT growth. The presence of at least 5% SWCNTs in the material generated by the growth process is confirmed by ex situ Raman Spectroscopy.

## MATERIALS, EQUIPMENT AND METHODS

### Materials

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was obtained from Merck, GPR acetone and SiO<sub>2</sub> powder (*Cab-O-sil®*) from Sigma Aldrich and Ar(g) and CH<sub>4</sub>(g) from BOC. All materials were used as received.

### Equipment

A Q500 TGA was used to grow the CNTs. Table 1 details the instrument settings used for all procedures described. High resolution thermogravimetric analysis (Hi-res TGA™) uses a sensitive mass balance enclosed in a platinum wound ceramic furnace to measure weight change in a controlled environment. High accuracy weight and temperature measurements allow catalytic processes, such as CNT growth, to be continuously monitored for a range of growth conditions with reproducible results.

Instrument Setting	Value
Gas Flow	100 mL min <sup>-1</sup>
Ramp Rate	50 °C min <sup>-1</sup>
Temp Precision	± 0.1 °C
Temp Accuracy	± 1 °C
Weighing Precision	± 0.01%
Weighing Sensitivity	0.1 µg
Mode	Hi-Res

Table 1: Instrument settings used for the Q500 TGA

A Raman spectrometer, Renishaw system 1000 with a 632 nm HeNe laser, was used for ex situ characterisation of the CNTs grown. The spectrometer was initially calibrated with a single SiO<sub>2</sub> crystal at 520 cm<sup>-1</sup>.

### Methods

#### Ex situ catalyst precursor synthesis

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.99 g) was dissolved in a minimal amount of acetone before SiO<sub>2</sub> powder (0.80 g) was added and the solution stirred for 16 hours. Once the acetone had evaporated the resulting precipitate was ground to a fine powder.

#### SWCNT synthesis

Prior to CNT growth the Q500 TGA was purged by decomposing animal charcoal in an inert argon atmosphere. The temperature was increased from 50 - 1000 °C until no further mass loss was observed. This was repeated to ensure the furnace was well purged of oxygen.

Catalyst precursor was placed in a Pt pan to cover the pans

base (see Figure 1). The catalyst was produced *in situ* in the Q500 TGA, under a flow of Ar(g), by first maintaining a temperature of 50°C for 15 minutes to remove moisture from the precursor. The temperature was then increased to the desired growth temperature and an isotherm held until the Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was fully decomposed to NiO (after about 30 minutes in Figure 2). At this point the gas flow was changed to 10% CH<sub>4</sub>(g) in Ar(g) causing the NiO to reduce to metallic Ni. Once reduced, the Ni:SiO<sub>2</sub> ratio was calculated to be 1:4. CVD CNT growth could then be observed as a rapid increase in mass in the Q500 TGA. Isothermal programs of 600°C and 575°C were used to grow CNTs.

### SWCNT characterization

The CNTs grown were analyzed by Raman spectroscopy to determine if SWCNTs or Multi Walled Carbon Nanotubes (MWCNTs) had been synthesized. Spectra for samples grown at 575°C and 600°C were obtained by pentuple and triple accumulations respectively; each accumulation lasted 10 s. The accumulations were summed to average out statistical noise contributions. Multiple spectra per sample were obtained to account for variation within the sample.

## RESULTS AND DISCUSSION

Figure 2 shows the Thermogravimetric (TG) plot obtained using an isothermal growth temperature of 600°C for SWCNT synthesis. Initially a number of weight losses are observed which are associated with the thermal decomposition of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to NiO and these can be assigned to the reaction steps detailed in Table 2.<sup>6</sup> Figure 3 shows a TG plot of just the catalyst decomposition process, without the subsequent CNT growth, obtained by maintaining a 100% Ar(g) gas flow.

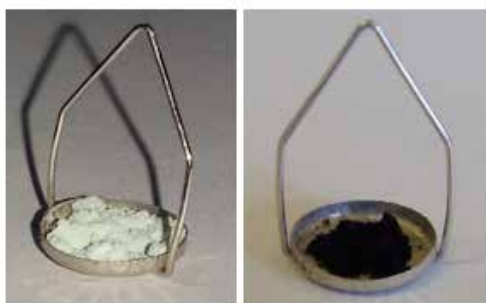


Figure 1: Catalyst before CNT growth (left) and after CNT growth (right).

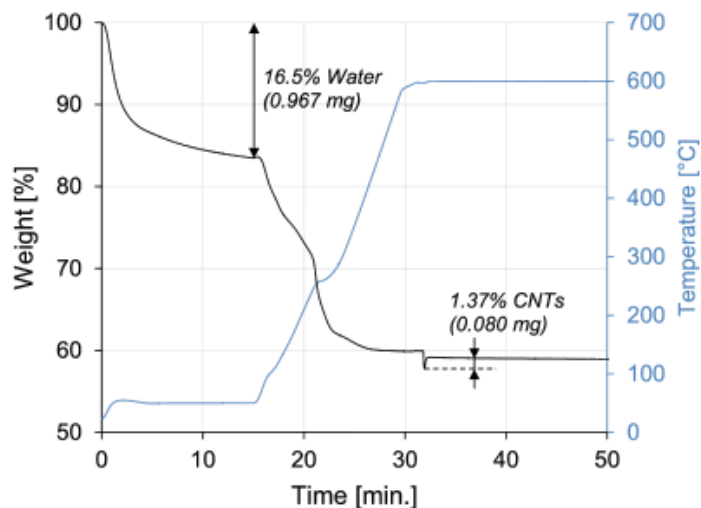


Figure 2: TG measurement showing the thermal decomposition of the nickel catalyst and carbon nanotube growth at 600°C. The percentage weight loss and temperature are both shown on the plot. Initial mass: 5.865 mg.

Step	Mechanism
Loss of free water	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} (\text{wet}) \rightarrow \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} (\text{dry})$
Loss of hydrates	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
Reconfiguration of complex around Ni centre	$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ni}(\text{NO}_3)(\text{OH})_2 \cdot \text{H}_2\text{O} + \text{NO}_2$ $\text{Ni}(\text{NO}_3)(\text{OH})_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ni}(\text{NO}_3)(\text{OH})_{1.5}\text{O}_{0.25} \cdot \text{H}_2\text{O} + 0.25\text{H}_2\text{O}$
Oxide formation	$\text{Ni}(\text{NO}_3)(\text{OH})_{1.5}\text{O}_{0.25} \cdot \text{H}_2\text{O} \rightarrow 0.5\text{Ni}_2\text{O}_3 + \text{HNO}_3 + 1.25\text{H}_2\text{O}$
Oxide decomposition	$3\text{Ni}_2\text{O}_3 \rightarrow 2\text{Ni}_3\text{O}_4 + 0.5\text{O}_2$ $\text{Ni}_3\text{O}_4 \rightarrow 3\text{NiO} + 0.5\text{O}_2$

Table 2: The thermal decomposition process of the nickel catalyst. Adapted from Brockner et al.

The weight derivative has been included in the plot in order to demonstrate these reaction steps more clearly. Figure 3 associates the reaction steps from Table 2 with the individual weight losses in the TG plot.

The catalyst then remains as NiO until the introduction of CH<sub>4</sub>(g) (at 31 minutes in Figure 2) where a sharp decrease in the weight can be seen as NiO is reduced to Ni. This allows for nucleation to occur and CNT growth to begin, observed as an immediate increase in weight. The growth continues steadily for a minute before stopping, observed as a plateau in the TG plot. In addition physical changes were observed upon removal of the pan from the Q500 TGA. The sample had changed from pale green, the color of the catalyst, to a charcoal black color (see Figure 1). These observations suggested growth of CNTs.

In order to confirm CNT growth had been achieved, rather than amorphous carbon growth, and whether the growth was of SWCNTs or MWCNTs *ex situ* Raman spectroscopy was performed. Figure 4 shows the Raman spectrum of the CNTs grown at an isothermal temperature of 600°C. Duplicate measurements were obtained using different areas of the material in order to account for variation within the sample. This characterization confirms that SWCNTs have been grown. The D peak (~1350 cm<sup>-1</sup>) representing defects is much less intense than the G peak (~1580 cm<sup>-1</sup>). The two components of the G peak, G<sup>+</sup> and G<sup>-</sup>, are resolved representing the LO and TO phonons which are parallel and perpendicular to the tube folding diameter respectively. The 2D peak (~2640 cm<sup>-1</sup>) representing two phonon scattering is larger than the D peak and Radial Breathing Mode (RBM) peaks (50-760 cm<sup>-1</sup>) can also be seen, which are only present in samples containing SWCNTs.<sup>7</sup>

As the presence of SWCNTs was observed in samples grown at 600°C it was decided to reduce the isothermal temperature to 575°C in order to determine if SWCNTs could be grown at lower temperatures. Figures 5 and 6 show the TG plot and the Raman spectrum obtained respectively. The TG plot again shows the thermal decomposition of the nickel catalyst and a sharp decrease in weight as CH<sub>4</sub>(g) is introduced followed by an increase in weight representing growth of CNTs.

Triplicate measurements were obtained for the Raman spectroscopy to account for variation within the sample. These spectra show the presence of both SWCNTs and MWCNTs. RBM peaks can still be seen as in Figure 4 however the ratio between the D and G peaks is now much lower (and the G<sup>+</sup> and G<sup>-</sup> peaks are no longer resolved) indicating MWCNTs are also contributing to the signal. In addition the intensity of the 2D peak is now lower than that of the D peak. As both MWCNTs and SWCNTs are contributing to the Raman spectra it can be said that SWCNTs are definitively present but that they constitute less of the sample than in samples grown at 600°C.

To the authors' knowledge this is the first time SWCNTs have been grown *in situ* using a TGA and at such a low temperature.

## CONCLUSION

SWCNTs were synthesized for the first time by CVD in a Q500 TGA on a SiO<sub>2</sub> supported Ni catalyst generated *in situ*. Due to the CVD process being performed in the Q500 TGA it was possible to monitor the SWCNT growth in real time.

It is possible to generate material by the CVD process which was confirmed to contain SWCNTs by Raman Spectroscopy.

Future work will focus on how temperature affects rate of growth, the amount of growth and the composition of the growth material in terms of the relative presence of SWCNTs and MWCNTs.

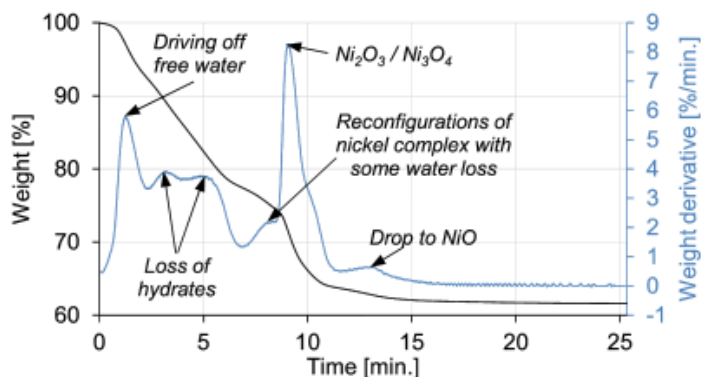


Figure 3: The thermal decomposition process of the catalyst from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to NiO.

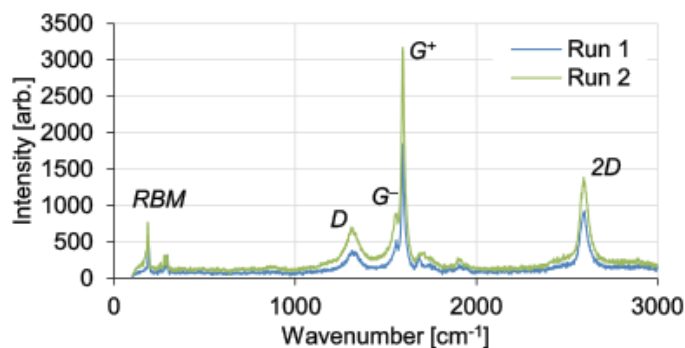


Figure 4: Raman spectra of the CNT material grown at 600°C.

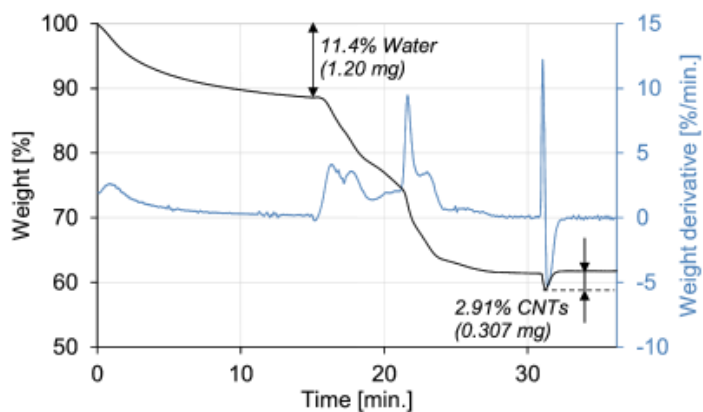


Figure 5: TG measurement showing the thermal decomposition of the nickel catalyst and carbon nanotube growth at 575°C. The percentage weight loss and weight derivative are both shown on the plot. Initial mass: 10.539 mg.

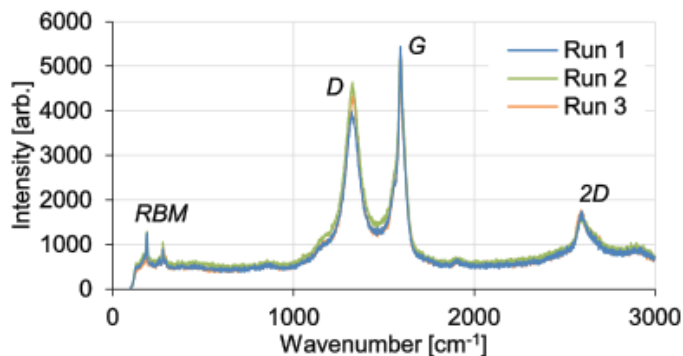


Figure 6: Raman spectra of the CNT material grown at 575°C.

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